## Photo-Mechanical and Optical Effects in Crystals of Azobenzene Photoswitches

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actuator upon UV and visible irradiation. Figure reproduced with permission from ref. 139. Copyright 2012 Wiley. (c) Irradiation of gold-coated diarylethene crystals with UV and visible light enables the ON/OFF photoreversible current switching of an electric circuit. Figure reproduced with permission from ref. 140. Copyright 2015 Royal Society of Chemistry. (d) Superimposed photographs of a crystal cantilever lifting a lead ball with a mass 275 times larger than the crystal upon irradiation with UV light from the underside of the actuator. Figure reproduced with permission from ref. 138. Copyright 2010 American Chemical Society. ....... 31 Figure 1.19 (a) Photo-induced proton transfer in the S-enantiomers of chiral salicylidenephenylethylamines upon keto-enol tautomerism (b) Superimposed photographs of a chiral enol-(S)-1 crystal before and after irradiating the top of the crystal actuator with ultraviolet light. The crystalline cantilever achieved 26 nJ of work by lifting a 4.00 mg metal ring a height,  $\delta$ , of 0.65 mm. Various photo-mechanical lifting work was achieved with different enantiomeric compositions within the crystal: the racemic crystal, enol-(rac)-1, achieved 59 nJ of work by lifting a weight with mass 300 times larger than that of the crystal (not shown). Figure reproduced with Figure 2.1 4-diethylamino-4'-nitroazobenzene microcrystal (700×600×2 µm) exhibits fast reversible photo-mechanical motion upon irradiation of the (001) face with visible light. The scale bar is 200 µm. Molecular geometry was optimized by molecular mechanics using the universal **Figure 2.3** Deflection angle  $(\theta)$  dependence on power of incident irradiation for crystals of similar dimensions and ca. 2 µm thickness of Disperse Red 13 (DR13), 4-diethylamino-4'-Figure 2.4 a) Molecular orientation in crystals of Disperse Red 13. Grey planes represent the irradiated face, blue planes — the least squares plane drawn through the azobenzene fragment; Molecules align nearly perpendicular to the (001) face and crystals exhibit significant bending; b) molecular orientation in crystals of Disperse Orange 1. Molecules are strongly tilted with respect Figure A1.1 Representation of the molecular tilt of Para Red with respect to the irradiated (010) 

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#### Abstract

This thesis makes contributions in the areas of photo-mechanical effects and crystal engineering of azobenzene crystals and cocrystals. Photo-mechanical effects are important phenomena, which deal with the direct transformation of light into mechanical motion by materials incorporating photoswitchable molecules. Only recently it was realized that once thought chemically and mechanically inert, single crystals may in fact exhibit motion in response to light irradiation. Azobenzene, which is a molecule of choice for photo-mechanical materials, was underexplored in crystals prior to this work.

The contribution of Chapter 2 lies in the observation of photo-induced motions in single crystals of pseudostilbenes, a spectral class of azobenzene derivatives with very short thermal lifetimes of the *cis*-state. The study provided insights into the structural dependence of this reversible solid state process. Bending of crystals, which can be initiated by various wavelengths of visible light, proved to be fully reversible at room temperature and ambient illumination on the timescale milliseconds. Chapter 3 provides the first observation and X-ray diffraction proof of irreversible *cis*-*trans* crystal-to-crystal isomerization in azobenzenes by utilizing the newly discovered perhalogenated chromophores with an ultra-long-lived *cis*-state. Such solid state photoisomerization is accompanied by a controllable and thermally irreversible change of crystal shape, which was the first observation of such permanent photo-mechanical modification in a crystal of azobenzene chromophores. Chapter 4 builds on this discovery and presents a cocrystallization strategy to develop better photo-mechanical cocrystals. As a result, the best photo-mechanical cocrystals allowed a study of the mechanism of the transformation *in situ* and confirmed unambiguously that isomerization in the crystals of azobenzenes proceeds through an amorphous intermediate and in a topotactic manner.

While the observations of motion of single crystals is an extremely curious phenomenon, it poses a question of how to predictably assemble chromophores in the crystal that ensures photomechanical behaviour. Chapter 5 reports a new supramolecular interaction between the azo group and a fluorinated phenyl group that directs the assembly of various fluorinated azobenzenes into 'pringle chip'-like stacks. The interaction persists in the halogen-bonded cocrystals of such azobenzenes, which allows one to arrange aliphatic and aromatic halogen bond acceptor molecules in a columnar fashion. Chapter 6 continues the crystal engineering efforts, but from a different perspective. Combining the linear nature of the azobenzene chromophore and high directionality of the halogen bond it reports the first deliberate formation of highly dichroic molecular crystals prepared by design. Chapter 7 reports unexpected reactivity in fluorinated azobenzenes, which allows one to prepare highly strained azobenzenes with bulky morpholine substituents in *ortho*-positions. The resulting molecules are unusually strained, as terminal phenyl rings of the azobenzene unit adopt a mutually nearly completely orthogonal orientation. Such heavily substituted azobenzenes serve as useful building blocks in crystal engineering by serving as halogen bond donors and acceptors simultaneously.

#### Résumé

Cette thèse apporte des contributions dans les domaines de l'effet photomécanique et de l'ingénierie de cristal de cristaux d'azobenzène. Effet photomécanique est un phénomène important qui traite de la transformation directe de la lumière en mouvement mécanique par les matériaux incorporant des molécules photoactives. Seulement récemment, il a été réalisé qu'une fois pensée chimiquement et mécaniquement, des monocristaux inertes peuvent, en fait, montrer un mouvement en réponse à une irradiation lumineuse. L'azobenzène, qui est une molécule de choix pour les matériaux photomécaniques, a été peu exploré dans les cristaux avant ce travail.

La contribution du chapitre 2 réside dans l'observation des mouvements photo-induits dans des monocristaux de pseudostilbènes, qui sont des dérivés azobenzène avec des durées de vie très courtes thermiques de l'état-cis. L'étude a fourni un aperçu de la dépendance structurelle de ce processus à l'état solide réversible. Les flexions de cristaux, qui peuvent être initiées par différentes longueurs d'onde de la lumière visible, révèlent être entièrement réversible à la température ambiante et l'éclairage ambiant sur une échelle de temps en millisecondes. Le chapitre 3 fournit la première observation et preuve de isomérisation irréversibles de *cis*→*trans* cristal à cristal par diffraction des rayons-X en utilisant les azobenzènes perhalogénés nouvellement découverts avec l'état-cis ayant une ultra-longue durée de vie. Cette photoisomérisation dans l'état solide est accompagnée par le changement contrôlable et thermiquement irréversible de la forme des cristaux, qui était la première observation d'une telle modification photomécanique permanente dans un cristal d'azobenzène. Chapitre 4 repose sur cette découverte et présente la stratégie de cocristallisation de développer de meilleurs cocristaux photomécaniques. Par conséquent, les meilleurs cocristaux photomécaniques ont permis d'étudier le mécanisme de la transformation in situ et de confirmer sans ambiguïté que l'isomérisation dans les cristaux se produit à travers un azobenzènes intermédiaire amorphe et d'une manière topotactique.

Bien que les observations du mouvement des monocristaux est un phénomène extrêmement curieux, il pose une question de comment assembler de manière prévisible les chromophores dans un cristal qui assure un comportement photomécanique. Chapitre 5 signale une nouvelle interaction supramoléculaire entre le groupe azoïque et le groupe phényle fluoré qui dirige l'ensemble des différents azobenzene fluoré en «piles de chip» comme Pringle. L'interaction persiste dans les cocristaux halogènes liés de ces azobenzènes, ce qui permet d'organiser des molécules par liaison halogène entre accepteurs aliphatiques et aromatiques en colonne. Chapitre 6 poursuit les efforts d'ingénierie de cristal, mais dans une perspective différente. Combinant la nature linéaire du chromophore azobenzène et directivité élevée de la liaison halogène, il signale la première formation voulue de cristaux moléculaires hautement dichroïques. Chapitre 7 rapporte la réactivité inattendue des azobenzènes fluorés, ce qui permet de préparer des azobenzènes très tendues avec des substituants de morpholine encombrant les positions ortho. Les molécules résultantes sont exceptionnellement tendues comme noyaux phényle terminaux ou l'unité d'azobenzène adoptent mutuellement une orientation presque complètement orthogonal. Ces azobenzènes fortement substitués servent de blocs de construction utiles pour l'effort d'ingénierie de cristal en se servant simultanément de donneurs de liaison halogène et accepteurs.

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#### **Preface & Contributions of Authors**

The main body of this thesis consists of six research chapters (Chapter 2-7). All of the chapters have been published therefore they are presented in their respective paper format ending with an appendix containing the supporting information for the papers. Chapter 1 (Introduction) was written entirely by Oleksandr S. Bushuyev, and part of the chapter (the section on photomechanical motion) was published in *ACS Nano* **2015**, *9*, 7746-7768 and is presented here in its reprinted (adapted) form with permission from: Abendroth, J. M.; Bushuyev, O. S.; Weiss, P. S.; Barrett, C. J. Copyright 2015 American Chemical Society. The photo-mechanical section of the article was written entirely by Oleksandr S. Bushuyev, Drs. Weiss and Barrett helped in final editing and manuscript preparation.

## Chapter 2. Fast, Reversible, and General Photo-Mechanical Motion in Single Crystals of Various Azo Compounds Using Visible Light

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All project design, synthesis, material preparation and X-ray analysis was conducted by Oleksandr S. Bushuyev, Thomas A. Singleton advised on best practices of laser experiments and helped with initial laser set-up. Dr. Barrett helped in final editing and manuscript preparation.

## Chapter 3. Shaping Crystals with Light: Crystal-to-Crystal Isomerization and Photo-Mechanical Effects in Fluorinated Azobenzenes

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## Chapter 4. Photo-Mechanical Azobenzene Cocrystals and *in situ* X-ray Diffraction Monitoring of their Optically-Induced Crystal-to-Crystal Isomerization

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# Chapter 5. Azo…Phenyl Stacking: a Persistent Self-Assembly Motif Guides the Assembly of Fluorinated *cis*-Azobenzenes into Photo-Mechanical Needle Crystals

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All project design, synthesis, material preparation, crystal transmittance studies, X-ray analyses was conducted by Oleksandr S. Bushuyev, Anna Tomberg performed theoretical calculations, Joanna R. Vinden synthesized some of the studied chromophores, Drs. Moitessier, Barrett and Friščić helped in final editing and manuscript preparation.

## Chapter 6. Controlling Dichroism of Molecular Crystals by Cocrystallization

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## Chapter 7. Fluorinated Azobenzenes with Highly Strained Geometries for Halogen Bond-Driven Self-Assembly

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All project design, synthesis, material preparation, and X-ray analyses was conducted by Oleksandr S. Bushuyev, Davin Tan performed theoretical calculations, Drs. Barrett and Friščić helped in final editing and manuscript preparation.

## **Chapter 1: Introduction**

#### 1.1 Molecular Photoswitches for Smart Functional Materials

One of the key goals of materials science is the design of smart, functional materials, which perform a function when acted upon by a defined stimulus. Visible light is oftentimes a preferred stimulus due to its non-invasive nature, tunability and ease of spatial and temporal control. A general strategy to prepare a material responsive to visible light is to incorporate light-responsive photochromic or photoswitching molecules into a passive material matrix. Common photoswitches utilized to this end include azobenzenes,<sup>1</sup> diarylethenes,<sup>2</sup> spiropyrans,<sup>3</sup> hydrazones,<sup>4</sup> furylfulgides,<sup>5</sup> etc. (**Figure 1.1**), each of them presenting a certain set of advantages and drawbacks.



**Figure 1.1.** Examples of common small-molecule switch isomerization reactions: a) azobenzene; b) diarylethene; c) spiropyran.

Despite the diversity of chemical structures of these chromophores, their common unifying characteristic is the ability to function as molecular switches. All of these molecules possess two stable states addressable and interconvertible by light, and thus can equip a material with unique properties. Some of the applications of photochromic materials may include optical switching, information and energy storage, holography, or a photo-induced shape change, known as the photo-mechanical effect. A leading photochromic molecule for light-responsive materials research that will be discussed in detail in the following chapters is azobenzene and its derivatives. Azobenzene is a popular photoswitching molecule owing to its high extinction coefficient, stability, and favourable fatigue resistance.

#### 1.2 Azobenzene

Azobenzene is an organic molecule composed of two phenyl rings linked together by the azo group. By varying the substituents in the conjugated structure the absorption of azobenzene can span the electromagnetic spectrum from ultraviolet (UV) to near-infrared (NIR) wavelengths. Azobenzene has been known for almost two centuries,<sup>6</sup> and up until now has been a major chromophore utilized by the dyes and pigments industry and is a base for many acid-base pH indicators.<sup>7</sup> What sets azobenzene apart from most of the other chromophores is its ability to isomerize from a thermally stable *trans*-form to a metastable *cis*-form upon absorption of a single photon of light.<sup>8</sup> The reaction is clean and occurs without a build-up of unwanted side products. Such isomerization proceeds with a dramatic change of geometrical shape of the molecule, resulting in out-of-plane movement of the phenyl rings and contraction of the molecule of nearly 40% along its longest linear dimension.<sup>9-11</sup> The isomerization can be reversed thermally or by absorption of a photon of different frequency. Clean, reversible and fatigue- resistant *trans-cis* azobenzene isomerization, which allows the molecule to function as a molecular photoswitch, has propelled the azobenzene molecule to the forefront of this area of materials science research.

#### 1.2.1 Azobenzene Isomerization

The first observation of azobenzene isomerization (**Figure 1.2**) dates back to experiments by Hartley, who noticed that upon exposure to light the solubility and molar extinction coefficient of a sample was changed. He posited that the observed change was due to the isomerization of the molecule to a *cis*-form and measured the dipole moment (*ca.* 3 Debye).<sup>12</sup> The isomerization event occurs by absorption of a photon of light corresponding to either of the highest occupied orbitals of azobenzene molecule, which are  $\pi$ , or n-orbitals. In both cases the electron is promoted to the  $\pi^*$  orbital.<sup>13</sup> For the parent centrosymmetric azobenzene molecule the  $n \rightarrow \pi^*$  transition is symmetry forbidden and consequently weak, while the  $\pi \rightarrow \pi^*$  is prominent. While most of its derivatives are centrosymmetric, the relative strength of the  $n \rightarrow \pi^*$  transitions for *trans*- and *cis*-isomers effectively overlap. While high degrees of conversion are often possible for *trans*-*cis* isomerization, the overlap of  $n \rightarrow \pi^*$  means the reverse process is incomplete and most of the times the *trans*-isomer is recovered *via* thermal relaxation.



**Figure 1.2** Azobenzene isomerization showing both isomers of the azobenzene chromophore. Planar t*rans*-azobenzene has no net dipole moment while *cis*-azobenzene has a dipole moment of 3 Debye.

For a long time azobenzenes were classified into three discreet spectral classes proposed by Rau: azobenzene-type, which included chromophores with the longest half-lives of the *cis*-form (on the timescale of hours), aminoazobenzenes (lifetime of minutes and redshifted absorbance) and pseudostilbenes (milliseconds to microseconds and even more redshifted absorbance).<sup>14</sup> Structurally the three classes broadly implied the lack of strong electron donating or withdrawing substituents for azobenzene-type, presence of one (generally donating) for aminoazobenzene-type and presence of both electron-donating and withdrawing ('push-pull') substituents for the pseudostilbene-type. Energetic differences between the azobenzene and pseudostilbene classes are demonstrated in **Figure 1.3**. Introduction of push-pull substituents results in a simultaneous lowering of the LUMO energy and an increase of  $\pi$  orbital energy levels resulting in near coalescence of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions and concomitantly dramatically decreases the thermal half-life of the *cis*-form. While convenient for certain applications, the discovery of new chromophores with absorbance maxima shifted far in the red region, or exhibiting lifetimes of years, limits the utility of the original classification.<sup>15</sup>



**Figure 1.3** Representation of HOMO-1, HOMO, and LUMO, transition energies, and oscillator strengths for  $n-\pi^*$  and  $\pi-\pi^*$  transitions for azobenzene and 4-dimethylamino-4'-nitroazobenzene calculated using the TDDFT/B3LYP/6-31G(d) method. Figure reproduced with permission from ref. 13. Copyright 2006 American Chemical Society.

#### **1.2.2** Thermal Lifetime of the *cis*-Isomer

For many practical applications an important characteristic of a photo-active molecule is its ability to function as a bistable switch. Thermal stability of azobenzene photoswitches might then limit their practical utility. The first attempts to stabilize the cis-form and enhance thermal stability of azobenzenes involved steric considerations, and these attempts were focused primarily on creating steric bulk around the azo group or forcing the *cis*-geometry by various constraints.<sup>16</sup> In this vein, two investigations merit attention. Siewertsen et al. discovered that a bridged azobenzene derivative 5,6-dihydrodibenzo[c,g][1,2]diazocine exhibited highly unusual behaviour.<sup>17</sup> Unlike most other azobenzenes for which the *trans*-form was energetically preferred, in the strained bridged configuration the cis-isomer was more stable. The half-life of the less stable *trans*-isomer was 5 hours, while the ring strain also resulted in the significant separation of  $n \rightarrow \pi^*$ absorption maxima and allowed switching between the isomers with near quantitative efficiency. Beharry *et al.* reported a photoswitch possessing *ortho*-methoxy groups sporting the half-life of 14 days capable of switching both ways under visible light.<sup>15</sup> It was estimated that the proximity of oxygen atoms of methoxy groups was raising the energy of the HOMO and resulting in good  $n \rightarrow \pi^*$ separation. A similar type of approach, involving electronic stabilization was put forth by Blegér et al. and consisted of the incorporation of fluorine atoms in the ortho-position of the azobenzene phenyl rings (Figure 1.4).<sup>18</sup>

Reasoning that reduction of n-electron density on the azo group would lead to lower orbital energy, the researchers introduced *ortho*-fluorine atoms into the azobenzene structure. The resulting tetrafluoroazobenzene photoswitch had a thermal half-life of ca. 700 days, producing the first bistable azobenzene photoswitch. Furthermore, over 50 nm spectral separation between the  $n\rightarrow\pi^*$  absorption maxima for *trans*- and *cis*-forms was observed, which allowed such molecules to be switched with over 90% efficiencies by blue and green light. Thermally stable orthofluoroazobenzenes are central to this Thesis and will feature in various capacities throughout Chapers 3–7.


**Figure 1.4** a) Chemical structure of tetrafluoroazobenzene; b) and c) Energetic diagram of n,  $\pi$ , and  $\pi^*$  orbitals for the parent azobenzene molecule and tetrafluoroazobenzene calculated at the B3LYP/6-31G(d) level of theory with arrows representing the n $\rightarrow\pi^*$  transition. Figure reproduced with permission from ref. 18. Copyright 2014 American Chemical Society.

## **1.2.3** Optical Properties of Azobenzene

Owing to the linear rod-shape of the *trans*-isomer of azobenzene, the molecule interacts with polarized light, demonstrating strong dichroism and birefringence. While the effect is not easily observed in the studies of azobenzenes in solution, it was investigated in the polymeric matrices. Uznanski *et al.* studied azobenzene incorporated into the matrix of polyethylene films.<sup>19</sup> Upon mechanical stretching of the film azobenzene molecules become aligned along the stretch direction. This allowed for the determination of the orientation of transition dipole moments of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions and for the first time definitively showing that their direction closely followed the molecular axis and N=N group orientations. For the bent *cis*-azobenzene the polarization of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition dipole moments was found to be mutually perpendicular.<sup>20</sup> Such properties of azobenzene molecules gave rise to numerous investigations and even entire fields of study. Specifically, combining the dichroic properties and light induced photoisomerization azobenzenes quickly became a molecule of choice for the development of materials for polarization holography.<sup>21</sup> Optically induced birefringence patterns were studied in various materials for information storage applications.<sup>22</sup> One of the solutions — Verbatim CD-R

was even for a limited time exploited commercially. Studies of birefringence in azobenzenecontaining materials were responsible for the discovery of surface mass-transport and photomechanical effects in azobenzenes, which will be discussed in greater detail in Section 1.4. In Chapter 6 of this Thesis we will revisit basic dichroic properties of azobenzene to demonstrate that a permanently dichroic crystalline material can be engineered from azobenzene building blocks.

## **1.3** Crystals of Azobenzenes

Most of the material presented in this Thesis revolves around crystals of azobenzenes. Basic crystallographic information about azobenzene was obtained in 1939 and 1941 with the first crystal structure determination of the parent azobenzene chromophore in *trans* and *cis*-states, respectively.<sup>9,10</sup> Since then and until the beginning of the 21<sup>st</sup> century crystallographic reports on azobenzene derivatives focused on classic structural parameters of crystals without much regard for possible photochemistry. Photoswitching did not seem to occur in crystalline azobenzene samples, which was easily rationalized by the absence of needed free volume for photoisomerization to occur within crystal lattice. Chapters 2-5 of this Thesis demonstrate that photo-induced reactions are in fact possible in certain azobenzene crystals especially if crystals are optimized, or engineered, to maximize the chance of obtaining photo-active crystals. The next section introduces the concepts of crystal engineering as a design tool for crystal growth. Chapters 4, 5 and 6 will exploit crystal engineering tools such as cocrystallization and halogen-bonding to generate new photo-mechanical and optical crystals of azobenzene.

## **1.3.1** Crystal Engineering as a Means to Control Crystal Packing

Crystal engineering is a term that was first introduced in 1956 by Pepinsky,<sup>23</sup> but its origin is more often associated with the work of Schmidt on photochemistry of [2 + 2] photodimerization of *trans*-cinnamic acids.<sup>24</sup> It became apparent to Schmidt that reactive crystals can be engineered because two molecules could be arranged in a position favourable for photodimerization *via* the supramolecular Cl···Cl interactions. In the broadest sense, the goal of crystal engineering is to predict and design a functional crystal structure given only a molecular structure as an input.<sup>25</sup> The problem that arises is that crystal structure is an emergent property and is not simply related to

molecular structures or functional groups. An important leap in understanding of crystal packing was made with the introduction of the close-packed principle by Kitaigorodskii, who stated that assembly of a crystal structure was to a large extent driven by considerations of size and shape.<sup>26</sup> The work of M.C. Etter highlighted the importance of hydrogen bonding in driving the formation of molecular crystals because of its strength and directionality.<sup>27</sup> Subsequently, G. Desiraju brought together the considerations of size and shape of Kitaigorodskii (physical approach) and directionality of interactions noted by Etter (chemical approach). He stated that minor deviations from close-packing are possible and are in fact of great importance, because they provide insight into the design of crystals and allow the construction of them in a systematic manner.<sup>28</sup> He introduced a concept of a supramolecular synthon as an analogy to synthons of organic synthetic chemistry. Such synthons serve as a handle for the predictable assembly of molecules into crystals.

Attempts to control crystal packing historically mostly involved the utilization of hydrogen bonding,<sup>27</sup> until coordination bonding in metal organic architectures emerged as another useful tool.<sup>29,30</sup> Apart from these two interactions, the toolbox of crystal engineering now consists of forces such as  $\pi \cdots \pi$ -stacking, aurophilic interaction and halogen bonding. Cocrystallization utilizing some of these interactions has been demonstrated to favourably modify solid-state physical and chemical properties of pharmaceutical precursors and was applied in photochemical synthesis.<sup>31,32</sup> From the standpoint of azobenzene research, cocrystallization was attempted utilizing  $\pi \cdots \pi$ -stacking,<sup>33</sup> molecular inclusion,<sup>34</sup> hydrogen<sup>35</sup> and halogen bonding.<sup>36</sup> None of thus prepared cocrystals of azobenzene, however, demonstrated any photochemical activity nor incorporated *cis*-isomers.

# **1.3.2 Halogen Bonding**

Arguably one of the least explored strong directional supramolecular interactions for crystal engineering applications is the halogen bond. It represents an attractive interaction between an electrophilic halogen atom and a Lewis base, where the internuclear distance between the two interacting parties is less than the sum of their van der Waals radii. Curiously, the existence of halogen bonds was noted even prior to the very first synthesis of azobenzene, when in 1814 a complex of iodine and ammonia was observed.<sup>37</sup> The prominent property of a halogen bond is its

linearity, as the angle between two interacting molecules typically lies in the range of 175-180°. In strength a halogen bond is comparable to a hydrogen bond with energies up to 200 kJmol<sup>-1</sup>.<sup>38</sup>

The (near) linearity of a halogen bond is explained by the  $\sigma$ -hole developing along the C-X bond of the halogen and can be illustrated by the series of CF<sub>3</sub>X molecules (**Figure 1.5**).<sup>39</sup> When fluorine is substituted for Cl in the CF<sub>4</sub> molecule, a positive potential develops on the outermost portion of its surface opposite to the C-Cl axis. This positive region is referred to as a  $\sigma$ -hole in the belt of negative potential around the chlorine atom. Similar but more pronounced positive regions are observed in CF<sub>3</sub>Br and CF<sub>3</sub>I molecules.



**Figure 1.5** Molecular electrostatic potential, in Hartrees, at the 0.001 e/Bohr<sup>-3</sup> isodensity surface of  $CF_3X$  (from left to right, X = F, Cl, Br, I). Reprinted with permission from ref. 39 Copyright 2007 Springer.

It is these regions and their predictable location opposite to the C-X bond that determines the linearity of the halogen bond. The localization of the  $\sigma$ -hole can be explained by considering the electron distribution around a bound halogen atom. In a CF<sub>3</sub>X molecule a halogen atom is bound to a carbon through a  $\sigma$ -bond and also possesses three unshared pairs of electrons. Two of these pairs occupy p-orbitals perpendicular to the C-X axis. The third orbital is essentially of *s*character, with some degree of *p*-hybridization along the C-X axis. Iodine and to a lesser extent bromine and chlorine ensure the lower level of *sp*-hybridization, which means that the unshared electron pairs approximate the configuration of a Cl<sup>+</sup> with an empty p-orbital developing a large positive charge opposite to the C-X bond.

Highly electron-withdrawing substituents, such as F-atoms, increase the size of a  $\sigma$ -hole and consequently increase the propensity towards halogen bonding. Various other molecules, which are activated for halogen bonding, also exhibit  $\sigma$ -holes and thus can be reliably used for crystal engineering purposes. The examples of most successful halogen bond donors utilized by crystal engineers are presented in Figure 1.6.<sup>40</sup>



**Figure 1.6** Examples of strong halogen bond donor molecules: a) diiodotetrafluorobenzene; b) iodopentafluorobenzene; c) dibromotetrafluorobenzene; d) 1-iodoethynyl-4-iodobenzene; e) 1-bromoethynyl-4-bromobenzene.

## **1.4** Photochromism in the Solid State

All of the research chapters of this Thesis deal with various manifestations of photochromism in the solid state. To better contextualize the following content, this section will give a brief overview of different photochromic processes occurring in the solid state that involve molecular and macroscale motion. Photochromism is the reversible transformation of two chemical species between two energetic states caused by absorption of visible light or, in a more broad sense, electromagnetic radiation. In principle, any double-well potential system, or photoswitch, which reversibly cycles between two energetic states by absorption of light is photochromic. Practical photochromic systems do so cleanly without the build up of unwanted side products and possess sufficiently high potential barriers to ensure the stability of both of the energetic states. Some of the most extensively studied small-molecule motifs include (but are far from limited to) azobenzenes, whose isomerization between *E* and *Z* conformations about a double bond mimic flapping motions;<sup>13,14</sup> diarylethenes and spiropyrans, in which conformational changes are accompanied by ring-opening or closing reactions;<sup>15-17</sup> anthracene and coumarin

derivatives that reversibly dimerize with one another;<sup>18-21</sup> and overcrowded alkenes, hydrazones, and imines, which behave as rotors that can revolve about a rigid internal axis.<sup>22,25</sup> Photoswitches are extensively studied in solution where each of the isomerization reactions can be considered to occur independently. The focus of this section, however, is the reversible transformation of photochromic molecules in the solid state, when they are incorporated into an amorphous polymer matrix, liquid crystalline (LC) elastomers, or single crystals.

Since two different energetic states of photoswitching molecules are generally differently coloured, photochromism in the narrow sense means the change of colour of a material upon absorption of electromagnetic radiation. The effect can be accompanied by a change of other parameters such as electrical or thermal conductivity, transparency, loss of order etc. At the same time, chemical isomerization between two energetic states brings about motion. In order for a molecule to change conformation, movement of a part or of a whole molecule has to occur. Such molecular motion may be carefully engineered and harnessed to produce a useful function and makes solid state photochromism an extremely useful phenomenon. Depending on whether the function is performed on a micro, meso or macroscopic scale different phenomena may be observed. They are studied in materials chemistry as molecular machines, surface mass-transport, switchable network materials or photo-mechanical materials.

## 1.4.1 Surface Mass-Transport and Phase Change Effects

Studies of light-induced birefringence for optical storage applications briefly discussed in section 1.2.3 gave rise to an all new direction in photo-induced patterning of the surfaces. Two independent investigations nearly simultaneously observed formation of large-scale patterns on the Disperse Red 1 (DR1) surface irradiated with a light interference pattern.<sup>41,42</sup> The experiments involved the intersection of two coherent laser beams with a wavelength corresponding to the DR1 absorption band at the surface of the thin flat sample. The interference of the two beams resulted in translation of a sinusoidal pattern to the surface of the material. The effect was called surface relief grating (SRG) formation, but in a broad sense it represents a manifestation of photo-induced transport of the material. The typical depth of the spin-cast azobenzene-containing layers for SRG generation experiments was 10-1000 nm and the magnitude of the gratings observed reached hundreds of nanometers (**Figure 1.7**).



**Figure 1.7** Example of a surface relief grating (SRG) produced on an azo-polymer film. Grating amplitudes comparable to the original film thickness were achievable. Figure reproduced with permission from ref. 43. Copyright 2012 Springer Publishing Company.

Importantly, the SRG formation was initiated at room temperature well below the  $T_g$  of the material and the grating could be removed by heating above the  $T_g$ . The observed mass transport effects required the presence of photo-switchable azobenzene chromophores. Efficient diffraction of photo-generated SRGs warranted their further extensive studies as all optically-patterned materials.<sup>43-46</sup>

Mass-transport effects are not limited to the polymeric azo materials, but can also occur in crystals of photochromic molecules. Primarily, such observations represent directional melting and crystal growth as well as self-propulsion in a medium. A first entry into this field was provided by Milam *et al.* with the observation of swimming, sinking, and stationary azobenzene crystals in a triacrylate solution.<sup>47</sup> The motility was rationalized by the creation of concentration/surface tension gradients around the crystal/liquid interface upon the exclusion of triacrylate solvent from the growing crystal front. More recently, Hoshino *et al.* demonstrated how irradiation induced *trans-cis* conversion in crystals of azobenzenes can lead to directed melting by UV light by careful choice of the position and identity of a substituent on the azobenzene core (**Figure 1.8**) and utilized this phase transition to selectively pattern copper surfaces.<sup>49</sup>



**Figure 1.8** a) Structures and b) photographs of the crystalline powders of azobenzenes utilized in the study; c) The same powders after irradiation with 365 nm light for 30 mins at 100 mW cm<sup>-2</sup>. Figure reproduced with permission from ref. 49. Copyright 2014 American Chemical Society.

These observations once again proved the feasibility of reversible *trans-cis* azobenzene isomerization in carefully tailored single crystals. The observation of light-mediated melting also led to a completely new phenomenon — apparent directional 'crawling' of single crystals on a glass surface driven by the melting transition. Upon simultaneous visible and UV irradiation, single crystals of *trans-3,3*'-dimethylazobenzene 'crawl' along the flat glass surface (and even vertically) away from the UV light source (**Figure 1.9**).<sup>50</sup>



**Figure 1.9** a) and b) Motion of single crystals of *trans*-3,3'-dimethylazobenzene on the glass surface; c) Schematic representation of the irradiation setup; d-i) Microscope images for translational motion of *trans*-3,3'-dimethylazobenzene after irradiation time, *t*, min 0 (d), 3 (b), 6 (f), 10 (g), 15 (h), 20 (b) White and blue dashed lines represent the initial positions of crystals and droplets, respectively. Figure reproduced with permission from ref. 50. Copyright 2015 Nature Publishing Group.

The motion is driven by melting and crystallization of the crystals at the front and rear edge and while the shape of the crystal continuously changes, the optical axis remains constant. Meltingdriven motility of crystals is an important step in the development of self-propelled objects<sup>51,52</sup> and enhances the understanding of the crawling phenomena already observed in photochromic azobenzene-containing glasses and polymers.<sup>53,54</sup> Such directed surface transport of azobenzene materials is a complimentary (and inverted) observation of the liquid mass-transport on the surface of azobenzene functionalized surfaces pioneered by Ichimura *et al.*<sup>55-57</sup>

#### 1.4.2 Photochromic Reactions in Framework Architectures

A new avenue of research in solid-state photochromic reactions started with the development of metal-organic frameworks (MOFs) and similar network-type crystalline systems.<sup>58</sup> Specifically, upon realizing that MOFs can survive relatively harsh environments and are capable of post-functionalization while retaining tremendous surface area,<sup>59,60</sup> efforts were made to prepare and study photoswitchable MOFs with the goal of carbon dioxide absorption (**Figure 1.10**).<sup>61,62</sup> Following the idea that azobenzene molecules can only isomerize when used as pendant groups on linkers, photo-active MOFs were prepared and successfully tested to regulate methane absorption.<sup>63</sup> The azobenzene chromophore usually does not act as a truly bistable switch as the lifetime of the *cis*-form is usually short. Recently, however, the Hecht group has reported *o*-fluorinated azobenzenes which have *cis*-form lifetimes of over 2 years in solution.<sup>18</sup> Castellanos *et al.* utilized such fluorinated azobenzenes to prepare a MOF which is addressable by green and blue light and has potential as a bistable gas storing material.<sup>64</sup>

A simple and elegant approach to photo-switchable gas absorption in MOFs was proposed by Lyndon *et al.* Instead of covalent modification of a MOF or a linker unit, they opted for postsynthetic treatment of the surface of a MOF by methyl red azobenzene dye. The dye would coat the surface and prevent absorption of CO<sub>2</sub> inside the MOF.<sup>65</sup> However, upon irradiation the pores would open and the MOF would be ready to absorb CO<sub>2</sub>. In the same vein, photochromism of azobenzene molecules inside the pores of a MOF was shown by the Kitagawa group to direct structural changes in the network and as a consequence regulate gas sorption.<sup>66</sup> Incorporation of the azobenzene chromophore as a guest molecule into the network lead to a phase change of the network from tetragonal to orthorhombic crystal system upon UV-irradiation, which resulted in drastically different uptake profiles. Whereas most of the research is performed under the assumption that switching of azobenzene is only possible in a MOF when chromophores are used as pendant groups,<sup>62</sup> a recent report by Baroncini *et al.* may warrant a closer inspection of this idea. Tetrameric star-shaped azobenzene molecules assemble a porous network and then undergo reversible isomerization aided by partial amorphization of the sample.<sup>67</sup> The isomerization in turn changes the porosity and consequently the gas uptake of the network.



Figure 1.10 (Top) Isomerization of the azobenzene ligand within a MOF PCN-123. (Bottom) Schematic illustration of  $CO_2$  uptake in the parent MOF-5 structure and PCN-123 network in a *trans*- and *cis*-states. Figure reproduced with permission from ref. 61. Copyright 2012 American Chemical Society.

While most of the effort in photo-responsive MOFs was directed towards the study of azobenzene type chromophores, Walton *et al.* produced photochromic architectures utilizing diarylethene-type chromophores.<sup>68,69</sup> Irradiation of a crystal of the UBMOF-1 with UV light would turn the crystal red, indicating a successful ring closure reaction of the diarylethene chromophore. However, unlike in the work of Irie *et al* on photochromic crystals,<sup>70</sup> when diarylethene photochromes are introduced into the MOF scaffold the reverse reaction can only take place upon digestion of the MOF into its constituents by a strong acid. The reversible switching of a diarylethene unit inside a network was since achieved by Luo *et al.*, which allowed light-triggered desorption of up to 75% of CO<sub>2</sub> upon UV and visible irradiation.<sup>71</sup>

## 1.4.3 Azobenzene-Powered Molecular Machines

A recent definition states that a molecular machine is a multicomponent system with defined energy input that is capable of performing a measureable and useful secondary function either at the nanoscale, or if amplified through collective action, at the macroscale.<sup>72</sup> The system should ideally act in a reversible manner, with the capacity to complete repeated mechanical

operations. Spatial and temporal control over this motion, and work performed, are further hallmarks of successful machines.

The integration of switchable molecular systems with inorganic nanostructures and nanoparticle assemblies enables the manipulation of the optical properties of the hybrid materials in situ. Two common methods to direct the optical properties of nanostructured materials are the active tuning of refractive indices at the surface of plasmonic nanoparticles functionalized with switchable molecules,<sup>73-75</sup> and physically modulating interparticle distances or orientations.<sup>76</sup> The intelligent functionalization of larger organic or inorganic nanostructures with small molecular switch and rotor components expands the versatility of these dynamic systems for applications such as drug delivery and to tune the chemical and physical properties of the hybrid materials.<sup>77,78</sup> Exemplary demonstrations of artificial molecular machinery that employ functionalized nanostructures are mesoporous nanocrystals modified with molecular nano-impellers, valves, or gates for the capture and release of cargo with external control.<sup>79</sup> Numerous switch motifs have been utilized as gatekeepers to control payload release from these versatile materials including coumarins,<sup>80,81</sup> and azobenzenes.<sup>82,83</sup> Besides the necessity for biocompatibility, tissue specificity, and high loading capability, to implement these systems in vivo for biomedical applications such as controlled drug release, non-invasive actuation mechanisms are also required because some stimuli may be detrimental to biological environments.<sup>84</sup> In a recent example, a nano-impeller system developed by Croissant et al. utilizes azobenzene photoisomerization as a driving force to release the anti-cancer drug camptothecin from mesoporous silica nanoparticles (Figure 1.11).<sup>85</sup> Contrary to classic designs in which azobenzene trans to cis isomerization is triggered by UV light which is harmful to living cells, this prototype system is based on two-photon excitation (TPE) of a fluorophore with NIR light. The use of NIR light facilitates isomerization of the azobenzene moieties through Förster resonance energy transfer (FRET) from a nearby fluorophore. Isomerization of the azobenzene nano-impellers subsequently kicks out the camptothecin cargo, leading to cancer cell death in vitro.



**Figure 1.11** Two-photon excitation (TPE) of a fluorophore to facilitate Förster resonance energy transfer (FRET) to photoizomerize azobenzene nanoimpellers on mesoporous silica nanocrystals, and subsequent cargo release. (a) Overlap of the emission spectrum of the fluorophore and absorption spectrum of the azobenzene nanoimpeller enables FRET; (b) Structure of the azobenzene moiety; (c) Structure of the two-photon fluorophore. (d) Photoisomerization of azobenzene using two-photon (760 nm) excitation of the fluorophore; (e) Schematic of the mesoporous silica nanocrystal; (f) Transmission electron microscopy image of a single nanocrystal. Light-activated nanovalves that utilize near-infrared irradiation such as this TPEbased mechanism show promise for targeted drug delivery applications, and should be further explored to extend their scope. Figure reproduced with permission from ref 85. Copyright 2013 Wiley.

Using TPE with NIR light to trigger drug release from mesoporous nanoparticles has not yet been extensively explored, but offers the benefits of deeper tissue penetration in the biological spectral window (700-1000 nm), and lower scattering loss.<sup>86,87</sup> The TPE-based designs illustrate how the actuated mechanics of photoswitches can be tailored by their immediate surroundings by coupling simple switches or rotors to their nanostructured environment, provided that the fluorophores have large two-photon absorption cross sections and sufficient emission quantum yields (> 0.5) for FRET.

To leverage the mechanical motion of ensembles of molecules, some directing interaction is mandatory to overcome the chaotic application of force. Similar to Archimedes' need for just a lever and place to stand to move the Earth, a surface may be utilized to instill directionality to harness the power of large numbers of photochromic molecular machines. Two-dimensional coverage by molecular switches and rotors on planar surfaces provides advantages over isolated molecules or functionalized nanoparticles by facilitating the manipulation of physical and chemical properties of a material at the micro-, meso-, and macroscales. For example, through the amplification of collective molecular mechanical motion, the integration of small-molecule switches and rotors into ordered arrays has resulted in dynamic control over the work function, refractive index, and surface wettability.<sup>88-92</sup> Molecular pumps based on host-guest interactions composed of cyclodextrin and azobenzene designed by Sen and coworkers perform such a function by external stimulation with light.<sup>93</sup> These hybrid systems are organized within gels or adsorbed directly on glass substrates (Figure 1.12a,b). Upon UV light absorption, azobenzene molecules isomerize and leave their cyclodextrin hosts. The created cavity is then promptly filled with water molecules. The amplified and collective actions of the multitude of neighboring pumps create a steady flow of fluid around the surface at the rate of *ca*. 2 µm/s (Figure 1.12c,d). The pump can also be activated by chemical stimuli and recharged by visible light irradiation. Despite these impressive examples, there exist few reports of integration of molecular switches and rotors in planar assemblies because of the challenging design rules that accompany surface functionalization, as described below. Self-assembled monolayers (SAMs), Langmuir-Blodget (LB) films, and layer-by-layer (LBL) assemblies are all well-understood organic thin-film technologies that can be utilized to fabricate nanoscale functional surfaces.<sup>94</sup> Within SAMs, intermolecular distances, molecular orientation, and substrate-molecule interactions strongly influence whether assembled switches and rotors retain their functionality due to the varied chemistries of their interfaces.<sup>95</sup>



**Figure 1.12** (a) Schematic of a dual responsive micropump on a glass surface. Light or chemical stimuli may be used to induce fluid flow by a  $\beta$ -cyclodextrin-polyethylene glycol ( $\beta$ -CD-PEG) gel upon isomerization of the azobenzene moiety; (b) Schematic of the direct functionalization of glass surfaces by covalently tethering azobenzene containing molecules. Reversible formation or disassociation of the host/guest complex with  $\alpha$ -cyclodextrin results in fluid pumping; (c) Optical microscopy image of tracer particles in solution above a  $\beta$ -CD-PEG gel on a glass surface before and (d) after irradiation with ultraviolet light for 1 h. Figure reproduced with permission from ref 93. Copyright 2013 American Chemical Society.

Physically and electronically decoupling these functional moieties from surfaces or from neighboring molecules is often necessary to avoid steric constraints or quenching of excited states.<sup>96-98</sup> For example, molecular rotors can be tethered such that the axis of rotation is aligned parallel or perpendicular to the surface, in either altitudinal or azimuthal orientations, respectively. Feringa and coworkers reported the tunable and reversible wettability of gold surfaces modified with SAMs of altitudinal rotors based on light-driven overcrowded alkenes bearing perfluorinated alkyl chains.<sup>99</sup> Taking advantage of unhindered rotation enabled by the superior altitudinal orientation of the rotor units dramatically modified the surface energy with resulting water contact angle changes of as much as 8–22° owing to differences in the orientation of the hydrophobic perfluorobutyl group. The photoconversion efficiency and rotation speed of these surface-bound rotors are still generally lower than for free molecules in solution, highlighting how proper spatial arrangement and sufficient room to rotate are necessary parameters to optimize for these dynamic molecular motifs to retain their large-scale functionality.<sup>100</sup>

## **1.5** Photo-Mechanical Effects

The photo-mechanical effect is the change of shape of a material upon exposure to light and is a property of some materials incorporating light-switchable chromophores. In its essence, it refers to the direct transformation of the energy of visible light into mechanical motion. For ease of observation and with the goal of maximising photo-mechanical efficiency, the materials are generally fabricated into high aspect ratio rods, sheets, or films, forming thin actuators. In most simple terms, actuators are the systems which convert a given type of stimulus, in this case the energy of photons, into mechanical motion. Photo-mechanical effects can be observed in a variety of materials ranging from amorphous polymers to hard and brittle single crystals and can be produced by most known photochromic molecules.

#### **1.5.1** Photo-Mechanical Effects in Amorphous Azo Polymers

Perhaps not surprisingly, the photo-mechanical effect in organic materials was first noted for the azobenzene chromophore. Merian is often credited with the first observation of photo-mechanical effect in azobenzenes, when in 1966 he observed that the azobenzene treated nylon filament shrank upon irradiation with a Xe daylight lamp.<sup>101</sup> The relatively unimpressive overall

contraction of under 0.1% of the original length and complexity of the sample meant that it was not until 1980s that further research into this interesting phenomenon followed. In 1980s Eisenbach prepared poly(ethyl acrylate) networks cross-linked with azobenzene chromophores.<sup>102</sup> The samples experienced photo-induced contraction of around 0.2% upon irradiation with UV light and corresponding expansion after visible light irradiation. In further investigations Matejka *et al.* reported that upon the increase of loading of azobenzene into the material above 5% the photo-induced contraction of nearly 1% was achieved.<sup>103-105</sup>

The requirements of processing to generate materials best suited for scientific research dictated that the materials be prepared in the form of thin films. This is most easily achieved in azobenzene-containing amorphous polymers. Primarily, those offer the possibility to generate free-standing films with varying thickness from nanometre to centimetre scales. In a study of thin films Tanchak and Yager evaluated the photo-mechanical motion of azobenzene containing acrylate polymers. Utilizing atomic force microscopy, *in situ* neutron reflectometry and ellipsometry they observed that photo-mechanical expansion had irreversible and reversible components.<sup>106-108</sup> Upon irradiation, films of thicknesses ranging from 25 to 140 nm would irreversibly expand by 1.5-4%. After that, upon repeating irradiation cycles the films would expand reversibly by 0.6-1.6 %, for many hundreds of cycles without visible film quality deterioration. This marked the first quantification of hysteresis in amorphous azobenzene films and also demonstrated how the extent and direction of photo-mechanical motion could be controlled.

The azobenzene chromophore holds promise for artificial muscles through linear polymerization. By incorporating azobenzene within the main chain of a linear assembly, modest dimensional changes of merely a few Ångströms for each chromophore can result in dramatic changes in the contour length of the polymer. Utilizing this strategy, Gaub and coworkers demonstrated the capability of individual polyazobenzene peptides to perform mechanical work by tethering one end of the chain to a substrate and the other to a flexible cantilever to measure the force exerted by the contracting polymer upon photoisomerization.<sup>109</sup> The extent of polymer deformation, and thus the usefulness of the molecules for opto-mechanical applications, was found to depend on both the conformational rigidity of the backbone and minimization of electronic coupling between azobenzene moieties.<sup>110</sup> The synthesis of rigid-rod polymers that include

azobenzene within a poly(*para*-phenylene) backbone is one strategy to maximize photodeformation, enabling accordion-like compression and extension of chains upon cycling with UV and visible light (**Figure 1.13a**).<sup>111</sup> Lee *et al.* demonstrated that these single-chain polymeric assemblies may even exhibit crawling movements when deposited onto an octadecylaminemodified graphite surface and imaged with scanning force microscopy (**Figure 1.13b**).<sup>112</sup>



**Figure 1.13** (a) Schematic of a main-chain azobenzene-containing polymer (P1;  $R = C_{12}H_{25}$ ) with a poly(*para*-phenylene) backbone. Irradiation with ultraviolet (UV) or visible light facilitates photoisomerization of azobenzene and conversion to the compressed and extended conformations, respectively. Figure reproduced with permission from ref 111. Copyright 2011 Wiley. (b) Scanning force microscopy images of P1 deposited on a modified graphite surface. The polymer crawls along the surface as it contracts upon UV irradiation. Demonstrating control over movement direction, and the functionalization or tethering of the polymer strands to scaffolds may enable the macromolecules to perform work by lifting weights or transporting cargo. Figure reproduced with permission from ref. 112. Copyright 2014 American Chemical Society.

### **1.5.2** Polymers and Liquid Crystals

The main difference between photo-mechanical amorphous polymers and liquidcrystalline elastomers (LCEs) is the order inherent in the assemblies of the latter. While in amorphous azo materials photo-mechanical motion occurs isotropically, in ordered LCEs the direction of actuation can be controlled. In lightly crosslinked LCEs the alignment order of mesogens is coupled to the large scale movement of the whole network. UV-irradiation of azobenzene-containing elastomers disturbs the mesogen alignment in the surface layers of the film due to *trans-cis* isomerization. The introduced disorder generates asymmetric strain and causes the bending of the film. The alignment can be re-established by visible light irradiation and thus the film restores its initial shape. <sup>113,114</sup>

The major advances covered in this section were made possible specifically because of the directionality of motion of LCEs. Firstly, it is possible to utilize linearly polarized light to control the bending direction of poly-domain LCEs as was demonstrated in a seminal report by Yu *et al.*<sup>115</sup> (**Figure 1.14**) The studied film was comprised of many small domains of azobenzene liquid-crystal moieties. The alignment of mesogens was uniform in each domain but macroscopic alignment of domains was random. Upon irradiation with linearly polarized light, absorption of light and concomitant *trans-cis* isomerization only occurred in domains where chromophores were aligned along the direction of polarization. Anisotropic distribution of reacted chromophores led to bending in the direction parallel to the mesogen alignment and direction of polarization. The rotation of the plane of light polarization thus allowed for fine control over the direction of film bending.

While the bending direction in experiments by Yu *et al.* was correlated to mesogen alignment, Priimagi *et al.* demonstrated that the bending direction can also depend on the position of the azobenzene unit inside the crosslinked polymer network.<sup>116</sup> In isostructural LCE films, in which azobenzenes molecules were serving as cross-linkers bending upon UV irradiation proceeds towards visible light. In the same polymer where azobenzene was serving as a side chain, the whole film would move away from UV irradiation. Directional control over movements of azo-containing cross-linked liquid crystalline polymers was also demonstrated in mechanical prototypes. A continuous belt of azobenzene film laminated onto the thin polyethylene (PE) sheet was applied to rotate a set of pulleys by simultaneous UV and visible light irradiation of two

different regions of the film (**Figure 1.15a**). <sup>117</sup> Utilizing the same concept of an azo laminated PE film Yamada *et al.* have demonstrated several other possible device applications.<sup>118</sup>



Figure 1.14 a) Chemical structures of the liquid-crystal monomer (1) and cross-linker (2);
b) Photographs of film bending in different directions in response to irradiation by linearly polarized light of different angles of polarization (white arrows) at 366 nm, and flattening again by visible light longer than 540 nm. Figure reproduced with permission from ref. 115. Copyright 2003 Nature Publishing Group.

Laminating the film in two different positions created a simple arm-like device, which could be addressed separately in two locations. Sequential bending and unbending of the azo-treated segments (**Figure 1.15b**) allowed for precise positioning of the film in space, imitating robotic arm motions. Unidirectional motion was made possible in asymmetrically shaped laminated films with one flat and one sharp edge. The film lying flat on the surface can move forward upon alternate irradiation with UV and visible light, because upon UV exposure the sharp edge acts as a stationary point and pushes the entire film in the extension motion. Upon visible light irradiation, the film retracts from the rear side and flat edge acts as the stationary point while the sharp edge is drawn against the surface.



**Figure 1.15** a) Series of photographs showing the rotation of a light-driven plastic motor with a LCE laminated film moved by simultaneous irradiation with UV and visible light. Figure reproduced with permission from ref. 117 Copyright 2008 Wiley. b) Series of photographs of the flexible 'robotic arm' motion of an azo-LCE laminated film induced by irradiation with UV and visible light. Arrows indicate the direction of light irradiation. Figure reproduced with permission from ref. 118. Copyright 2009 Royal Society of Chemistry.

Fast bending and unbending film motions may also serve as a means to design a high frequency oscillator. White and coworkers have designed such high-frequency photo-driven oscillators capable of achieving oscillation frequencies of up to 270 Hz.<sup>119,120</sup> The key to faster bending was to increase the azobenzene concentration in the polymer, reduce thickness, and attain a mono-domain orientation. Oscillation of azo polymer cantilevers was also possible under a focused beam of sunlight, paving the way for a possible solar light-driven microscopic flying apparatus.

Chemically or physically cross-linked supramolecular assemblies of these linear photomechanical polymers may be envisioned to behave as actuators, to lift weights, and to perform other types of work with greater resistance to deformation fatigue than individual strands.<sup>121</sup> For example, Fang *et al.* reported using a simple melt spinning method to fabricate hydrogen-bonded cross-linked fibers of azobenzene-containing main chain polymers that were prepared *via* a Michael addition reaction (**Figure 1.16**).<sup>122</sup>



**Figure 1.16** a) Synthetic route and chemical structures of acrylate-type azobenzene monomers; b) Supramolecular hydrogen bonding interactions between main-chain polymers to facilitate physical cross-linking; c) Photographs of a polymeric fiber fabricated by simple melt spinning. The fiber reversibly bends upon irradiation with ultraviolet and visible light. The fibers demonstrate robust photodeformation fatigue resistance and high thermal stability, and show promise for applications as photo-mechanical actuators. Figure reproduced with permission from ref. 122. Copyright 2013 American Chemical Society.

These authors also investigated the photo-induced mechanical properties of the fibers, reporting a maximum stress generated by a single fiber of 240 kPa upon UV irradiation at 35 °C. This force is similar to the maximal tension forces of some chemically cross-linked azobenzene containing polymer fibers and even human striated muscles (*ca.* 300 kPa).<sup>123</sup> More recent notable advances in the field of photo-mechanical polymers report the development of more complex movement patterns and designs that respond to a broader range of stimuli with better addressability or spatial precision.<sup>124,125</sup> Katsonis and coworkers, for example, recently described impressive control over the helical motion of azobenzene-containing liquid-crystalline polymer springs, mimicking the extensile function of plant tendrils.<sup>83</sup> (**Figure 1.17**)



**Figure 1.17** Central kink in the mixed helicity ribbon a) incorporating azobenzene chromophore undergoes a piston-like shuttling motion upon irradiation with visible b) and UV c) light. A magnet connected to the kink and is transported and transmits the push-pull shuttling motion to a second magnet placed 10 mm below. Figure reproduced with permission from ref. 83. Copyright 2014 Nature Publishing Group.

Here, helical deformations are pre-programmed by including chiral azobenzene dopants and controlling the relative orientation of the aligned liquid-crystals within each spring, respectively. Chiral dopants induce left-handed or right-handed twists in the liquid crystalline film. Depending on the direction of the cut of such a film it will curl, twist, or do both upon irradiation with light. Complex extensile and contractile coiling and twisting helical motions are possible, and mechanical energy can be exported from the system by the use of a pair of magnets. (**Figure 1.17b,c**)

#### **1.5.3** Thermo- and Photo-Salient Crystals

While polymeric materials offer ease of processing and fabrication, crystalline motifs offer a path to near-perfect three-dimensional arrangements of dynamic molecular building blocks, as well as a facile means to monitor the motion of the crystals using nuclear magnetic resonance (NMR) and X-ray diffraction. Furthermore, energy transduction in crystals is faster and the actuating motion is generally of larger magnitude compared to polymeric assemblies, because rigidly packed molecules have to work as an assembly. In a less-ordered medium, motion of the same molecular switches may be less directionally biased and ultimately less efficient. Often derided as a "chemical cemetery" after Leopold (Lavoslav) Ružička's famous remark, crystal machines have witnessed a remarkable resurgence in recent years with discoveries of controlled or spontaneous actuation, reversible or irreversible movements, and reactivity.<sup>126-128</sup>

Entire crystals of photochromic molecules can serve as actuators and transfer the external stimulus such as light into mechanical energy. Depending on the photo-mechanical response, such crystal actuators can be categorized as photo-salient or photo-mechanical crystals.<sup>129-131</sup> Photo-salient crystals, which exhibit spontaneous actuation (jumping) upon heating or irradiation, are an interesting subset of a more general thermo-salient materials. Thermo-salient crystals developed by Naumov and coworkers harness the energy of polymorphic transformations that occur upon heating in crystals. The effect is driven by extremely rapid anisotropic expansion and contraction of the unit cell axes upon a phase transition that was found to be 10<sup>4</sup> times faster than in regular crystal-to-crystal phase transformations.<sup>132</sup> This class of crystalline compounds is comprised of a diverse range of materials including brominated organic molecules, terephthalic acid, and organometallic complexes.<sup>133,134</sup> Although there exists little directional control or foresight into

which compounds will exhibit the effect, the explosive 'popcorn' crystals nonetheless exhibit impressive centimeter-scale jumping movements that greatly exceed the crystal dimensions. Lightactivated chemical processes within crystals, such as changes in the coordination sites of small ligands or [2+2] cycloaddition reactions have also been shown to result in 'popping' under ultraviolet irradiation.<sup>130,135</sup> Similar to thermo-salient materials, little control is possible over 'popping' crystals and thus their utilization as functional molecular machines is difficult to envisage. To circumvent this problem, Sahoo *et al.* developed smart hybrid materials that incorporate thermo-salient microcrystallites on flexible sodium caseinate films to impart directionality to the crystals' movements.<sup>136</sup> The material represents a successful marriage of crystals with biocompatible polymeric films in one system, combining the benefits of the plasticity of soft polymers and the efficient, fast actuation of leaping crystalline solids.

#### **1.5.4** Photochromic and Photo-Mechanical Crystals

Alternatively, photo-mechanical materials move, bend, twist, or curl when exposed to light. Some of the most promising photo-mechanical crystalline systems for converting light into mechanical work have been proposed by Irie and coworkers and are based on diarylethene photoswitches.<sup>70</sup> Light absorption triggers pericyclic ring-opening and closing reactions of this photoswitch throughout the crystal and is responsible for expansion and contraction, respectively, of the unit cell that consequently leads to photo-mechanical bending of the crystal. Structural studies on crystals of diarylethene derivatives link the initial speed of curvature change to crystal thickness.<sup>137</sup> The bending behaviour is also dependent on the crystallographic face that is irradiated, which could be attributed to differences in molecular packing. While the geometric change that occurs during the isomerization of a single diarylethene photoswitch is modest, the collective action of arrays of molecules in the crystal lattice can produce macroscopic motion. Cleverly engineered, such actuating crystals can perform work pushing or lifting objects many times their weight,<sup>70,138</sup> rotating gears,<sup>139</sup> or acting as an electrical circuit switch (**Figure 1.18**).<sup>140</sup>



**Figure 1.18** Photo-mechanical systems based on diarylethene crystals that convert light into mechanical work. (a) A rod-like crystal pushes a gold micro-particle that is 90 times heavier than the crystal when irradiated with ultraviolet (UV) light. Bending of the crystal pushes the micro-particle up to 30 µm. Figure reproduced with permission from ref. 70. Copyright 2007 Nature Publishing Group. (b) Rotation of gears facilitated by the reversible bending of a crystalline actuator upon UV and visible irradiation. Figure reproduced with permission from ref. 139. Copyright 2012 Wiley. (c) Irradiation of gold-coated diarylethene crystals with UV and visible light enables the ON/OFF photoreversible current switching of an electric circuit. Figure reproduced with permission from ref. 140. Copyright 2015 Royal Society of Chemistry. (d) Superimposed photographs of a crystal cantilever lifting a lead ball with a mass 275 times larger than the crystal upon irradiation with UV light from the underside of the actuator. Figure reproduced with permission from ref. 138. Copyright 2010 American Chemical Society.

Other commonly studied photo-mechanical crystalline architectures are composed of anthracenes or salicylidenephenylethylamine molecules. Bardeen and co-workers investigated the [4+4] dimerization reaction of anthracenes where the photoreaction results in reversible or irreversible twisting of crystalline microribbons.<sup>141,142</sup> The curling and twisting motion may be attributed to strain between spatially distinct reactant and product domains as a result of differential absorption by different regions of the crystal or intrinsic solid-state reaction kinetics.<sup>143</sup> Another crystalline molecular machine was proposed by Koshima *et al.* based on photo-mechanical action in platelike crystals of salicylidenephenylethylamine (**Figure 1.19**).<sup>144</sup>



**Figure 1.19** (a) Photo-induced proton transfer in the *S*-enantiomers of chiral salicylidenephenylethylamines upon keto-enol tautomerism (b) Superimposed photographs of a chiral enol-(*S*)-1 crystal before and after irradiating the top of the crystal actuator with ultraviolet light. The crystalline cantilever achieved 26 nJ of work by lifting a 4.00 mg metal ring a height,  $\delta$ , of 0.65 mm. Various photo-mechanical lifting work was achieved with different enantiomeric compositions within the crystal: the racemic crystal, enol-(*rac*)-1, achieved 59 nJ of work by lifting a weight with mass 300 times larger than that of the crystal (not shown). Figure reproduced with permission from ref. 144. Copyright 2013 Wiley.

These actuators are capable of lifting weights up to 300 times the crystal weight. The motion is linked to geometric changes in the molecules produced upon tautomeric transformation triggered by light absorption and consequent proton migration. Collective reorganization of the molecules within the lattice leads to small uniaxial cell expansion, which in turn results in bending of the crystal.

The workhorse of many photo-mechanical studies, the azobenzene chromophore has been extensively probed on surfaces, in polymers, and within liquid crystals.<sup>145-149</sup> It has been far less studied in the crystalline state however, for photo-mechanical applications. This is due, in part, to the sterically demanding *trans* to *cis* isomerization process which may be impeded in a crystal. Surprisingly, Koshima *et al.* demonstrated reversible photo-mechanical bending of thin *trans*-4-(dimethylamino)azobenzene plates upon ultraviolet irradiation, concluding that isomerization can still occur inside the crystal.<sup>150</sup> That report was followed by a study of thin crystalline plates and needles of pseudostilbenes (azobenzenes with short-lived *cis*-states) which were capable of sub-millisecond bending and relaxation upon irradiation with visible light. The study is presented as Chapter 2 of this Thesis.<sup>151</sup> Pseudostilbene bending crystals offer the fastest speed of bending-relaxation cycles as the whole event can take less than a second and is the only system that completely circumvents the need for ultraviolet light to induce isomerization. More recent reports have focused on elucidating the mechanistic aspects of azobenzene isomerization in crystals focusing on *in situ* X-ray diffraction studies of irreversible *cis-trans* isomerization in crystals (Chapter 3),<sup>152</sup> and cocrystals (Chapter 4),<sup>153</sup> of the molecule.

These reports demonstrated that  $cis \rightarrow trans$  isomerization in crystals is mediated by a transient amorphous state. While the sterically demanding azobenzene isomerization reaction requires considerable free volume to occur and is rarely possible in a single-crystal-to-single-crystal fashion, an amorphization mechanism enables the photochemical reaction to proceed despite the constraints of the crystal lattice. Amorphous intermediates in the crystal were corroborated by the loss of diffraction spots upon irradiation with visible light at low-temperature. Remarkably, isomerization within the crystals of azobenzene represents a topotactic process in which the orientation of the resultant *trans*-crystal phase is dependent on the initial crystal orientation and effectively represents template crystal growth directed by light.

The growing number of investigations on dynamic molecular crystals that can perform as actuators demands new theoretical models. Various models have been reported in the context of polymer films, rods, or plates, such as the analysis derived by Warner and Mahadevan on photodeformation of nematic elastomers.<sup>154</sup> However, careful structural and kinetic considerations based on the spatial density and uniform orientations of photoactive molecules must be taken into account for these models to be fully applicable to crystalline systems. While the molecular motifs responsible for crystal motions are diverse, an attempt to unify photo-mechanical processes was done by Nath *et al.* who proposed a mathematical treatment of photo-mechanical crystal bending by accounting for the gradual profile of the product in the crystal, irradiation time, direction and power using the azobenzene dye, Disperse Red 1, as a model compound.<sup>155</sup> The model is applicable for any photo-mechanical crystal system and allows an easier comparison between the different platforms for efficiency, modulus, stress, and other parameters critical for optimization of the process for practical use. Ultimately, with the help of theoretical frameworks and empirical data, the goal of future development of photo-mechanical systems needs to be directed toward robust and fatigue resistant designs capable for even faster and reliable actuation over thousands of cycles.

#### **1.6** Thesis Scope and Overview

The work presented in this Thesis falls into the context of previous research on photomechanical and optical properties of azobenzene chromophores performed in our group over the last decade. The major difference lies in studying azobenzene in a well-defined crystalline matrix. Chapters 2 and 3 will lay out the possibility of photochemical reactions of azobenzene inside crystals while also highlighting the limitations of crystal growth by traditional techniques. Cocrystallization is the simplest approach to alter crystal properties and Chapter 4 will examine the utility of halogen bond-driven cocrystallization as a design tool for photo-mechanical azobenzene crystals. The crystal engineering approach taken in Chapter 4 will be further expanded upon in Chapter 5 by recognizing and exploiting a new supramolecular interaction enabled by fluorination of *cis*-azobenzenes. Chapter 6 will build on the crystal engineering efforts developed previously to propose a cocrystallization-driven approach to control optical properties of molecular crystals of *trans*-azobenzenes *via* halogen bonding. In conclusion, Chapter 7 will highlight the possibility of designing polydentate halogen bond donor and acceptor ligands by simple room temperature substitution reactions.

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# Rationale for Chapter 2: Fast, Reversible, and General Photo-Mechanical Motion in Single Crystals of Various Azo Compounds Using Visible Light

Investigation of photo-mechanical motion in the solid state is a fascinating topic in materials chemistry, and the azobenzene chromophore is the cornerstone molecule of the field. Suprisingly though, since almost all of the studies were performed with amorphous polymeric or liquid crystalline materials very little evidence about azobenzene isomerizations in the ordered crystalline phase existed in the literature. It was with the goal of filling the gaps in the understanding of photo-mechanical motion of azobenzene materials that the study presented in the following chapter was conceived. The contribution 'Fast, Reversible, and General Photomechanical Motion in Single Crystals of Various Azo Compounds Using Visible Light' that was published in *Advanced Materials* provides insight that the isomerization of azobenzenes is in fact possible in crystalline materials and can produce fast milli- or micro-second scale motions of thin organic crystals upon irradiation with visible light.



# Chapter 2: Fast, Reversible, and General Photo-Mechanical Motion in Single Crystals of Various Azo Compounds Using Visible Light

#### 2.1 Abstract

Examination of single crystals of six azobenzene derivatives demonstrates that all undergo photo-mechanical motion given appropriate stimulus. This general, fast and reversible bending was observed for the first time using only visible light as the transformation source. The process was characterized by single crystal XRD measurements which provide insight into the structural dependence of this reversible solid state process. The bending is conveniently initiated by various wavelengths of visible light and is fully reversible at room temperature and ambient illumination on the timescale of fractions of seconds. The motion was quantified by rate and deflection angle with respect to irradiation intensity, and correlated to the solid state structure of the compounds. High quality single crystal structure determination for several azobenzene derivatives was also performed for the first time.

# 2.2 Introduction

Harnessing molecular motion to reversibly control macroscopic properties such as shape and size is a subject of much current interest in the scientific and engineering research communities. Various clever systems have been designed to exploit this motion at the nanoscale yielding new classes of smart materials including molecular switches,<sup>1</sup> motors,<sup>2</sup> and even 'nanocars',<sup>3</sup> each driven by some external stimuli such as chemicals, heat or electromagnetic fields. Light-activated materials are especially interesting due to ongoing parallel research into alternative materials for solar energy harvesting,<sup>4</sup> with molecular chromophores being designed to respond to light sources that mimic solar wavelengths and intensities.<sup>5</sup> Here, we demonstrate how to convert the concerted, fast, visible light-induced molecular isomerization to an easily-observable reversible motion of various macroscopic azobenzene and pseudostilbene single crystals (**Figure 2.1**).



**Figure 2.1** 4-diethylamino-4'-nitroazobenzene microcrystal ( $700 \times 600 \times 2 \mu m$ ) exhibits fast reversible photo-mechanical motion upon irradiation of the (001) face with visible light. The scale bar is 200  $\mu m$ . Molecular geometry was optimized by molecular mechanics using the universal force field algorithm in Avogadro 1.03.

Photo-mechanical motion in bulk crystalline materials was first observed recently, most notably in a reversible shape and colour change of diarylethene crystals,<sup>6</sup> where the visible structural change was initiated by a pericyclic ring opening/closing reaction, and photoelongation of crystals of anthracene derivatives due to reversible [4 + 4] photodimerization.<sup>7</sup> Subsequent investigations followed, including studies of diarylethene cocrystals,<sup>8</sup> twisting of anthracene ester crystals,<sup>9</sup> and a salicylideneaniline system,<sup>10</sup> where shape change was governed by intramolecular proton migration under irradiation. It was postulated that the especially dramatic and facile photomechanical motion of diarylethene crystals arises from the relatively small free volume change of the transition state of the ring opening/closing reaction. Azobenzene trans-cis isomerization requires a much greater free volume change (between 120 and 250 Å<sup>3</sup>)<sup>11</sup> and thus harnessing such isomerization in the solid state poses a greater challenge. However, the examples of amorphous soft 'plastic motors'<sup>12</sup> and multiple photochromic effects in azobenzene functionalized polymer films<sup>13</sup> and liquid-crystalline actuators<sup>14</sup> suggested that *trans-cis* isomerization at least in the surface layers in the crystalline state was also feasible. The observation of photo-mechanical crystal bending of two azobenzene derivatives was indeed reported<sup>15</sup> with displacement magnitudes comparable to those of the other systems mentioned above.

# 2.3 Results and Discussion

# 2.3.1 Advantages of Visible Light Irradiation

One of the limitations of previous crystal photo-mechanical systems, however, was their reliance on high energy ultraviolet light for driving the underlying molecular transformation, whether it is a pericyclic reaction, *trans-cis* isomerization or proton migration. Using lower energy visible light is preferable since it is far less damaging to organic molecules, and comprises a larger portion of the solar spectrum available. Furthermore, the length of the photo-mechanical cycle (from the beginning of irradiation until the crystal returns to its original shape) for previously reported azobenzene crystals was on the order of minutes,15 consistent with the rates usual for this spectral class of dyes, which limits many practical applications. With azobenzene chromophores, however, the absorbance maximum can be easily red-shifted by substitution. A special case, where a strong 'pull' electron withdrawing group is combined with a strong 'push' donor gives rise to a class of azo molecules known as *pseudostilbenes*, which are characterized by comparatively short lifetimes of the *cis*-isomer, down to milliseconds, as well as absorption maxima in the visible spectrum deep into the blue or green.<sup>16</sup> In this paper, we establish that the electronic structure of pseudostilbenes indeed enables rapid and reversible photo-mechanical motion in response to visible light, and correlate photo-mechanical bending properties to structural features of the chromophore and their crystals such as crystal packing, crystal thickness, and relative orientation of the absorbing molecules to the irradiated crystal faces. While a UV-lamp was used as a light source in previous studies of crystal photo-mechanical properties, we instead employed a tunable Ar<sup>+</sup>-ion laser, for better localization, higher power, and better control over wavelength, intensity, and polarization. Crystals were grown by sublimation on glass microscope slides under reduced pressure at, or slightly below, the melting point of a particular compound. Crystals of larger sizes were chosen for X-ray single crystal structure determination (Bruker Smart Apex 2), while the thinner crystals were subjected to bending analysis with the laser light. (See Experimental section for sublimation conditions and the irradiation setup).

# 2.3.2 General Nature of Photo-Mechanical Effects in Pseudostilbenes

In contrast to isolated cases reported in previous studies where bending was observed in only some samples, here we demonstrate bending motion for all of the compounds investigated (Figure 2.2), suggesting the general nature of the photo-mechanical effect of the solid state in pseudostilbene derivatives, if suitable conditions are found. Another important difference was observed in the relaxation process, which occurs at least one order of magnitude faster than that for the aminoazobenzene crystals. Previously studied aminoazobenzene systems<sup>15</sup> thermally relax on a time scale of tens of seconds or minutes and the relaxation can be accelerated by irradiation with the light corresponding to the absorption of the *cis*-isomer. For the diarylethene derivatives the irradiation for the reverse motion is mandatory. At the same time, the crystals based on the pseudostilbene derivatives studied here revert back to their original shape naturally when irradiation is ceased on a time scale of miliseconds without any supplemental irradiation, owing to the extremely short lifetimes of the *cis*-isomer, thus demonstrating suitability to fast switching applications. The observation of forward bending rates on the microsecond timescale (faster than the millisecond video capture limit) represents the fastest azo photo-mechanical systems yet reported.



Figure 2.2 Structures of the studied chromophores.

To best characterize and compare photo-mechanical motion between different compounds with an inherent distribution of linear dimensions for crystals, we monitored deflection angle as opposed to deflection distance. Furthermore, as was noted in the preceding investigation,<sup>15</sup> bending magnitudes along different crystallographic axes in the unit cell can vary significantly; here the values are reported along the axis of maximum bending. Relaxation rates and maximum deflection magnitudes are summarized in **Table 2.1** alongside the dimensions of crystals for which they were obtained. The magnitude of bending depends on the power of incident radiation, as depicted in **Figure 2.3**. Noteworthy, the threshold power at which the photo-mechanical effect is observable varies significantly for different compounds. While for dimethylaminoazobenzene the motion initiates at the power as low as  $1 \text{ mW/cm}^2$ , 4-diethylamino-4'-nitroazobenzene at 50 mW/cm<sup>2</sup>, and Disperse Red 13 at 100 mW/cm<sup>2</sup>, the Para Red crystal can be moved only at 200 mW/cm<sup>2</sup>.



**Figure 2.3** Deflection angle ( $\theta$ ) dependence on power of incident irradiation for crystals of similar dimensions and *ca*. 2 µm thickness of Disperse Red 13 (DR13), 4-diethylamino-4'-nitroazobenzene (DEA) and Para Red. Inset: relaxation profile of DR13 in the dark.

The power dependence can be correlated with the size and/or rigidity of the substituents on the azobenzene parent structure and, as will be discussed further, with the density of crystal packing. As the size of the donor group substituents grows larger and with the inclusion of a nitro group, the free volume change required for the *trans-cis* isomerization increases, thus inhibiting the bending. Consequently, a larger number of simultaneously isomerizing molecules is needed to move the crystal which is achieved by a higher power density. Macroscopic crystal bending depends strongly on the thickness of the crystal specimen, and is driven only by a relatively thin 50-100 nm surface layer due to the high molar absorptivity of azobenzene-type chromophores.<sup>17</sup>

| Compound                              | Crystal<br>dimensions,<br>µm | Deflection,<br>degrees | Half -<br>life, s | Orientation of the<br>molecular plane with<br>respect to irradiated face,<br>degrees | Volume per non-<br>hydrogen atom in<br>the unit cell, Å <sup>3</sup> |
|---------------------------------------|------------------------------|------------------------|-------------------|--|--|
| Dimethylamino<br>azobenzene           | 600×400×1                    | 20*                    | 1                 | 83.3, 85.9**   | 18.1   |
| Disperse Red 13                       | 600×500×1                    | 15                     | < 0.1             | 87.2, 89.2**   | 17.1   |
| 4-diethylamino-4'-<br>nitroazobenzene | 500×300×3                    | 8                      | <0.1              | 85.6, 88.2**   | 16.7   |
| Para Red                              | 800×300×2                    | 5                      | < 0.1             | 25.6   | 14.9   |
| Disperse Orange 1                     | 600×100×5                    | 1                      | < 0.1             | 65.3   | 15.9   |
| Methyl Red                            | 400×100×5                    | 3                      | < 0.1             | 54.5   | 14.6   |

 Table 2.1 Summary of photo-mechanical behaviour of the studied compounds, orientation

 of the molecules and density of crystal packing.

\* using power density of 0.3 W/cm<sup>2</sup>. All other values were at 1 W/cm<sup>2</sup>

\*\* 2 values represent the two orientations in the herring-bone structures

This simple estimate can be made considering the appreciable extinction coefficients of the azo molecules of the order of 10-20  $\mu$ m<sup>-1</sup>, and a threshold depth for inactivation where light levels are reduced to 10% of the incident light on the surface. Consequently it is not surprising that only a modest net photo-mechanical effect was observed for crystals above 10  $\mu$ m in thickness, where the active driving layer comprises only 1% or less of the total thickness, and that plate-like crystals bend more than the needle-like ones.

The magnitude of bending of azobenzene crystals thus depends on the power of irradiation, the bulkiness of the ring substituents, and crystal shape and thickness. Another dependence, however, can be traced: that of the crystalline structure. The orientation of the constituent molecules relative to the most prominent faces of the crystal may also influence the photomechanical behaviour of the macroscopic crystal, so crystal structures of all compounds were obtained for comparison. Multiple bending experiments on various crystals of all of the tested compounds suggest strong dependence of the magnitude of bending its orientation with respect to the irradiating beam. Some of the systems, namely dimethylaminoazobenzene, 4-diethylamino-4'- nitroazobenzene and Disperse Red 13, which coincidentally form crystals of similar size and planar shape, exhibited the highest bending magnitudes. Other systems of Disperse Orange 1, Para Red and Methyl Red which form needle-like crystals exhibited a strong preference to bending at specific incident irradiation directions while showing no response upon irradiation of other faces. This suite of observations taken together leads us to believe that molecular orientation and packing in the crystals are largely responsible for the direction and magnitude of the photo-mechanical effect. As was noted in a prior investigation<sup>15</sup> the molecules in dimethylaminoazobenzene are arranged almost perpendicular to the (001) face of the irradiated crystal which is the most prominent face. We determined the orientation of the constituent molecules relative to the irradiated crystalline face in the studied crystals by single crystal X-ray diffraction and face indexing. In all three of the compounds showing the highest photo-mechanical effect, molecules run nearly parallel to the c-axis resulting in a roughly perpendicular arrangement relative to the irradiated (001) face (Figure 2.4a and Figure A1.1), which is in all cases the largest face of these plate-like crystals. The long c-axis characteristic of all three of the structures may be responsible for directing the preferential planar growth of the crystals under sublimation conditions, allowing for the most suitable plate-like photo-responsive crystals. For the other studied compounds (Disperse Orange 1 (Figure 2.4b), Para Red (Figure A1.2) and Methyl Red) the internal orientation of the molecules is not perpendicular to the largest irradiated (010) faces and the observed deflection magnitudes are lower than for crystals with perpendicular arrangement.

The density of the crystal packing likely plays a crucial role in determining the magnitude of the photo-mechanical effect by governing the free volume requirements for molecular isomerization. Calculated densities are not representative due to different elemental composition of the studied dyes, but a crystallographically determined density that remains accurate regardless of the elemental composition is the volume per non-hydrogen atom in the unit cell. For all of the crystals which exhibited maximum bending this volume was the highest (*ca.* 17-18 Å<sup>3</sup> per non-hydrogen atom) showing low packing density of these crystals compared with the other studied analogues (*ca.* 15 Å<sup>3</sup>). For a structure of 20 non-hydrogen atoms, such a difference amounts to a 40-60 Å<sup>3</sup> difference in free space, a value of the same order of magnitude as required for the isomerization of the parent azobenzene chromophore (120-250 Å<sup>3</sup>)<sup>11</sup>, which allows more facile crystal motion and higher net photo-mechanical effect.



**Figure 2.4** a) Molecular orientation in crystals of Disperse Red 13. Grey planes represent the irradiated face, blue planes — the least squares plane drawn through the azobenzene fragment; Molecules align nearly perpendicular to the (001) face and crystals exhibit significant bending; b) molecular orientation in crystals of Disperse Orange 1. Molecules are strongly tilted with respect to the irradiated (010) face and crystals exhibit relatively little bending.

Crystal structure also plays a crucial role in the resilience of crystals under different irradiation powers. While dimethylaminoazobenzene crystals crack at power densities greater than 1 W/cm<sup>2</sup> and with 4-diethylamino-4'-nitroazobenzene over 2 W/cm<sup>2</sup>, Para Red crystals survive irradiation with powers of up to 4 W/cm<sup>2</sup>. Such a four-fold increase in crystal resiliency can be attributed to an increase in strength of molecular interactions. The nitro group in 4-diethylamino-4'-nitroazobenzene and Para Red increases the strength of dipole interactions, while extra reinforcement is possible in Para Red due to intramolecular hydrogen bonds and more efficient  $\pi$ - $\pi$  interaction between naphthalene fragments.

### **2.3.3** Control Experiments

To confirm that the fast relaxation process was not caused by thermal effects of irradiation by the laser, we tested crystals of previously reported dimethylaminoazobenzene. Blue light of 457 nm wavelength was employed at power densities of 100-300 mW/cm<sup>2</sup> to initiate bending of a 600×400×1 µm crystal, with both forward bending (seconds) and the relaxation times (tens of seconds, Table 2.1) were comparable to values reported previously using UV-light.<sup>15</sup> Green light (532 nm) of the same power was unable to initiate bending due to the negligible absorption of the compound at longer wavelengths. In a separate set of experiments photo-mechanical bending was studied under the liquid nitrogen stream on a Bruker Smart Apex II diffractometer which allows controlled cooling to 90 K. In the course of the experiment we observed bending at as low as 180 K, at which point the studied crystals become too brittle and fracture under the stress generated by bending. Repeated attempts to cool crystals below 180 K all led to fracturing of the crystals. We observed a decrease of speed of the relaxation at low temperatures which is consistent with the slower thermal relaxation of the *cis*-azobenzenes at low temperatures. Additionally, as a test for photothermal contribution to photo-mechanical bending, needle-like single crystals of alizarin dye were grown by ethanol vapor diffusion into DMF and tested in identical conditions. At similar thickness (3-10 µm) and aspect ratios alizarin failed to produce any bending at any of the used irradiation wavelengths and power of up to 10 W/cm<sup>2</sup>. Furthermore, utilizing the previously developed model<sup>17</sup> for temperature increase in irradiated azo-containing polymer films we do not anticipate any significant thermal contribution to crystal bending, even at the relatively high irradiation powers employed. No significant dependence of the polarization direction of the light source on rate or magnitude of deflection was observed.

# 2.4 Conclusions

In conclusion, we examined the influences of electronic structure, molecular geometry, long-range crystal packing, and macroscopic crystal orientation on the photo-mechanical performance of azobenzene dyes. The push-pull electronic structure of donor/acceptor substituents on pseudostilbenes extends and enhances the photo-mechancial property of single crystals known from other azobenzene derivatives by simultaneously imparting sensitivity to visible light and spontaneous, rapid reverse motion of photo-mechanically bent single crystals. The latter property results from the extremely short thermal lifetimes of *trans-cis* isomerization in pseudostilbenes

relative to other azobenzenes. Such short lifetimes allow quick recovery without supplemental irradiation with other light sources as in the previously studied systems. It appears that a combination of lower packing density, lower crystal thickness and perpendicular arrangement of the molecules with respect to the irradiated surface all contribute significantly to the ability of a crystal to exhibit high magnitude photo-induced bending. After optimizing each of these structural-property relationships, no compounds were identified which failed to undergo photo-induced bending under some conditions, although less compliant systems require higher power density. Crystal structures for Disperse Red 13, 4-diethylamino-4'-nitroazobenzene, Disperse Orange 1 and a new Para Red polymorph were obtained for the first time.

# 2.5 Supporting Information

Complete experimental details, summary of crystallographic refinements and statistics, are presented in Appendix 1. This material as well as cif files, 3 videos of crystal motion upon irradiation are available free of charge online from Wiley InterScience or from the authors.

# 2.6 Acknowledgements

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# **Appendix 1: Supporting Information for Chapter 2**

### 1. Materials Synthesis and Characterization

Disperse Red 13, Disperse Orange 1, Para Red and Methyl Red were purchased from Sigma Aldrich and used for sublimation as is. Dimethylaminoazobenzene and 4-diethylamino-4'nitroazobenzene were synthesized in-house using the following procedures:

# Dimethylaminoazobenzene:

0.020 mol (2.53 mL) of aniline was dissolved in 50 mL of 1:1 water:acetone mixture and cooled to 0-5 °C in an ice bath. 0.020 mol (1.38 g) of sodium nitrite and 0.040 mol (3.5 mL) of concentrated HCl were dissolved in 20 mL of 1:1 water:acetone and cooled to 0-5 °C, then slowly added to the aniline solution with stirring (30 mins). 0.020 mol (1.86 mL) of dimethylaniline dissolved in 50 ml of acetone at 5 °C was slowly added to the mixture and left stirring for 1 hour. Orange precipitate formed overnight was filtered and washed with acetone yielding 1.52 g of wet product. The solvent in the mother liquor was partially removed by rotary evaporator yielding more orange precipitate. The product was re-crystallized from methanol yielding a total of 3.15 g (70%) dimethylaminoazobenzene (pure by TLC). The product was used for sublimation without further purification: the structure was confirmed by single crystal X-ray diffraction.

# 4-diethylamino-4'-nitroazobenzene:

0.010 mol (1.38 mL) of 4-nitroaniline was dissolved in 150 mL of 2:1 water:acetone mixture and cooled to 0-5 °C in an ice bath. 0.010 mol (0.69 g) of sodium nitrite and 0.020 mol (1.72 mL) of concentrated HCl were dissolved in 20 mL of water and cooled to 0-5 °C, then slowly added to the aniline solution with stirring (30 mins). 0.010 mol (1.61 mL) of N,N-diethylaniline was slowly added to the mixture with intensive stirring (red colouration was observed almost immediately) and left overnight. Acetone was removed by rotary evaporation and the product was extracted with diethyl ether. The diethyl ether was removed by rotary evaporation, yielding purple red crystals. The total yield of dry product was 2.216 g (74.3%). The structure was confirmed by NMR and single crystal X-Ray diffraction.

# 2 Sublimation conditions

Crystals for the photo-mechanical motion measurements were obtained by sublimation under reduced pressure in a ChemGlass sublimator at or below the melting point of the respective compound. Conditions and crystal morphology are summarized in **Table 2.2**.

| Compound                              | Sublimation      | Crystal shape and | Visible $\lambda_{max}$ |
|---------------------------------------|------------------|-------------------|-------------------------|
| Compound                              | temperature, °C. | colour            | (THF)                   |
| Disperse Red 13                       | 135              | purple plates     | 511                     |
| Methyl Red                            | 150              | red needles       | 487                     |
| Para Red                              | 180              | red needles       | 483                     |
| Dimethylamino<br>azobenzene           | 115              | yellow plates     | 415                     |
| Disperse Orange 1                     | 150              | orange needles    | 467                     |
| 4-diethylamino-4'-<br>nitroazobenzene | 145              | red plates        | 418                     |

Table A1.1 Sublimation conditions for the dyes used in the investigation

#### **3** Photo-Mechanical Motion Measurements

Crystals subjected to bending were irradiated on the edges of microscope slides or mounted on the tip of the Mitegen® 75  $\mu$ m aperture micromounts with the nominal tip thickness of 10  $\mu$ m. Irradiation was achieved by variable power Ar<sup>+</sup>-ion laser tuned to either 457, 488, 514 or 532 nm wavelength, depending on the absorption maximum of the compound being investigated. The light was normally linearly polarized. For the samples absorbing at 488 nm (Para Red and Methyl Red), experiments were conducted both with linearly polarized light, and with a <sup>1</sup>/<sub>4</sub> waveplate in place to alter the light to circular polarization, to check that polarization state had no effect on photomechanical motion. Circular polarization can be considered equivalent in effect to randomly polarized light in this case (equal field magnitude in all directions), since neither compound crystallizes in a chiral space group nor possesses molecular chirality. Photo-mechanical motion was recorded by a Sony CCD camera fitted with a zoom lens.

#### 4. Crystal Motion Observation

Videos of crystal motion are an integral part of this study and could be viewed on-line using the following digital object identifier: doi/10.1002/adma.201204831.

**Video 1.** Slow reversible bending of dimethylaminoazobenzene at 0.3 W/cm<sup>2</sup>, irradiation wavelength 457 nm. One cycle is shown.

**Video 2.** Fast and reversible bending of Disperse Red 13 single crystal under irradiation with 514 nm light at 0.5 W/cm<sup>2</sup>.

**Video 3.** Fast and reversible bending of Para Red single crystal under irradiation with 488 nm light at 1 W/cm<sup>2</sup>.

# 5. X-ray Data Collection and Analysis

X-ray diffraction data was obtained on Bruker Smart Apex II single-crystal X-ray diffractometer at 100 K. Multi-scan absorption correction (SADABS) was applied. Structures were solved by direct methods or dual space algorithm and refined using SHELX-97 software.<sup>18</sup> All hydrogen atoms where possible were calculated from the electron density map and refined using distance restraints or placed using the riding model. A data summary for Dispere Red 13, Disperse Orange 1, 4-diethylamino-4'-nitroazobenzene and a new polymorph of Para Red can be obtained from Cambridge Structural Database, deposition numbers 893536-893539.

|                                   | Disperse Red 13   | Para Red  | Disperse Orange 1    | 4-diethylamino-4'-     |  |
|-----------------------------------|---|---|----------------------|------------------------|--|
|                                   | _   |   |                      | nitroazobenzene        |  |
| CCDC number                       | 893536  | 893539  | 893538               | 893537                 |  |
| Formula                           | C <sub>16</sub> H <sub>17</sub> ClN <sub>4</sub> O <sub>3</sub> | C <sub>16</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> | $C_{18}H_{14}N_4O_2$ | $C_{16}H_{18}N_4O_2$   |  |
| Density (g/cm <sup>3</sup> )      | 1.430   | 1.468   | 1.386                | 1.346                  |  |
| Crystal System                    | Monoclinic  | Monoclinic  | Monoclinic           | Triclinic              |  |
| Space Group                       | P2(1)   | C2/c  | Cc                   | P-1                    |  |
| Colour and Shape                  | Purple plate  | Red needle  | Orange needle        | Maroon plate           |  |
| Cell Dimensions                   |   |   |                      |                        |  |
| $a h c (\lambda)$                 | 7.2622, 12.3952,  | 32.581, 3.7389,   | 10.1999, 16.892,     | 7 5088 11 080 10 088   |  |
| a, b, c (A)                       | 17.997  | 26.650 8.9859   |                      | 7.3988, 11.089, 19.088 |  |
| $\alpha, \beta, \gamma$ (°) (°)   | 90.00, 93.034, 90.00  | 90.00, 125.9820,  | 90.00, 99.817, 90.00 | 75.749, 85.573, 70.805 |  |
| Volume (Å <sup>3</sup> )          | 1617.8  | 2627.1  | 1525.6               | 1472.2                 |  |
| Ζ                                 | 4   | 8   | 4                    | 4                      |  |
| Resolution (°)                    | 25.00   | 28.44   | 28.27                | 25                     |  |
| Completeness (%)                  | 93.1  | 92  | 93.6                 | 83                     |  |
| Collected reflections             | 18384/7356  | 13750/3020  | 8523/3423            | 6021/6021              |  |
| /independent reflections          | 10304/7550  | 1373073020  | 052575425            | 0021/0021              |  |
| Data/restraints/parameters        | 7356/456/137  | 3020/203/0  | 3423/221/2           | 6021/402/0             |  |
| Goodness of fit on F <sup>2</sup> | 1.053   | 0.984   | 1.040                | 0.821                  |  |
| Final R indices $[I>4\sigma(I)]$  | 0.0384  | 0.0422  | 0.0401               | 0.0556                 |  |
| Dirding (all data)                | $R_1 = 0.0473$  | $R_1 = 0.0639$  | $R_1 = 0.0544$       | $R_1 = 0.1080$         |  |
| R indices (all data)              | $wR_2 = 0.0988$   | $wR_2 = 0.1480$   | $wR_2 = 0.0890$      | $wR_2 = 0.1471$        |  |
| Largest diff. peak and hole (e.   | 0.27 0.22   | 0.21 0.27   | 0.17 0.10            | 0.26 0.20              |  |
| Å- <sup>3</sup> )                 | 0.57, -0.52   | 0.51, -0.27   | 0.17, -0.19          | 0.20, -0.30            |  |

Table A1.2 Data collection and refinement statistics summary

Complete supplemental information for these crystal structures is available in the Crystallographic Information files (.cif files) from the Cambridge Crystallographic Data Centre using the accession codes listed above.



**Figure A1.1** Representation of the molecular tilt of Para Red with respect to the irradiated (010) face.



**Figure A1.2** Representation of the molecular tilt of 4-diethylamino-4'-nitroazobenzene with respect to the irradiated (001) face.

# Rationale for Chapter 3: Shaping Crystals with Light: Crystal-to-Crystal Isomerization and Photo-Mechanical Effects in Fluorinated Azobenzenes

Despite the encouraging results of the study described in Chapter 2 only limited structural information was obtained due to the time averaged nature of the X-ray experiments because the reverse isomerization in pseudostilbenes occurs much faster than the time-scale of the diffraction experiment. Chapter 3 presents the contribution 'Shaping Crystals with Light: Crystal-to-Crystal Isomerization and Photo-mechanical Effect in Fluorinated Azobenzenes' that was published in the *Journal of the American Chemical Society* and describes how the first definitive X-ray diffraction proof of *cis*—*strans* photo-mechanical azobenzene isomerization was obtained utilizing crystals of fluorinated *cis*-azobenzenes as a study material.



Chapter 3: Shaping Crystals with Light: Crystal-to-Crystal Isomerization and Photo-Mechanical Effects in Fluorinated Azobenzenes

# 3.1 Abstract

Unusually long thermal half-lives of perhalogenated *cis*-azobenzenes enabled their structural characterization and the first evidence of a crystal-to-crystal *cis*→*trans* azobenzene isomerization. Irradiation with visible light transforms a perhalogenated *cis*-azobenzene single crystal into a polycrystalline aggregate of its *trans*-isomer in a photo-mechanical transformation which involves a significant, controllable and thermally irreversible change of crystal shape. This is the first demonstration of permanent photo-mechanical modification of crystal shape in an azobenzene.

# 3.2 Introduction

The azobenzene (azo) chromophore is one of the best studied photochromic groups,<sup>1</sup> and its clean, reversible isomerization has been investigated in a variety of applications (Figure 3.1a).<sup>2</sup> While the isomerization efficiency and chemical stability of the chromophore under multiple isomerization cycles are high, a recent fascinating aspect of azobenzene-containing solids is the photo-mechanical effect,<sup>3</sup> *i.e.* the direct conversion of visible light into mechanical motion based on the ability of molecular building blocks to change shape upon irradiation. Such solid-state molecular motion alters bulk material properties, including shape, thickness, surface energy etc.<sup>4</sup> Photo-mechanical effect in azobenzene solids was studied in polymers,<sup>5</sup> thin films<sup>6</sup> or liquid crystals<sup>7</sup> and is manifested in macroscopic bending of the material or surface relief gratings formation<sup>8</sup> on its surface upon *trans* $\rightarrow$ *cis* conversion. Previous work has focused on reversible systems in which photochemical bending is accompanied by thermal  $cis \rightarrow trans$  relaxation which restored the object to its initial shape.<sup>3b,c,5-7</sup> However, azobenzene isomerizations in crystals remain almost unexplored, possibly due to a general opinion that underlying stereochemical change (120-250 Å<sup>3</sup>)<sup>9</sup> would be hindered in a crystal and, consequently, that crystalline azobenzenes are generally not capable of photo-mechanical effect. It was recently demonstrated, however, that sufficiently thin azobenzenes crystals allow photochemical  $trans \rightarrow cis$  isomerization and thermal relaxation<sup>10</sup> leading to a rapidly reversible photo-mechanical effect. A peculiarity of azobenzene

crystal chemistry is the paucity of *cis*-isomer structures, associated with their short half-lives hindering the isolation of single crystals.<sup>11</sup> The lack of crystallographic data on *cis*-azobenzenes is notable considering that azobenzene isomerization was reported nearly 200 years ago and addressed in tens of thousands of papers since.



Figure 3.1. (a) Azobenzene isomerization; (b) *cis*- and *trans*-forms of 1 and 2; (c)  $cis \rightarrow trans$  isomerization of 1 depicted with molecular structures based on single crystal X-ray diffraction; (d) irreversible bending of a thin crystal of *cis*-1 by 457 nm light, with the arrow at the top of the figures indicating the direction of irradiation.

We now report that photochemical  $cis \rightarrow trans$  azobenzene isomerization can take place in a crystal-to-crystal fashion. The very long half-lives (ca. 2 months) of *cis*-forms of azobenzenes **1** and **2** (Figure 3.1b,c) allowed their isolation as crystals capable of *cis* $\rightarrow$ *trans* isomerization<sup>12</sup> upon visible light irradiation. This photo-mechanical effect is irreversible, which is a new development in the area of photo-mechanical azobenzene solids, which has so far focused on reversible switching. Thin crystals of *cis*-1 and -2 can be shaped by light into thermally stable cyclic or zigzag forms (**Figures 3.1d**, also see Experimental section).

#### 3.3 **Results and Discussion**

# 3.3.1 Preparation of Azobenzenes with Very Long Thermal Half-Lives

Both 1 and 2 were synthesized by conventional oxidative coupling, and obtained predominantly as *cis*-forms. The long half-lives of *cis*-azobenzenes 1 and 2 are in agreement with the recent report by Hecht *et al.*<sup>13</sup> showed that *o*-fluorinated azobenzenes can exhibit significantly separated *trans*- and *cis*-form  $n-\pi^*$  absorption maxima leading to long *cis*-isomer half-lives. Indeed, the half-life of *cis*-1 and -2 determined by kinetic UV-Vis experiments in solution is 60 days in CH<sub>2</sub>Cl<sub>2</sub>. The *n*- $\pi^*$  transitions for both 1 and 2 are separated by 40 nm (420 nm *cis*, 460 nm *trans*, see Experimental section for details) which in solution allows for switching between photostationary states using visible green (*trans*-*cis*) and blue (*cis*-*trans*) light. The *trans*-*cis* isomerization is also achievable with ultraviolet light of 320 nm for 1 and 330 nm for 2 *via*  $\pi$ - $\pi^*$ excitation. Absorption maxima do not change appreciably with the solvent.

#### 3.3.2 Computational Analysis

Computational studies of **1** and **2** were done using a density functional theory (DFT) method used for similar systems.<sup>14</sup> Compound **1** and the parent azobenzene were treated with B3LYP level of theory with Pople 6-31G(d) basis set. For **2**, calculations required an increased basis set due to the presence of iodine and so DGDZVP was used. The calculations predict that the energy difference between *cis*- and *trans*-isomers of **1** and **2** are approximately half of the value calculated for azobenzene: 8.84 kcal mol<sup>-1</sup>, 8.88 kcal mol<sup>-1</sup> and 15.26 kcal mol<sup>-1</sup> respectively (**Figure 3.2**, also see Experimental section).



**Figure 3.2** Energy profiles for *trans-cis* isomerization of **1** (red) and the parent azobenzene (blue); the *cis*-form of **1** is relatively more stable with respect to the corresponding *trans*-isomer compared to azobenzene.

Long half-lives of *cis*-1 and *cis*-2 allowed the isolation of both *trans*- and *cis*-forms of 1 and 2 and their structural characterization by single crystal X-ray diffraction. Two concomitant polymorphs of *cis*-1 were found: *cis*-1 and *cis*-1a Only *cis*-1 could be obtained as thin needles suitable for photo-mechanical studies, and is the relevant form for this work. Crystal structures of *trans*-1 and -2 reveal planar molecules, while *cis*-1 and -2 are V-shaped with intramolecular angles between phenyl moieties between 74° and 82°.

#### 3.3.3 Photo-Mechanical Motion Examination

To study photoresponsive behaviour we irradiated thin needle crystals of *cis*-1 with blue 457 nm laser light. Remarkably, even relatively thick needles of ca. 10-20  $\mu$ m bent readily and irreversibly away from the light source, reaching deflection angles of up to 180° for the tip of the needle (**Figure 3.1d**). Controlled photo-mechanical bending of such magnitude is unprecedented in crystalline azobenzene systems, and has only very recently<sup>15</sup> been reported in alternative<sup>16,17</sup> crystalline photo-mechanical systems. Earlier *trans*-azobenzene or pseudostilbene photo-mechanical systems exhibited motion of considerably lower extent and only if crystal was less

than 5  $\mu$ m thick, with optimum effect at 1  $\mu$ m.<sup>10</sup> Bending of *cis*-1 was accompanied with change of colour of the irradiated part of the crystal from yellow to orange-red, consistent with *cis* $\rightarrow$ *trans* isomerization. Irradiation of the opposite face of the crystal allows bending in the opposite direction. This results first in straightening of the crystal, and then bending in the opposite direction (**Figure 3.1d**). After irradiating both prominent faces, the crystal became inactive to laser light, which was explained by isomerization of all *cis*-1 molecules on the surface to *trans*-1. With the provision of sufficient spatial control, such irreversible bending allows shaping of the crystalline material. A crystal can even be molded into an S-shape by irradiation from two different directions at two different regions. Similar behaviour was also observed for *cis*-2.

That photo-mechanical behaviour of *cis*-1 is related to isomerization is evidenced by powder X-ray diffraction, which demonstrated the concomitant disappearance of X-ray reflections of *cis*-1 and the appearance of those corresponding to *trans*-1 (see Experimental section) upon irradiating a powder sample of *cis*-1. We next attempted to follow the transformation of *cis*-1 into trans-1 via single crystal X-ray diffraction. Importantly, photo-mechanical isomerization of crystalline azobenzenes has never been ascertained in this manner. It was, therefore, surprising and gratifying to discover that a single crystal of *cis*-1 upon irradiation with 457 nm laser light transformed into a polycrystalline sample of *trans-1*. The transformation is clearly visible from composite diffraction images (Figures 3.3a-c show composite images for diffraction of h0l planes, further ones are provided in the Experimental section 3.5.6). The X-ray reflections of irradiated cis-1 single crystal could be completely indexed to several differently oriented domains with unit cell parameters identical to those of trans-1. In particular, 903 out of total 1125 X-ray reflections could be indexed by considering five such domains (details in the Experimental section). Indexing of all reflections was accomplished by considering a total of 16 domains with crystallographic parameters corresponding to those of *trans*-1. Although X-ray diffraction data collected from these domains was poor and highly overlapped, using reflections from one such domain allowed the structure of trans-1 to be solved and even refined, using a constrained isotropic model, to a reasonable degree with respect to data quality. Within the limitations of the available data, the resulting structure was identical to that of *trans-1* obtained from a separately grown single crystal, unambiguously confirming the crystal  $\rightarrow$  crystal nature<sup>18</sup> of the *cis* $\rightarrow$ *trans* transformation in 1.



**Figure 3.3** Composite diffraction images for the *h0l* planes of single crystals of: (a) *cis*-1; (b) *trans*-1 and (c) *cis*-1 after 4 hours irradiation at 457 nm, demonstrating the conversion of a single crystal of *cis*-1 into polycrystalline *trans*-1; (d) tentative model of the photo-mechanical bending of *cis*-1 crystal as *cis*-molecules progressively isomerize into *trans*-1 upon light penetration. Molecular stacks are parallel to the long axis of the crystal needle. Crystal structure of *cis*-1: (e) molecular stacks viewed in the crystallographic *ab*-plane perpendicular to irradiation and (f) down the crystallographic *b*-direction parallel to the crystal needle axis, displaying the retained zigzag motif of Br...Br contacts. (g) The (30-2) plane in *trans*-1 with molecular arrangement resembling that of *cis*-1 in (f).

The amenability of cis-1 and -2 crystals to photo-mechanical shaping is unique in azobenzene chemistry, compared to previously studied *trans*-azobenzenes and pseudostilbenes. Permanent bending in previously studied trans-azobenzene systems was not achievable due to the rapid equilibrium formed upon irradiation, in which molecules photochemically isomerize to the cisform but also thermally relax back to the *trans*-form. As a result, a sufficiently high concentration of the cis-form required for permanent photo-mechanical bending of the trans-crystal is difficult to achieve. In the case of cis-1, however, we have not observed any tendency for reversal of the  $cis \rightarrow trans$  isomerization in the crystal using either blue (457 nm), green (514 nm) or red (633 nm) light. While the irreversible nature of the isomerization in *cis*-1 is probably aided by the metastable nature of the cis-isomer, it is likely that thickness of the crystal or more efficient molecular packing of trans-azobenzene in the crystal is the key for permanent bending. The latter possibility is supported by the lower density of *cis*-1 compared to *trans*-1. For *cis*-1 the volume of the unit cell per molecule if 339.5 Å<sup>3</sup> while the corresponding value for *trans*-1 is 325.5 Å<sup>3</sup>. We note a similarity between the herein reported photo-mechanical shaping of perhalogenated azobenzene crystals and previously studied bending of haloarene crystals by mechanical force.<sup>19</sup> In crystals of *cis*-1 and cis-2 molecules are arranged into stacks which, we propose, could expand upon photochemical  $cis \rightarrow trans$  isomerization without generating extensive stress on the nearby stacks. In cis-1 the stacks are parallel to the crystallographic b-direction which coincides with the needle crystal long axis. Molecules in neighboring stacks interact by networks of Br...Br interactions parallel to and perpendicular to the needle axis (Figure 3.3d,e). Progressive photo-mechanical expansion of molecular stacks which are closer to the source of irradiation might allow the crystal to bend away from the light source with minimum fracturing by sacrificing only the Br...Br interactions along the needle axis (Figure 3.3e). Although no clear topochemical relationship was established between the photochemically generated domains of *trans*-1 and the parent *cis*-1 crystal,<sup>18</sup> we note a correspondence between arrangements of molecules populating the crystallographic (010) planes of cis-1 and the (30-2) planes of trans-1. Both planes exhibit a zigzag net of Br...Br contacts (3.95 Å in cis-1 and 4.02 Å in trans-1), suggesting that this supramolecular motif, normal to the needle axis of the starting crystal, might be conserved upon photo-mechanical bending (Figures 3.3e,f).

#### 3.4 Conclusions

In summary, the exploration of two new perhalogenated azobenzenes with long-lived *cis*forms provided the first demonstration of an irreversible photo-mechanical effect in a crystalline azobenzene solid. Single crystal and powder X-ray diffraction revealed that the photo-mechanical effect involved a single crystal  $\rightarrow$  polycrystal transformation, so far unprecedented in solid-state chemistry of azobenzenes. The metastable nature of the starting *cis*-azobenzene and its large photo-mechanical response highlight photo-mechanical shaping as a new exciting opportunity in the solid-state photochemistry of crystalline azobenzenes. We therefore believe that the irreversible photochemical effect of 1 and 2 opens new possibilities in the design of photoresponsive azobenzene solids.

# **3.5** Supporting Information

Details of synthesis, videos, images of crystal bending, selected UV-Vis spectra, powder X-ray diffraction data, DFT calculations and crystallographic data in cif format. This material is available free of charge *via* the Internet at <u>http://pubs.acs.org</u> as well as in Appendix 2 in the end of this Chapter.

# **3.6** Acknowledgments

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# **Appendix 2: Supporting Information for Chapter 3**

#### 1. Materials and Syntheses

4-Bromo-2,3,5,6-tetrafluoroaniline, 2,3,5,6-tetrafluoroaniline and mercury oxide were obtained from Sigma Aldrich and used without purification. Activated manganese dioxide was obtained in house from potassium permanganate and manganese sulfate utilizing a published procedure.

### 4,4'-dibromooctafluoroazobenzene (1)



600 mg of 4-Bromo-2,3,5,6-tetrafluoroaniline was mixed with 8.2 g of activated manganese dioxide in 100 ml of petroleum ether. After 6 days of stirring at room temperature the slurry was filtered, washed until clear washings with petroleum ether and then with dichloromethane (DCM). All fractions were combined, and solvent was removed on rotary evaporator. Product was purified on CombiFlash automated silica column, using 95% hexane 5% ethyl acetate gradient solvent system. Yield 182 mg of cis (30.5%) and 80 mg trans (13.4%).\*

4-iodo-2,3,5,6-tetrafluoroaniline



400 mg of yellow (1.84 mmol) HgO was added to a solution of 450 mg (2.45 mmol) of 2,3,5,6-tetrafluoroaniline in 20 ml of ethanol. Mixture was stirred for 30 minutes, and then 620 mg

(2.44 mmol) of I<sub>2</sub> was added. Mixture was stirred overnight and then filtered over celite. Solvent was removed on rotary evaporator, then product redissolved in ca. 40 ml of DCM and washed several times with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution and dried over MgSO<sub>4</sub>. Product was purified by sublimation yielding long needles 605 mg, (85%).<sup>1</sup>H-NMR: broad signal at 4.1 ppm.

#### 4,4'-diiodooctafluoroazobenzene (2)

600 mg of previously synthesized 4-iodo-2,3,5,6-tetrafluoroaniline was mixed with 8.0 g of activated manganese dioxide in 100 ml of petroleum ether. After 3 days of stirring at room temperature the slurry was filtered, washed until clear washing with petroleum ether and then with dichloromethane (DCM). All fractions were combined, and solvent was removed on rotary evaporator. Product was purified on CombiFlash automated silica column, using 95% hexane 5% ethyl acetate gradient solvent system. Yield 120 mg of *cis*-2 (20%) and 70 mg *trans*-2 (11.7%).\*

Chemical identities of the prepared compounds were confirmed by single crystal X-ray diffraction, powder X-ray diffraction (e.g. see **Figure A2.6**) and absence of proton signals in <sup>1</sup>H-NMR spectrum.

\*Yield of *trans*-form can be enhanced by refluxing the mixture. However, upon refluxing the amount of isolated *cis*-isomer drops significantly.

#### 2. UV-Vis Analysis

UV-Vis studies of *cis-trans* isomerization were performed using a Cary 300 Bio UV-Vis spectrometer. *K*-values and  $t_{1/2}$  were obtained for 1 in hexanes, THF, and DCM; for 2 in hexanes and are summarized in **Table A2.1** Example UV-Vis spectra are given in **Figure A2.1**,



Figure A2.1 (left) UV-Vis profile of *cis*-1 (red) and *trans*-1 (blue) in hexanes; (right)n- $\pi^*$ transitions for *cis*-1 (red) and *trans*-1 (black)

| compound         | cis-1 (hexanes)       | <i>cis</i> -1 (THF)   | cis-1(DCM)            | cis-2 (hexanes)       |
|------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| (solvent)        |                       |                       |                       |                       |
| $K, (s^{-1})$    | $2.75 \times 10^{-7}$ | $1.93 \times 10^{-7}$ | $1.34 \times 10^{-7}$ | $2.23 \times 10^{-7}$ |
| $t_{1/2}$ , days | 29                    | 42                    | 60                    | 36                    |

 Table A2.1 Half-lives of *cis*-isomers and reaction constants for 1 and 2.

# 3. Photo-Mechanical Motion Measurements

Needle-like crystals of 1 and 2 of approximately 10-20  $\mu$ m thickness were selected and subjected to irradiation on the tip of the Mitegen® 75  $\mu$ m aperture micromounts with the nominal tip thickness of 10  $\mu$ m. Irradiation was achieved by linearly polarized variable power Ar+-ion laser at 457 nm wavelength. Beam power used for experiments was 1-5mW, with beam diameter around 1 mm<sup>2</sup>. Photo-mechanical motion was recorded by the Infinity-1 CMOS microscopy camera fitted with a zoom lens.



**Figure A2.2** Permanent S-shape photo-mechanical modification of *cis*-1 crystal by irradiation: (a) crystal before irradiation; (b) crystal after irradiation; (c) crystal after rotation by 180 °C around its long axis and (d) crystal after second turn of irradiation. Direction of irradiation is indicated by the white arrow.

# 4. Single Crystal X-ray Diffraction Measurements and Crystallographic Summary

X-ray diffraction data was obtained on Bruker D8 single-crystal X-ray diffractometer equipped with a  $MoK_{\alpha}$  X-ray source and a graphite monochromator. Multi-scan absorption correction (SADABS) was applied. Structures were solved by direct methods and refined using SHELX-97 software.<sup>1,2</sup> Data can be obtained from Cambridge Structural Database, deposition numbers 1000907-1000912.

# **Description of Crystal Structures**

The *trans*-isomers of **1** and **2** in the solid state assemble into different motifs: *trans*-**1** forms  $\pi$ -stacks composed of identically oriented molecules, while *trans*-**2**, probably due to a larger radius of the iodine atom adopts a herringbone structure with two distinct orientations for the azo molecules. In both structures the fluorinated phenyl rings are coplanar, despite possible repulsive interactions between ortho-fluorine atoms. Both **1** and **2** in the *trans*-form exhibit pedaling motion observed as a disorder of the azo group.

Crystal structures of *cis*-1 and *cis*-2 contain alternately-oriented stacks of V-shaped molecules parallel to the crystallographic *b*-axis. A distinct difference in intramolecular angles between the phenyl planes can be seen when comparing to the parent azobenzene molecule. The

angle between the phenyl rings opens up from  $64^{\circ}$  in the parent azobenzene to  $81^{\circ}$  and  $74^{\circ}$  in *cis*-**1** and *cis*-**1a**, respectively, and  $82^{\circ}$  in *cis*-**2** (Figures A2.3 and A2.4). Such a difference is significant as the effective volume change upon azo isomerization is likely to be determined by the relative positioning of the phenyl rings and distance between the termini of the azo molecules. In most previous investigations, and angle of  $64^{\circ}$  between phenyl planes is quoted even for molecules significantly different than parent azobenzene.



**Figure A2.3** Molecular geometries for: (a) *cis*-1; (b) *cis*-1a and (c) *cis*-2 in corresponding single crystal structures. The depicted planes (red and green) correspond to best planes drawn through the benzene rings of the 4-bromo- and 4-iodotetrafluorophenyl groups. Figures drawn using Mercury CSD.



Figure A2.4 Crystal packing of: (top) *cis*-1 viewed perpendicular to the crystallographic *ab*-plane; (middle) *cis*-1a viewed down crystallographic *a*-axis and (bottom) *cis*-2 viewed perpendicular to the crystallographic *ab*-plane. Note the isostructural nature of *cis*-1 (top) and *cis*-2 (bottom). Figures were drawn using Mercury CSD.

# 5. Summary of Indexing a Crystal of cis-1 after Irradiation

Majority of the reflections (903 out of 1125) could be fitted to five major domains,<sup>2</sup> described below:

Domain 1: 446 reflections out of 1125

Domain 2: rotated by 178.8 degrees about reciprocal 1.000; -0.182; -0.515; 382 reflections, (204 exclusively)

Domain **3**: rotated by 7.0 degrees about reciprocal 1.000; -0.240; -0.178; 286 reflections (129 exclusively)

Domain 4: rotated by 103.1 degrees about reciprocal 0.024; 0.009; 1.000; 318 reflections (69 exclusively)

Domain 5: rotated by 174.1 degrees about reciprocal 1.000; -0.184; -0.508; 337 reflections (55 exclusively)

The remaining 222 reflections are all fitted if a total of 16 domains are considered. All 16 domains exhibit the same unit-cell (identical to the second decimal) resembling that of *trans*-1: a= 8.894 Å, b=7.790 Å, c= 10.572 Å,  $\beta$ =109.55°.


**Figure A2.5** Composite diffraction images for the *hk0* diffracting plane of: (a) *cis*-1; (b) *cis*-1 irradiated at 457 nm for 4 hours; (c) *trans*-1 and the 0kl diffracting plane of: (d) *cis*-1; (e) *cis*-1 irradiated at 457 nm for 4 hours; (f) *trans*-1. The d-spacings measured for images (b) and (e) clearly matched those in images (c) and (f), respectively.

## 6. Powder X-ray Diffraction Data



**Figure A2.6** Powder X-ray diffraction patterns for the bulk irradiation experiment. From top to bottom: sample of *cis*-1 after irradiation; sample of *cis*-1 before irradiation; simulated pattern of *trans*-1; simulated patterns for the two polymorphs of *cis*-1.

#### 7. Theoretical Calculations

All calculations were performed using the Gaussian package<sup>3</sup> and Avogadro<sup>4</sup> was used as visualization software. The basis set a level of theory were chosen based on the results of a validation study for azobenzene *trans*- and *cis*-conformations. As shown in **Table A2.2**, the best compromise between accuracy and time was a DFT hybrid method B3LYP yielding the right geometry. Also, Pople's 6-31G(d) basis set was found to be suitable for azobenzene parent molecules as well as for **1**, while **2** required a bigger basis set to suite Iodine, and DGDZVP was used.

The accuracy of the theoretical model was based on the best structural geometry obtained compared to experimental results for *cis* and *trans* azobenzene molecules. In order to effectively cover the various possibilities, a variety of theoretical model types were used: a semi-empirical PM6 method, two *ab initio* methods (HF, MP2), and a density functional method (B3LYP). Basis sets used in combination with these models had different levels of polarizability and different number of diffuse functions so that the impact of the size of basis set on the accuracy of results could be monitored.

As shown in **Table A2.3**, the MP2/6-31+G(d) combination displays the smallest average percent error, making it the most accurate. However, this computation is the only one that predicted a non-planar geometry for *trans*-azobenzene (torsion angle of  $17.5^{\circ}$ ), which makes its geometry optimization unacceptable. The next best combination was found to be MP2/6-311+G(d,p), yet computational time significantly exceeded the desired threshold of 2 hours. For these reasons, the third best combination, B3LYP/6-31G(d), was selected for geometry optimization of subsequent *trans*-azobenzene derivatives. Notably, polarization and the increased number of diffuse functions in the orbital approximation of basis sets yielded equivalent or worse results than the normal 6-31G(d) basis set. Other, least successful combinations were attempted but are not shown in **Table A2.2** 



Figure A2.7 Molecular model of *trans*-azobenzene (atoms are labeled as in Table A2.2).

| Bond lengths (Å)                                 |               |  |               |                  |                |                           |
|--|---------------|--|---------------|------------------|----------------|---------------------------|
|  | Atom 1        | Atom 2   | MP2/6-31+G(d) | MP2/6-311+G(d,p) | B3LYP/6-31G(d) | Experimental <sup>5</sup> |
|  | N (1)         | N (2)  | 1.279         | 1.271            | 1.261          | 1.243                     |
|  | C (1)         | N (1)  | 1.423         | 1.423            | 1.419          | 1.433                     |
|  | C (1)         | C (2)  | 1.402         | 1.403            | 1.401          | 1.384                     |
|  | C (1)         | C (6)  | 1.405         | 1.407            | 1.406          | 1.385                     |
|  | C (2)         | H (2)  | 1.088         | 1.087            | 1.086          | 1.102                     |
|  | C (6)         | H (6)  | 1.087         | 1.085            | 1.084          | 1.102                     |
| Bond ang   | les (degrees) |  |               |                  |                |                           |
| Atom 1   | Atom 2        | Atom 3   | MP2/6-31+G(d) | MP2/6-311+G(d,p) | B3LYP/6-31G(d) |                           |
| C (1)  | N (1)         | N (2)  | 113.4         | 113.9            | 114.8          | 113.6                     |
| C (2)  | C (1)         | N (1)  | 115.3         | 114.9            | 115.3          | 115.5                     |
| C (6)  | C (1)         | N (1)  | 124.0         | 124.7            | 124.8          |                           |
| C (2)  | C (1)         | C (6)  | 120.7         | 120.4            | 119.9          | 120.3                     |
| C (1)  | C (6)         | C (5)  | 119.1         | 119.2            | 119.6          | 119.6                     |
| C (1)  | C (2)         | C (3)  | 119.7         | 120.0            | 120.2          | 119.6                     |
| C (1)  | C (6)         | H (6)  | 119.5         | 119.4            | 118.8          |                           |
| C (1)  | C (2)         | H (2)  | 118.7         | 118.4            | 118.2          |                           |
| Torsion angles:                                  |               | $D(C_2,C_1, N_1,N_2)$  | 162.5         | 180.0            | 180.0          | 180.0                     |
| D(<br>,N   |               | D(C <sub>1</sub> ',N <sub>2</sub><br>,N <sub>1</sub> ,C <sub>1</sub> ) | 177.6         | 180.0            | 180.0          |                           |
| % error (average on 4 references) <sup>6</sup> : |               | 1.02   | 1.04          | 1.07             |                |                           |

 Table A2.2 Geometry optimization of trans-azobenzene.

Using the optimal B3LYP/6-31G(d) combination, the geometry of *cis*-azobenzene was also computed and the bond lengths, bond angles and the C-N=N-C torsion angle were compared with experimental values taken from the literature. The results were collected in **Table A2.3**, where the atoms are labeled as in **Figure A2.8**.



Figure A2.8 Molecular model for *cis*-azobenzene, atoms are labeled as in Table A2.3.

| Bond lengths (Å)          |             |             |                |                             |        |  |  |
|---------------------------|-------------|-------------|----------------|-----------------------------|--------|--|--|
|                           | Atom 1      | Atom 2      | B3LYP/6-31G(d) | Experimental <sup>[7]</sup> | %error |  |  |
|                           | N (1)       | N (2)       | 1.243          | 1.253                       | 0.8    |  |  |
|                           | C (1)       | N (1)       | 1.436          | 1.448                       | 0.9    |  |  |
|                           | C (1)       | C (2)       | 1.401          | 1.385                       | 1.2    |  |  |
|                           | C (2)       | C (3)       | 1.391          | 1.377                       | 1.0    |  |  |
|                           | C (3)       | C (4)       | 1.394          | 1.389                       | 0.4    |  |  |
|                           | C (4)       | C (5)       | 1.395          | 1.374                       | 1.5    |  |  |
|                           | C (5)       | C (6)       | 1.390          | 1.378                       | 0.9    |  |  |
|                           | C (6)       | C (1)       | 1.398          | 1.401                       | 0.2    |  |  |
| Bond angle                | s (degrees) |             |                | •                           |        |  |  |
| Atom 1                    | Atom 2      | Atom 3      |                |                             |        |  |  |
| C (1)                     | N (1)       | N (2)       | 124.2          | 121.9                       | 1.8    |  |  |
| C (2)                     | C (1)       | N (1)       | 122.9          | 122.5                       | 0.3    |  |  |
| C (1)                     | C (2)       | C (3)       | 120.1          | 120.8                       | 0.6    |  |  |
| C (2)                     | C (3)       | C (4)       | 120.5          | 119.0                       | 1.2    |  |  |
| C (3)                     | C (4)       | C (5)       | 119.8          | 121.7                       | 1.6    |  |  |
| C (4)                     | C (5)       | C (6)       | 120.1          | 118.7                       | 1.2    |  |  |
| C (5)                     | C (6)       | C (1)       | 120.0          | 119.8                       | 0.2    |  |  |
| C (2)                     | C (1)       | C (6)       | 119.9          | 120.0                       | 0.1    |  |  |
| Torsion angle: D(6,7,5,14 |             | D(6,7,5,14) | 51.0           | 53.0                        | 3.7    |  |  |
|                           |             |             | Total %error:  |                             | 1.0    |  |  |

**Table A2.3** Optimized geometry of *cis*-azobenzene using B3LYP/6-31G(d).

The values obtained were in agreement with literature displaying a similar percent error as the one for *trans*-azobenzene. Especially, the torsion angle of the C-N=N-C bond was found to be 51°, which was shown to be the correct geometry of *cis*-azobenzene in several studies.<sup>8</sup> It was concluded that B3LYP/6-31G(d) is the optimal combination for computations on *trans*-azobenzene molecules and their derivatives.

To ensure that the results obtained for **1** and **2** were realistic, their geometry was compared to the parent azobenzene molecule. For all structures, first a geometry optimization was performed, followed by a vibrational analysis, were no imaginary frequencies were found, meaning that the geometries obtained correspond to the ground state structures in gas phase. In order to compare the isomers of each compound, the difference in their single point energies were computed. The result obtained for azobenzene corresponds to the values seen in literature.<sup>9</sup> Energy differences between *cis*- and *trans*-isomers of **1** and **2** are very similar, approximately half the value for azobenzene. All these results are summarized in **Table A2.4**.

| Structure                       | 1        |                | 2      |              | Parent azobenzene |                |        |
|---------------------------------|----------|----------------|--------|--------------|-------------------|----------------|--------|
| Method                          |          | B3LYP/6-31G(d) |        | B3LYP/DGDZVP |                   | B3LYP/6-31G(d) |        |
|                                 | Units    | cis            | trans  | cis          | trans             | cis            | trans  |
| $\Delta$ SP( <i>trans-cis</i> ) | kcal/mol | 8.84           |        | 8.88         |                   | 15.26          |        |
| Dipole moment                   | Debye    | 1.74           | 0.06   | 2.52         | 0.10              | 3.21           | 0.00   |
| Δ LUMO-HOMO                     | eV       | 3.78           | 3.55   | 3.66         | 3.40              | 3.76           | 3.95   |
| CN=NC Torsion angle             | 0        | 10.58          | 178.18 | 9.97         | 177.07            | 9.36           | 179.97 |
| N=NCC Torsion angle             | 0        | 56.37          | 23.21  | 57.57        | 23.21             | 51.03          | 0.01   |

Table A2.4 Results of DFT calculations.

Finally the molecular orbitals of all isomers were computed. The corresponding figures of HOMO and LUMO orbitals are shown below:



cis-azobenzene (HOMO)

cis-1 (HOMO)

cis-2 (HOMO)



cis-azobenzene (LUMO)

cis-1 (LUMO)



cis-2 (LUMO)





## 6. References for Appendix 2

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# Rationale for Chapter 4: Photo-Mechanical Azobenzene Cocrystals and *in situ* X-ray Diffraction Monitoring of their Optically-Induced Crystal-to-Crystal Isomerization

In Chapter 3 we have established that single crystals of fluorinated *cis*-azobenzenes can be shaped in the irreversible crystal-to-crystal photo-mechanical process. Chapter 4 describes the possiblity of significant improvement of photo-mechanical potential of azobenzene crystals by halogen bond-driven cocrystallization. Specifically, by fine-tuning the cocrystal composition, photo-mechanical motion can proceed at much lower irradiation powers. The relative ease of photo-mechanical transformation prompted the *in situ* study of the photochemical reaction and revealed that crystal-to-crystal transformations in azobenzenes are topotactic and mediated by an amorphous state. The contribution 'Photo-mechanical azobenzene cocrystals and *in situ* X-ray diffraction monitoring of their optically-induced crystal-to-crystal isomerization' was published in *Chemical Science*.



## Chapter 4: Photo-Mechanical Azobenzene Cocrystals and *in situ* X-ray Diffraction Monitoring of their Optically-Induced Crystal-to-Crystal Isomerization

#### 4.1 Abstract

We demonstrate the first supramolecular cocrystallisation strategy to generate crystalline azobenzene materials with a range of photo-mechanical and thermochemical properties: from those that exhibit isomerization without any change in crystal shape to those that undergo a crystal-to-crystal *cis*-trans isomerization accompanied by large scale bending. The latter permitted the use of variable temperature single crystal X-ray diffraction for the first in situ monitoring of structural changes behind the *cis*-trans isomerization in the solid-state, which revealed a topotactic process mediated by an amorphous phase. While the design of photo-mechanical azobenzene solids has so far focused on polymer matrices and gels, the herein presented cocrystallisation approach represents the first methodology for generating new photo-mechanical azobenzene crystals from a limited number of photo-active building blocks, opening a route to potential bio-mimetic and light-harvesting materials based on crystalline solids

## 4.2 Introduction

Photo-mechanical materials, that undergo light-induced changes in shape<sup>1-5</sup> or even exhibit motion<sup>6,7</sup> are being extensively explored for applications in light-harvesting, molecular robotics, and in the design of nano-actuators and bio-mimetic artificial muscles.<sup>8,9</sup> Azobenzenes are a prominent family of photo-mechanical molecules whose *cis-trans* isomerization (**Figure 4.1a**)<sup>10,11</sup> causes large-scale changes in molecular shape. This change was used in the design of photo-mechanical liquid crystals<sup>12,13</sup> and polymer-based<sup>14</sup> solids, some of which have been likened to molecular muscles capable of exerting force on objects several times their weight.<sup>15</sup> Due to their close-packed structure, crystalline photo-mechanical systems offer access to faster energy transfer than their polymer-based counterparts and, in principle, should also allow the direct structural studies of the photo-mechanical effect by X-ray diffraction.<sup>7,16</sup> However, the development of photo-mechanical azobenzene (azo) crystals has only just begun: photo-induced bending of a thin azo crystal under ultraviolet irradiation was first reported in 2009<sup>17</sup> and, recently, rapid photo-mechanical bending<sup>18</sup> induced by visible light was observed in pseudostilbenes, *i.e.* azo

compounds containing complementary electron-donating and withdrawing groups. While a molecular-level mechanistic understanding of photo-mechanical effect in azo crystals is not yet accessible, a mathematical description of crystal bending and associated kinetics of isomerization have recently been reported.<sup>19,20</sup> An exciting development in photo-mechanical azo crystals has been provided by perfluorinated azo compounds,<sup>21</sup> whose *cis*-isomers have sufficiently long thermal half-lives to be isolated as single crystals. Single crystals of the perfluorinated azobenzene *cis*-1 and its iodo-analogue *cis*-2 (Figure 4.1b) undergo apparently irreversible photo-mechanical bending<sup>22</sup> caused by light-induced *cis*-*trans* azo isomerization.



**Figure 4.1** Schematic representation of: a) azo-isomerization; b) herein studied halogen bond donors (left) and acceptors (right) and c) a general halogen bonding motif.

Irreversibility of this transformation permitted the deliberate shaping of micrometer-sized crystals and was explained by the higher density of the *trans*-crystal which hinders the opposite transformation to the *cis*-form. This photo-mechanical transformation proceeded in a crystal-to-crystal manner, which transformed a single crystal of *cis*-1 into polycrystalline *trans*-1, suggesting X-ray diffraction could be utilised to study the azo photo-mechanical bending.

Further studies and the design of photo-mechanical azo crystals are inherently limited by the number of available chromophores, challenges of their synthesis and, ultimately, their crystal morphology.<sup>23</sup> In principle, all of these limitations can be circumvented by crystal engineering, that allows the modification of a number of solid-state properties through the formation of multi-component crystals (cocrystals). Cocrystallisation has previously been employed to tune solid-state physicochemical properties of molecules, especially for pharmaceutical applications and photochemical synthesis.<sup>24,25</sup> Whereas the formation of azo cocrystals was previously explored through  $\pi \cdots \pi$ -stacking,<sup>26,27</sup> molecular inclusion,<sup>28,29</sup> hydrogen<sup>30-33</sup> and halogen-bonding,<sup>34-36</sup> there have been no reports of photo-mechanical activity in the resulting solids. Moreover, there have not yet been any reports of design or structural characterisation of cocrystals of *cis*-azobenzenes, most likely due to often short lifetimes preventing the isolation of single crystals.

We now demonstrate halogen bond-driven cocrystallisation as a simple, rapid strategy to deliberately generate a diversity of azo-based crystalline materials involving *cis*- or *trans*-azo moieties or their combination, with different photo-mechanical and thermal properties. Most importantly, we report a halogen-bonded *cis*-azo cocrystal that undergoes large-scale irreversible photo-mechanical bending in crystal-to-crystal fashion. We have used this photo-mechanically active cocrystal for the first *in situ* single crystal X-ray diffraction study of solid-state azo isomerization. The *in situ* studies at different temperatures revealed that the transformation of the *cis*- to the *trans*-cocrystal is topotactic and mediated by an amorphous phase.

## 4.3 Results and Discussion

### 4.3.1 Preparation of Cocrystals

Cocrystallisation is enabled by the highly polarizable bromine or iodine atoms on the electron-deficient perfluorphenyl moiety in 1 and 2 (Figure 4.1b,c), making them potentially suitable as halogen bond<sup>37</sup> donors. The halogen bond donors are expected to form a linear interaction with acceptor pyridine nitrogen atoms.<sup>38</sup> By pairing of either the *cis*- or the *trans*-isomer of 1 or 2 with suitable azo- or olefin-based pyridine derivatives (Figure 4.1c), we aimed to obtain first crystalline solids containing diverse combinations of azo and/or olefin geometric isomers. Cocrystals were prepared by slow evaporation of solutions containing equimolar amounts of a halogen bond donor (1 or 2) in cis- or trans-form and one of the following acceptors: cis- and trans-1,2-bis(4-pyridyl)ethylene (cis- and trans-bpe, respectively) and trans-4,4'-azopyridine (apy) (Appendix 3, Section 1). Attempts to obtain *cis*-4,4'-azopyridine as a potential cocrystallisation partner were not successful. Furthermore, none of the attempts to obtain the cocrystal (cis-1)(cis-bpe) was successful. As revealed by single crystal X-ray diffraction, all prepared cocrystals exhibit the expected Br…N (with 1) and I…N (with 2) halogen bonds with donor...acceptor distances below 3.2 Å (Appendix 3, Section 2).<sup>39</sup> The halogen bonds associate cocrystal components into infinite one-dimensional chains of alternating halogen bond donors and acceptors, whose topology is dictated by the choice of their geometric isomer. The bent "V-shape" of cis-1, cis-2 or cis-bpe dictates a zigzag geometry of the chains with a chain undulation distance of ca. 40 Å (Figure 4.2a). Chains involving trans-components only are linear, with adjacent molecules in each chain being either coplanar (in cocrystals with *trans*-bpe, Figure 4.2b) or rotated around the chain direction by 66.0° for (cis-1)(apy) (Figure 4.2c) and 65.2° for (cis-2)(apy). Two cis-building blocks in (cis-2)(cis-bpe) dictate the undulation of the supramolecular chain to be twice that found in cocrystals composed of *cis*- and *trans*-molecules (Figure 4.2d, wavelength 20.3 Å). Another important structural distinction between (*cis*-**2**)(*cis*-**bpe**) and other prepared cocrystals is the absence of intermolecular  $\pi \cdots \pi$  interactions. The latter suggests a potential explanation of the inability to obtain the analogous (cis-1)(cis-bpe); presumably, the Br...N interactions expected in (cis-1)(cis-bpe) would be too weak to hold together a cocrystal in the absence of such  $\pi \cdots \pi$  interactions.<sup>40</sup> In all cocrystals the supramolecular chains assemble so as

to segregate perfluorinated and hydrocarbon residues, as often observed in halogen-bonded cocrystals (Figure 4.2e).<sup>41</sup>



**Figure 4.2** (a) Zigzag structure of a supramolecular chain in the (cis-1)(trans-bpe) cocrystal, with the repeat distance of the chain undulation indicated. Linear structure of supramolecular chains in the: (b) (trans-1)(trans-bpe) cocrystal and (c) (trans-1)(apy) cocrystal. Chain components in (trans-1)(trans-bpe) are coplanar, while in (trans-1)(apy) the best planes drawn through molecules of *trans*-1 and **apy** are rotated by 66°.(d) In the zigzag structure of a (cis-2)(cis-bpe) chain the repeat distance of undulation is roughly half of that seen in cocrystals of *cis*-1 or -2 with *trans*-halogen bond donors. (d) The spacefill representation of molecular packing in (cis-1)(apy) illustrates the segregation of hydrocarbons (blue) and perfluorocarbons (red) residues into columns.

#### 4.3.2 Photo-Mechanical Behaviour

Cocrystallisation of *cis*-1 and *cis*-2 with all explored pyridines gave materials with very different photo-mechanical properties in terms of: 1) the power of irradiation required to induce bending and 2) of the magnitude of resulting deformation expressed as the deflection angle of the crystal tip. Upon irradiation with a 532 nm laser all prepared *cis*-azo cocrystals underwent a colour change from orange to red, consistent with solid-state isomerization.<sup>†</sup> However, an overview of the photo-mechanical properties of the cocrystals (**Table 4.1**) reveals that photo-mechanical behaviour of a *cis*-azobenzene is significantly modified by the choice of a cocrystallisation partner. Photo-mechanical characteristics of cocrystals follow the differences in the efficiency of their crystal packing, given as calculated volume per non-hydrogen atom in the unit cell. As planar *trans*-molecules are expected to more readily achieve a close-packed structure than their V-shaped *cis*-analogues,<sup>22</sup> there might also be a tentative relationship between cocrystal composition and photo-mechanical activity.

| Cocrystal          | Irradiatio         | Deflectio  | Volume per                    | Volume per non-H atom in the              |  |
|--------------------|--------------------|------------|-------------------------------|---|--|
|                    | n power,           | n angle, ° | non-H atom in                 | unit cell for corresponding               |  |
|                    | mW/cm <sup>2</sup> |            | the unit cell, Å <sup>3</sup> | cocrystal of <i>trans</i> -1 or -2, $Å^3$ |  |
| (cis-2)(cis-bpe)   | 5                  | > 90       | 16.6                          | 16.1                                      |  |
| (cis-2)(trans-bpe) | 60                 | 10         | 15.8                          | 15.1                                      |  |
| (cis-1)(trans-bpe) | 60                 | 9          | 15.4                          | 15.0                                      |  |
| (cis-2)(apy)       | 200                | 4          | 15.4                          | 15.4                                      |  |
| (cis-1)(apy)       | 200                | 3          | 14.8                          | 14.8                                      |  |

Table 4.1 Photo-mechanical behaviour of prepared cocrystals<sup>a,b</sup>

a) the thickness for all crystals ranged between 15  $\mu$ m and 20  $\mu$ m; b) cocrystals of *trans*-1 and -2 were not photo-mechanically active; c) for comparison, previously reported irreversible transformation in single-component crystals of *cis*-1 reliably generated deflection angles of > 90° at an irradiation power of 200 mW/cm<sup>2</sup>.<sup>22</sup>

Indeed, the only cocrystal in our study based only on *cis*-molecules, (*cis*-2)(*cis*-bpe), also exhibits the highest calculated volume per non-hydrogen atom of 16.6 Å<sup>3</sup>. Crystals of (cis-2)(cis**bpe**) readily bend at a low irradiation power of 5 mW/cm<sup>2</sup>, with the deflection angle of the crystal tip exceeding 90° (Figure 4.3, see also Appendix 3 Section 3, Table A3.2). The cocrystals of *cis*and *trans*-components, such as (*cis*-1)(*trans*-bpe) and (*cis*-2)(*trans*-bpe), are more closely packed with respective volumes of 15.4 Å<sup>3</sup> and 15.8 Å<sup>3</sup> per non-hydrogen atom. These cocrystals require an irradiation power of at least 60 mW/cm<sup>2</sup> for deflection. Similarly, the cocrystals (*cis*-1)(apy) and (cis-2)(apy) are photo-mechanically inactive up to the irradiation power of 200 mW/cm<sup>2</sup> and even then undergo only a minimal deformation of the crystal shape (Table A3.2 in Section 3 of the Appendix 3). Variation in crystal thickness between different samples (ranging between 15 µm and 20 µm) was too small to play a significant role in the described differences in photomechanical behaviour. No photo-mechanical bending was observed in cocrystals involving trans-1 and -2. This is consistent with our previous observation that pure trans-1 and trans-2 do not exhibit photo-mechanical bending, presumably due to much more efficient molecular packing compared to their *cis*-analogues.<sup>22</sup> As **apy** itself does not exhibit photochemical switching in solution,<sup>22</sup> it was unsurprising that pure apy and its cocrystals with *trans*-1 and 2 did not exhibit bending.

## 4.3.3 Crystal-to-Crystal Photo-Mechanical Bending in (cis-2)(cis-bpe)

Photo-mechanical bending of thin (ca. 20 µm) needles of (*cis*-2)(*cis*-bpe) was accompanied by a change in crystal colour from yellow to brick-red (**Figure 4.3b**), consistent with *cis*→*trans* isomerization of *cis*-2. After irradiation the crystal<sup>22</sup> exhibited an X-ray diffraction pattern of sufficient quality for crystal structure determination, revealing the crystal structure of (*trans*-2)(*cis*-bpe) identical to that obtained from separately grown crystals. Although this transformation did not take place in a single-crystal-to-single-crystal<sup>42,43</sup> fashion, the majority (ca. 75%) of the Xray reflections collected from the irradiated crystal could be indexed to only two crystalline domains of (*trans*-2)(*cis*-bpe), and the rest to several smaller crystalline domains of (*trans*-2)(*cis*bpe) (Appendix 3, Section 4). Such photochemical behaviour is significantly more susceptible to structural studies by X-ray diffraction than the previously investigated pure *cis*-1 which, upon irradiation, typically produced five or more crystalline domains that were difficult or impossible to index.



(cis-2)(cis-bpe) (trans-2)(cis-bpe) (cis-2)(cis-bpe) (after irradiation)

**Figure 4.3** a) Schematic illustration of the deflection of crystal tip upon photo-mechanical motion. b) Permanent photo-mechanical change in shape of a (cis-2)(cis-bpe) cocrystal upon photochemical transformation into (trans-2)(cis-bpe), the blue arrow indicates the direction of irradiation. c) Comparison of a (cis-2)(cis-bpe) cocrystal before and after irradiation with 532 nm laser, the photochemical  $cis \rightarrow trans$  isomerization is indicated by the colour change of the irradiated cocrystal. d) A highly bent crystal of (cis-2)(cis-bpe) with a tip deflection angle >90°. e) Fragments of cocrystal structures of the parent (top) and the daughter (bottom) phase involved in the photochemical transformation  $(cis-2)(cis-bpe) \rightarrow (trans-2)(cis-bpe)$ . f) Composite diffraction images of the *h0l* plane for the starting (cis-2)(cis-bpe) cocrystal (left), the (trans-2)(cis-bpe) cocrystal (center) and (trans-2)(cis-bpe) obtained by irradiation of (cis-2)(cis-bpe) (right). Analogous composite images for (0kl) and (hk0) planes are given in the Appendix 3, Figures A3.2 and A3.1

In contrast, the presence of only two major crystalline domains in irradiated (cis-2)(cisbpe) enabled indexing and structure solution using conventional protocols.<sup>‡</sup> Photochemical transformation underlying crystal bending is apparent from the comparison of composite diffraction images of the h0l diffraction planes for the (cis-2)(cis-bpe) cocrystal before irradiation, the separately grown (trans-2)(cis-bpe) cocrystal and the (cis-2)(cis-bpe) cocrystal after irradiation (Figure 4.3f, also Appendix 3, Section 4, Figures A3.2, A3.3). The reaction also proceeds in the bulk powder, as confirmed by powder X-ray diffraction (PXRD), which revealed the transformation of the powder diffractogram of (cis-2)(cis-bpe) into one consistent with (trans-2)(cis-bpe) upon irradiation. (Appendix 3 Section 5, Figure A3.5). The high quality of X-ray diffraction patterns observed from single crystals of (cis-2)(cis-bpe) irradiated ex situ encouraged us to explore the mechanism of this apparent crystal-to-crystal transformation by in situ monitoring of changes in the X-ray reflections in the reciprocal (001) plane of a single crystal of (cis-2)(cisbpe) during irradiation. Importantly, in situ diffraction studies on azo crystals undergoing photoisomerization have never previously been reported. The intensity of the reflections was found to rapidly diminish upon irradiation with 532 nm laser at 5 mW/cm<sup>2</sup>, with concomitant appearance and strengthening of reflections consistent with (trans-2)(cis-bpe) (Figure 4.4a). Disappearance of reflections of the starting phase and appearance of those of the product suggests a transformation mediated by amorphisation and recrystallisation. To verify the appearance of an amorphous intermediate, we conducted an analogous experiment with the crystal cooled to 200 K. Irradiation of a (cis-2)(cis-bpe) single crystal produced the expected change in crystal colour and shape, but also led to a complete loss of features in the diffraction image, consistent with amorphisation (Figure 4.4b). Presumably, 200 K is a sufficiently low temperature to hinder the crystallisation of the product (trans-2)(cis-bpe) from the amorphous phase generated by photochemical transformation. The reflections of the nascent daughter phase do not correspond to any simple (e.g. h0l, hk0 or 0kl) diffraction planes of (trans-2)(cis-bpe). However, repeating the experiment on a different crystal of (cis-2)(cis-bpe), with the same positioning of the laser source and the identical initial crystal orientation, yielded the same product diffraction pattern, indicating an identical orientation of the (trans-2)(cis-bpe) daughter phase (Appendix 3, Figure A3.4).



**Figure 4.4** X-ray diffractograms collected *in situ* on single crystals of (cis-2)(cis-bpe) while being irradiated with a 532 nm laser. (a) A single crystal of (cis-2)(cis-bpe) being irradiated at room temperature at 5 mW/cm2. (b) A single crystal of (cis-2)(cis-bpe) being irradiated at 200 K at 15 mW/cm2. These images reveal that room-temperature irradiation leads to the disappearance of parent (cis-2)(cis-bpe) and simultaneous formation of (trans-2)(cis-bpe). In contrast, low-temperature irradiation leads only to the appearance of an amorphous material, as evidenced by the loss of diffraction spots. The *in situ* diffraction data strongly indicates that "crystal-to-crystal"  $(cis-2)(cis-bpe) \rightarrow (trans-2)(cis-bpe)$  transformation is mediated by an amorphous phase.

Repeating the experiment with a different position of the laser source, but retaining the initial crystal orientation again provided the same diffraction pattern. Modification of the incident laser light polarisation also did not have any noticeable effect on the diffraction pattern and, therefore, crystallographic orientation of the product. The described experiments indicate that the solid-state photoisomerization of (*cis-2*)(*cis-bpe*) is a topotactic reaction,<sup>43</sup> *i.e.* the molecular arrangement of the parent phase appears to, at least partially, determine the crystallographic orientation of the daughter (*trans-2*)(*cis-bpe*) phase.

#### 4.3.4 Thermochemical Behaviour of cis-Azo Cocrystals

Cocrystallisation also affected the thermal behaviour of *cis*-1 and -2 in the solid state. Thermal analysis by combined differential scanning calorimetry and thermogravimetric analysis (DSC/TGA) revealed that *cis*-1 and -2 exhibit different solid-state thermal properties as pure solids than in the form of cocrystals. DSC thermograms of pure *cis*-1 and -2 display an endothermic event, immediately followed by a broad exotherm (**Figure 4.5a**, Appendix 3, Section 6). The two events are not associated with a loss of sample weight (Appendix 3, **Figures A3.6** and **A3.7**) and are interpreted as endothermic melting, followed by exothermic isomerization into the *trans*-isomer (it was previously calculated that the *cis*-forms of 1 and 2 are ca. 37 kJ mol<sup>-1</sup> higher in energy than the corresponding *trans*-isomer).<sup>22</sup> Thermal isomerization is confirmed by another endothermic event at a higher temperature, corresponding to the melting point of *trans*-1 or -2. In contrast, DSC thermograms of all prepared halogen-bonded cocrystals of *cis*-1 and -2 display an exothermic event first, (**Figure 4.5a**) taking place at a significantly lower temperature (130 °C-160 °C) than any other endothermic signal or weight loss detected in the combined DSC/TGA measurement.

We conclude that the exothermic  $cis \rightarrow trans$  isomerization in prepared cocrystals can take place in the solid state, *i.e.* without prior melting observed for pure cis-1 and -2. Interpretation of the first exothermic event as the  $cis \rightarrow trans$  isomerization is supported by the measured enthalpy change which is consistent with the previously calculated<sup>22</sup> differences in energy between cis- and trans-forms of 1 and 2, *e.g.* 37 kJ mol<sup>-1</sup> for (cis-1)(trans-bpe) and 33 kJ mol<sup>-1</sup> for (cis-2)(cis-bpe).



Figure 4.5 a) Overlay of DSC thermograms for pure solid *cis*-1 and cocrystals (*cis*-1)(*trans*-bpe) and (*cis*-2)(*cis*-bpe). b) A selected elongated crystal of (*cis*-1)(*trans*-bpe) on the hotstage microscope at 37 °C and c) the same crystal at 130 °C. These two images demonstrate the slight thermomechanical bending of the (*cis*-1)(*trans*-bpe) cocrystal, followed by chemical decomposition upon further heating. d) Image of an aggregate of crystals of pure *cis*-1 at 25 °C; e) image of the same sample at 139 °C, demonstrating partial melting of the sample and f) image of the same sample at 205 °C, demonstrating the recrystallisation of the sample. The images d) and e) demonstrate that pure *cis*-1 does not undergo solid-state *cis*-*trans* isomerization and thermomechanical bending, but instead melts and then undergoes *cis*-*trans* isomerization.

Next, we undertook a more detailed study of thermal behaviour of (cis-2)(cis-bpe) and (cis-1)(trans-bpe) cocrystals (Figure 4.5b,c), as well as pure solid cis-2 (Figure 4.5d,e) via thermal hot-stage microscopy. The cocrystals underwent slight mechanical bending upon heating to 140 °C and 120 °C, respectively, followed by thermal decomposition above 200 °C. In contrast, pure cis-2, as anticipated from bulk DSC measurements, underwent melting accompanied with colour change and solidification, both due to the formation of trans-2. The combined DSC and hot-stage microscopy data on cocrystals clearly show that cocrystallisation enabled the thermochemical  $cis \rightarrow trans$  isomerization to take place in the solid, without prior melting, potentially explaining the thermo-mechanical bending of cocrystals that was not observed in pure cis-1 or -2 crystals.<sup>¶</sup>

#### 4.4 Conclusions

The presented work demonstrated the first solid-state supramolecular strategy to generate new photo-mechanical azo crystals. Halogen bond-driven cocrystalisation enabled modification of the photo-mechanical behaviour of a particular azobenzene in a crystalline solid, and permitted the first use of single crystal X-ray diffraction for *in situ* study of azo isomerization. Using only one photo-mechanically active component (e.g. cis-2), cocrystallisation yielded one cocrystal exhibiting crystal-to-crystal photo-mechanical motion, several cocrystals that exhibited lesser photo-mechanical activity, and several cocrystals that displayed no photo-mechanical bending at all, demonstrating a means to modify the photo-mechanical response of a crystal to solid-state azo isomerization. Thermal measurements reveal that cocrystallisation also allows decoupling of thermal isomerization and melting, leading to new crystalline solids that can undergo thermal azo isomerization in the solid state. The facile crystal-to-crystal azo isomerization in (*cis*-2)(*cis*-bpe) enabled the use of X-ray single crystal diffraction to follow the structural changes behind photomechanical bending, revealing that the apparent crystal-to-crystal reactivity is topotactic and proceeds via an amorphous phase.<sup>45</sup> The presented cocrystallisation strategy offers rapid access to new structurally and photo-mechanically diverse azo crystals, including those susceptible to fundamental structural studies by X-ray single crystal diffraction. Complemented by the ongoing development of detailed kinematic studies,<sup>7,19</sup> this will be of paramount importance for understanding the structure-property relationships and, therefore, the design and optimisation of azo crystals for energy harvesting and transduction of light into mechanical motion. In that context,

the demonstrated ability to synthesise photo-mechanically active cocrystals opens up the opportunity to design materials in which photo-mechanical behaviour could be based on more than one type of chromophore. Our particular interest lies in exploring the potential of irreversible photo-mechanical behaviour for precise shaping of materials at the micrometer scale.

#### 4.5 Supporting Information

Appendix 3 contains the details of experimental procedures, selected PXRD, FTIR-ATR and thermal (TGA/DSC) data, summary of crystallographic data and indexing of the (*cis-2*)(*cis-bpe*) cocrystal after irradiation, crystallographic data for all prepared cocrystals. (CCDC code 984291-984300)

#### 4.6 Acknowledgements

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#### 4.7 Notes

<sup>†</sup> Spectral characterisation of *cis*-1 and -2, as well as *trans*-1 and -2 was reported previously<sup>21</sup>. Irradiation wavelengths were selected according to solid-state UV/Vis absorption profiles for *cis*-1/*trans*-1 and *cis*-2/*trans*-2 systems, which effectively coincide and allow irradiation with wavelengths up to 550 nm for irreversible solid-state *cis*→*trans* transformation. Vibrational (Fourier-transform infrared attenuated total reflectance) spectroscopy (Appendix 3 **Figs A3.23-3.39**) confirms the presence of both components in all prepared cocrystals.

‡ The differences between photo-mechanical behaviour of previously reported single crystals of  $cis-1^{22}$  and the herein investigated cocrystal (cis-2)(cis-bpe) merit some discussion. While both materials undergo photo-mechanical crystal-to-crystal transformation, a crucial

difference was observed in the quality of the irradiated crystals as measured by single crystal Xray diffraction. Irradiation of *cis*-1 crystals<sup>22</sup> always yielded multiple domains, which allowed for structural characterisation only in select few *ex situ* irradiated crystals. For the (*cis*-2)(*cis*-**bpe**) cocrystal nearly any specimen irradiated *in situ* produced a diffraction pattern of sufficient quality for routine indexing and structure determination. Cocrystal material of (*cis*-2)(*cis*-**bpe**) more easily accommodated the structural changes in the material upon isomerization and bending, and was less brittle upon irradiation than single-component crystals of *cis*-1; thus, cocrystallization allowed study of the process *in situ*.

We consider it unlikely that the difference in thermal behaviour of pure *cis*-1 or *cis*-2 and corresponding cocrystals would affect the mechanism of their photo-induced bending, as the low irradiation powers are not likely to significantly increase the temperature of the irradiated crystal.

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## **Appendix 3: Supporting Information for Chapter 4**

## 1. Experimental

#### 1.1 Materials:

4,4'-dibromooctafluoroazobenzene (1) and 4-iodo-2,3,5,6-tetrafluoroaniline(2) were synthesized and as outlined in our prior report which also reported their spectroscopic properties, including UV/Vis spectra and K,  $t_{1/2}$  and molar extinction coefficient values in different solvents.<sup>1</sup> Precursors such as 4-bromo-2,3,5,6-tetrafluoroaniline, 2,3,5,6-tetrafluoroaniline and mercury oxide were obtained from Sigma Aldrich and were used without purification.

#### 1.2 Cocrystal synthesis

Cocrystals were prepared by mixing equimolar quantities of halogen bond donors and acceptors in suitable solvent, most often dichloromethane (DCM). Samples of *cis*-1 and -2 after weighing and dissolving in a solvent were irradiated by 532 nm light to ensure ~100% *cis*-isomer content. Single crystals were obtained by slow evaporation of the solvent, while samples for thermal and Fourier-transform infrared attenuated total reflection (FTIR-ATR) spectroscopy analyses were made by quick evaporation to limit partial thermal isomerization of *cis*-1 and -2.

#### Cocrystal (*trans*-1)(apy)

10.0 mg (0.021 mmol) of *trans*-1 was dissolved in 2.5 ml of DCM and added to a solution of 3.80 mg (0.021 mmol) of **apy** in 2.5 ml of DCM. Solution remained clear after mixing and cocrystals precipitated when nearly all solvent evaporated. The cocrystal melts with decomposition at 204°C, different from the melting points of **apy** (111 °C) and *trans*-1 (222°C).

#### Cocrystal (*trans*-1)(*trans*-bpe)

10.0 mg (0.021 mmol) of *trans*-1 was dissolved in 2.5 ml of DCM and added to the solution of 3.80 mg (0.021 mmol) of *trans*-1,2-bis(4-pyridyl)ethylene (*trans*-bpe) in 2.5 ml of DCM. Solution remained clear after mixing and cocrystals precipitated when the solvent evaporation was nearly completed. The cocrystal melts with decomposition at 209°C.

## Cocrystal (cis-1)(apy)

10.0 mg (0.021 mmol) of *cis*-1 was dissolved in 2.5 ml of DCM and added to the solution of 3.80 mg (0.021 mmol) of **apy** in 2.5 ml of DCM. Solution remained clear after mixing and cocrystals precipitated when the solvent evaporation was nearly completed. On the DSC plot, a broad exotherm between 150-180°C can be observed corresponding to thermal *cis-trans* reconversion. The cocrystal melts with decomposition at 203°C.

## Cocrystal (cis-1)(trans-bpe)

10.0 mg (0.021 mmol) of *cis*-1 was dissolved in 2.5 ml of DCM and added to the solution of 3.80 mg (0.021 mmol) of *trans*-**bpe** in 2.5 ml of DCM. Solution remained clear after mixing and cocrystals precipitated when the solvent evaporation was nearly completed. In the course of thermal analysis an exothermal peak between 140-170°C can b observed which corresponds to thermal *cis*-*trans* reconversion. The cocrystal then melts with decomposition at 209°C.

## Cocrystal (*trans-2*)(**apy**)

10.0 mg (0.017 mmol) of *trans*-2 was dissolved in 25 ml of DCM and added to the solution of 3.18 mg (0.017 mmol) of **apy** in 15 ml of DCM. Solution turned cloudy as predominantly microcrystalline product precipitated. The cocrystal melts with decomposition at 263°C.

## Cocrystal (trans-2)(trans-bpe)

10.0 mg (0.017 mmol) of *trans*-2 was dissolved in 25 ml of DCM and added to the solution of 3.18 mg (0.017 mmol) of *trans*-bpe in 15 ml of DCM. Solution turned cloudy as predominantly microcrystalline product precipitated. The cocrystal melts with decomposition at 271 °C

## Cocrystal (cis-2)(apy)

10.0 mg (0.017 mmol) of *cis*-2 was dissolved in 25 ml of DCM and added to the solution of 3.18 mg (0.017 mmol) of **apy** in 15 ml of DCM. Solution turned cloudy as predominantly microcrystalline product precipitated. The cocrystal melts with decomposition at 247 °C.

## Cocrystal (cis-2)(trans-bpe)

10.0 mg (0.017 mmol)of *cis*-**2** was dissolved in 25 ml of DCM and added to the solution of 3.18 mg (0.017 mmol) of *trans*-**bpe** in 15 ml of DCM. Solution turned cloudy as predominantly microcrystalline product precipitated. The cocrystal melts with decomposition at 266 °C.

## Cocrystal (cis-2)(cis-bpe)

10.0 mg (0.017 mmol) of *cis*-2 was dissolved in 25 ml of DCM and added to the solution of 3.18 mg (0.017 mmol) of *cis*-1,2-bis(4-pyridyl) ethylene (*cis*-2) in 15 ml of DCM. Cocrystals precipitated when the solvent evaporation was nearly completed. Melting with decomposition was observed at 196 °C.

## Cocrystal (*trans-2*)(*cis-bpe*)

10.0 mg (0.017 mmol) of *trans*-2 was dissolved in 25 ml of DCM and added to the solution of 3.18 mg (0.017 mmol) of *cis*-**bpe** in 15 ml of DCM. Cocrystals precipitated when the solvent evaporation was nearly completed. Melts with decomposition at 200  $^{\circ}$ C.



2. Single Crystal X-ray Diffraction Measurements and Crystallographic Summary

**Figure A3.1** Fragments of crystal structures of prepared cocrystals, illustrating the formation of halogen-bonded chains, with representative halogen bond acceptor…donor distances

highlighted. Thermal ellipsoids are drawn at 50% probability. Element colours: grey (carbon), blue (nitrogen), green (fluorine), purple (iodine) and brown (bromine).

#### **3. Photo-Mechanical Motion Measurements**

X-ray single crystal diffraction data was obtained on Bruker D8 single-crystal X-ray diffractometer equipped with a Mo $K_{\alpha}$  X-ray source and a graphite monochromator. Multi-scan absorption correction (SADABS) was applied for all collected datasets. Structures were solved by direct methods and refined using SHELX-97 software.<sup>2</sup> Crystallographic data for all prepared cocrystals has been deposited with the Cambridge Structural Database (deposition codes 984291-984300)

For a typical exploration of photo-mechanical motion, cocrystals of *cis*-1 or -2 of the approximate thickness between 10  $\mu$ m and 20  $\mu$ m were subjected to irradiation on the tip of the Mitegen® 75  $\mu$ m aperture micromounts. Irradiation was achieved by linearly polarized variable power Ar<sup>+</sup>-ion laser at 488 nm and 532 nm wavelengths and power in the range between of 5 mW/cm<sup>2</sup> and 400 mW/cm<sup>2</sup>. Photo-mechanical motion was recorded by an Infinity-1 CMOS microscopy camera fitted with a zoom lens.

| Cocrystal                      | Snapshot before irradiation | Snapshot after irradiation |  |  |
|--------------------------------|-----------------------------|----------------------------|--|--|
| (cis-2)(cis-bpe)               |                             |                            |  |  |
| (cis-2)(trans-bpe)             |                             |                            |  |  |
| (cis-1)(trans-bpe)             |                             |                            |  |  |
| (cis-2)(apy)                   |                             |                            |  |  |
| ( <i>cis</i> -1)( <b>apy</b> ) |                             |                            |  |  |

Table A3.1 Images of photo-mechanical *cis*-azobenzene cocrystals before and after irradiation

## 4. Summary of Indexing the Crystal of (cis-2)(cis-bpe) after Irradiation

Cell indexing was performed in the basis of 747 reflections. Majority of the reflections (557 out of 747) could be fitted to two major domains<sup>3</sup>, described below:

domain 1: 420 reflections, 7.019, 7.06, 27.273 (reduced cell)

domain 2: 351 reflections, 137 exclusively, 190 unassigned

The unitcell was identical for the two domains, but rotated 2.3° about the reciprocal 0.315, 0.362, 1.000 axis and the real 0.792, 1.000, 0.220 axis

The remaining 190 reflections could be assigned to 10 domains with gradually diminishing size. All of them exhibit the same unitcell (identical to the second decimal) of (*trans-2*)(*cis-bpe*).

(cis-**2**)(cis-**bpe**)



(trans-2)(cis-bpe)



(*cis*-**2**)(*cis*-**bpe**) irradiated



**Figure A3.2** Composite diffraction images for the *0kl* diffracting plane of studied crystals. Irradiation of the cocrystal (right image) was performed by 488 nm laser light for 10 hours at 20  $mW/cm^2$ 



**Figure A3.3** Diffraction images for the *hk0* diffracting plane of studied crystals. Irradiation of the cocrystal (right image) was performed using 488 nm laser light for 10 hours at 20 mW/cm<sup>2</sup>.

an irradiated co-crystal usual settings b) a co-crystal irradiated with laser rotated by 90°





a)

c) co-crystal irradiated with linearly polarized light



d) co-crystal irradiated with circularly polarized light



**Figure A3.4** Diffraction images taken for identically oriented single crystals of (*cis*-**2**)(*cis*-**bpe**) after irradiation under different conditions: (a) standard experiment geometry; (b) irradiation with the laser rotated 90° around the sample; (c) irradiation using linearly polarized light and (d) irradiation using circularly polarized light. All the diffraction images are very similar, indicating that the orientation of the crystalline product phase (*trans*-**2**)(*cis*-**bpe**) is identical and that the photochemical isomerization is topotactic.

#### 5. Powder X-ray Diffraction Data



**Figure A3.5** Seclected powder X-ray diffraction patterns. From top to bottom: simulated pattern of (*cis*-2)(*cis*-bpe); experimental pattern for a sample of (*cis*-2)(*cis*-bpe) before irradiation; experimental pattern for (*cis*-2)(*cis*-bpe) after irradiation for 1 hour; experimental pattern for a sample of (*cis*-2)(*cis*-bpe) after irradiation for 20 hours and simulated pattern for (*trans*-2)(*cis*-bpe). The comparison of the PXRD patterns shows that the product of extended irradiation of crystalline (*cis*-2)(*cis*-bpe) is the (*trans*-2)(*cis*-bpe) crystal. The broadness of the (*trans*-2)(*cis*-bpe) X-ray reflections after irradiation is consistent with the presence of an amorphous phase indicated by *in situ* single crystal X-ray diffraction measurements.

## 6. Thermal Analysis Data



Figure A3.6 TGA (top) and DSC (bottom) thermograms of *cis*-1.



Figure A3.7 TGA (top) and DSC (bottom) thermograms of *cis*-2.


Figure A3.8 TGA (top) and DSC (bottom) thermograms of *trans*-1.



Figure A3.9 TGA (top) and DSC (bottom) thermograms of *trans-2*.



Figure A3.10 TGA (top) and DSC (bottom) thermograms of azopyridine (apy).



Figure A3.11 TGA (top) and DSC (bottom) thermograms of *trans*-bpe.



Figure A3.12 TGA (top) and DSC (bottom) thermograms of *cis*-bpe.



Figure A3.13 TGA (top) and DSC (bottom) thermograms of (*trans-1*)(*trans-bpe*) cocrystal.



Figure A3.14 TGA (top) and DSC (bottom) thermograms of (*cis*-1)(*trans*-bpe) cocrystal.



Figure A3.15 TGA (top) and DSC (bottom) thermograms of the (*cis*-1)(apy) cocrystal.



Figure A3.16 TGA (top) and DSC (bottom) thermograms of (*trans*-1)(apy).



Figure A3.17 TGA (top) and DSC (bottom) thermograms of (cis-2)(apy) cocrystal.



Figure A3.18 TGA (top) and DSC (bottom) thermograms of (cis-2)(trans-bpe) cocrystal.



Figure A3.19 TGA (top) and DSC (bottom) thermograms of (*cis*-2)(*cis*-bpe) cocrystal.



Figure A3.20 TGA (top) and DSC (bottom) thermograms of (*trans*-2)(apy) cocrystal.



Figure A3.21 TGA (top) and DSC (bottom) thermograms of (trans-2)(cis-bpe) cocrystal.



Figure A3.22 TGA (top) and DSC (bottom) thermograms of (*trans-2*)(*trans-bpe*) cocrystal.

# 7. Vibrational Analysis Data

Fourier-transform infrared attenuated total reflection (FTIR-ATR) spectra were obtained using Nicolet 6700 FTIR spectrometer and were analyzed with Bruker OPUS software, version 7.2.



Figure A3.23 FTIR-ATR spectrum of azopyridine (apy).



Figure A3.24 FTIR-ATR spectrum of *trans*-bpe.



Figure A3.25 FTIR-ATR spectrum of *cis*-bpe.



Figure A3.26 FTIR-ATR spectrum of *cis*-1.



Figure A3.27 FTIR-ATR spectrum of *cis*-2.



Figure A3.28 FTIR-ATR spectrum of *trans-*1.



Figure A3.29 FTIR-ATR spectrum of *trans-2*.



Figure A3.30 FTIR-ATR spectrum of (cis-1)(apy).







Figure A3.32 FTIR-ATR spectrum of (trans-1)(apy).



Figure A3.33 FTIR-ATR spectrum of (*trans-1*)(*trans-bpe*).



Figure A3.34 FTIR-ATR spectrum of (cis-2)(apy).



Figure A3.35 FTIR-ATR spectrum of (cis-2)(trans-bpe).



Figure A3.36 FTIR-ATR spectrum of (trans-2)(apy).



Figure A3.37 FTIR-ATR spectrum of (*trans-2*)(*trans-bpe*).



Figure A3.38 FTIR-ATR spectrum of (cis-2)(cis-bpe).



Figure A3.39 FTIR-ATR spectrum of (trans-2)(cis-bpe).

# 8. References for Appendix 3

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# Rationale for Chapter 5: Azo…Phenyl Stacking: a Persistent Self-Assembly Motif Guides the Assembly of Fluorinated *cis*-Azobenzenes into Photo-Mechanical Needle Crystals

The findings reported in Chapters 3 and 4 establish the underlying mechanism of photomechanical transformations in needle-shaped single crystals and cocrystals of fluorinated *cis*azobenzenes. The success of those investigations, however, raised a new question: what is the underlying driving force that is reliably directing the assembly of various fluorinated *cis*azobenzenes into needle-shaped crystals? Chapter 5 reveals a new supramolecular interaction between an azo group and electron deficient phenyl rings of fluorinated systems. This interaction is in fact responsible for the fast growth of needle shaped crystals and when combined with orthogonally directed supramolecular interactions, such as halogen bonds, allows one to assemble crystals in which both structure and morphology can be largely predicted.



Chapter 5: Azo…Phenyl Stacking: a Persistent Self-Assembly Motif Guides the Assembly of Fluorinated cis-Azobenzenes into Photo-Mechanical Needle Crystals

## 5.1 Abstract

We describe a novel, persistent motif of molecular assembly in photo-mechanical crystals and cocrystals of fluorinated *cis*-azobenzenes. The azo…phenyl stacking motif, which is preserved upon either chemical substitution or upon halogen-bonded cocrystallization, guides the assembly of fluorinated *cis*-azobenzenes into columnar stacks and drives the formation of crystals with needle-like morphologies optimal for photo-mechanical motion.

#### 5.2 Introduction

Control over molecular assembly in crystals is central to a range of applications for molecular materials, such as pharmaceuticals,<sup>1,2</sup> organic semiconductors,<sup>3</sup> and energy transduction and storage materials.<sup>4</sup> The latter have recently received much interest, as they include lightharvesting systems which can deform mechanically upon irradiation, and function as artificial muscles, photo-mechanical robots, and 'molecular machines'.<sup>5</sup> The understanding and prediction of solid-state molecular assembly, which is key to such designer crystalline materials, has been greatly advanced by an understanding of hydrogen-bonded supramolecular synthons<sup>6</sup> which, along with a variety of other interactions (e.g. halogen bonds,  $\pi$ - $\pi$  interactions), enable the design of crystals of high complexity and functional nature, including pharmaceuticals, explosives, or photoswitchable materials.<sup>7-10</sup> A recent development in the latter context is the discovery that azobenzenes, if obtained as sufficiently thin crystalline plates or needles, readily undergo largescale light-induced photo-mechanical motion associated with photochemical switching of transand cis-geometries.<sup>11-13</sup> Specifically, crystals of trans-azobenzenes undergo rapid, reversible motion upon exposure to ultraviolet or visible light,<sup>11,13</sup> while fluorinated *cis*-azobenzenes, such as *cis*-1 and *cis*-2 (Figure 5.1a), undergo light-induced  $cis \rightarrow trans$  isomerization accompanied with irreversible bending.<sup>14,15</sup> Critical to both types of photo-mechanical motion is the formation of crystals sufficiently long and thin to permit macroscopic bending.



**Figure 5.1** a) Fluorinated *cis*-azobenzenes synthesized in this work; b) typical needle-like crystal morphology observed for fluorinated *cis*-azobenzenes; c) stacking of *cis*-**3** parallel to the long axis of crystal needle growth. Molecular electrostatic potential (MEP) calculated for: d) a single *cis*-**3** molecule and e) for a pair of *cis*-**3** molecules in an azo…phenyl stack (contours at 0.02 a.u.; red: repulsion; blue: attraction), highlighting the short contact between the azo nitrogen and a *meta*-positioned C-F bond. f) The NCI plot for two molecules of *cis*-**3** in an azo…phenyl stack (NCI contours at 0.5, electron density threshold 0.2), demonstrating notable areas of attraction and repulsion.

We now report a persistent, previously undescribed azo…phenyl stacking motif in crystalline fluorinated *cis*-azobenzenes, leading to the formation of columnar 'pringle chip'-like supramolecular architectures,<sup>16</sup> and potentially driving the formation of crystals with thin needle-like morphologies (**Figures 5.1b,c, A4.2**), optimal for photo-mechanical motion. For the first time,

this molecular assembly motif offers an opportunity to design crystal structures and ensure crystal morphologies ideal for photo-mechanical behaviour, hence advancing applications in light-driven robotics, molecular machines, and artificial muscles.<sup>5</sup>

#### 5.3 **Results and Discussion**

#### 5.3.1 Azo…Phenyl Stacking in Fluorinated cis-Azobenzenes

The azo…phenyl stacking in fact can be recognized from careful inspection of previously published<sup>14b</sup> crystal structures of *cis*-1 and the two polymorphs of *cis*-2. These consist of onedimensional molecular stacks with repeat distances 5.324(1) Å (*cis*-1, CSD code DOCCOP), 5.597(1) Å (*cis*-2, CSD code DOCCEF01) and 5.316(1) Å (*cis*-2, CSD code DOCCEF01) along the crystallographic *b*-axis, respectively (**Figure A4.1**, Appendix 4). Importantly, stacks exhibit unusually short N…C contacts between azo groups and fluorinated phenyl rings of neighbouring molecules (3.190(5) Å in *cis*-1, 3.210(3) Å and 3.157(3) in polymorphs of *cis*-2, compared to N…C separation of ca. 3.3 Å expected from van der Waals radii<sup>17</sup>. Importantly, almost identical stacking is seen in reported<sup>14a</sup> cocrystals of *cis*-1 and *cis*-2, but not in non-fluorinated *cis*-azobenzenes,<sup>18</sup> suggesting it may be characteristic for only the fluorinated derivatives. To verify the presence of a persistent stacking motif, we first prepared the fully fluorinated *cis*-3 (**Figure 5.1a**).<sup>‡</sup> Crystallization of *cis*-3 from hexane gave thin needles (**Figure 5.1b**), established by single crystal X-ray diffraction to consist of one-dimensional stacks are arranged in parallel, characterized by a short N…C separation (3.073(4) Å) and a repeat distance of 5.569(3) Å.

#### 5.3.2 Computational Analysis

Formation of identical stacks independent of *para*-substituent is remarkable and points to a robust self-assembly motif. We undertook a computational analysis of interactions between molecules in stacks of cis-1, *cis*-2 (for one polymorph only, CSD code DOCCEF01) and *cis*-3 (see also Appendix 4). The molecular electrostatic potential (MEP) analysis revealed that stacking may be supported by two attractive interactions (**Figures 5.1c-e, A4.3, A4.4**). One arises between the lone electron pair on each of the azo group nitrogen atoms and *meta*-carbon atoms in the fluorinated phenyl group of the neighbouring molecule. The other attractive interaction involves the negatively charged rim of the halogen *para*-substituents and the positively charged carbon atoms in perfluorinated phenyl groups of neighbouring molecules. We also evaluated these noncovalent interactions between two neighbouring molecules by calculating the non-covalent interactions (NCI) index using NCIplot,<sup>19</sup> which depicts intermolecular interactions by an electron density gradient isosurface. The NCI calculations (**Figures 5.1f, A4.3, A4.4**) confirm that the above interactions are attractive and may help formation of molecular stacks.

In order to evaluate the importance of azo--phenyl stacking in the crystal packing of *cis*-3, we calculated intermolecular potentials using the UNI force field, implemented in MercuryCSD (version 3.5.1.).<sup>20,21</sup> Results reveal that stacking of *cis*-3 is the single most dominant stabilization factor in the crystal structure, with an intermolecular potential of -34 kJ mol<sup>-1</sup> (see Appendix 4, **Figures A4.5-A4.13**). The next most negative intermolecular potential in crystal structure of *cis*-3 was at -16 kJ mol<sup>-1</sup>. Similar results were obtained for the published structure of *cis*-1 (CSD code DOCCOP), where molecular stacks provide a stabilization of -54 kJ mol<sup>-1</sup>, the next lowest intermolecular potential being -25 kJ mol<sup>-1</sup>. For both known *cis*-2 polymorphs (CSD codes DOCCEF and DOCCEF01), azo--phenyl stacks provide a stabilization of -44 kJ mol<sup>-1</sup> and -50 kJ mol<sup>-1</sup>, with the next most negative intermolecular potential at -22 kJ mol<sup>-1</sup> (see Appendix 4, **Figures A4.5-A4.13**). These calculations point to azo--phenyl stacking as the most stabilizing interaction in crystalline fluorinated *cis*-azobenzenes.

#### 5.3.3 Generality of Azo…phenyl Stacking Extended to Substituted Substrates

To explore the robustness of azo…phenyl stacking to modification of the fluorinated *cis*azobenzene, we synthesized and grew single crystals of compounds *cis*-4 and *cis*-5, in which the fluorinated phenyl rings bear a bromine atom in 2-position, and a hydrogen atom in positions 3 and 5, respectively (**Figure 5.1a**). Both compounds form thin needle-shape crystals, and crystal structure determination revealed the persistent formation of molecular stacks along the crystallographic *b*-direction, coincident with the crystal needle axis. In crystals of *cis*-4, the molecular stacks arrange in antiparallel, with a 5.661(3) Å repeat distance. Crystal structure of *cis*-**5** consists of antiparallel azo…phenyl stacks, with neighbouring molecules in each stack mutually rotated by 90° and separated by 5.608(4) Å (**Figure 5.2**).



Figure 5.2 Azo...phenyl molecular stacking in single crystals of a) cis-4 and b) cis-5

All herein explored fluorinated *cis*-azobenzenes, as well as previously reported *cis*-1, *cis*-2 and their cocrystals,<sup>14</sup> persistently form thin needle crystals from different solvents (dichloromethane, acetonitrile, hexanes, ethyl acetate), with the needle axis always parallel to the direction of molecular stacks in the crystal, suggesting that azo…phenyl stacking governs macroscopic crystal shape and, therefore, potential photo-mechanical behaviour.

#### 5.3.4 Photo-Mechanical Performance of Stacked cis-Azobenzenes

Photo-mechanical properties were explored for needles of *cis*-**3** which underwent bending under irradiation with visible (488 nm) laser light. In contrast to crystals of *cis*-**1** and *cis*-**2**, that bend away from the light source, needles of *cis*-**3** initially bend *away* and, after a few seconds of continuous irradiation, reverse the direction of motion and instead bend *towards* the light source (**Figure 5.3a-d**).



**Figure 5.3** Bending of a single crystal of *cis*-**3** upon irradiation with a 5 mW, 488 nm laser (arrow indicates direction of irradiation): a) before irradiation; b) after 10 seconds of irradiation; c) after 30 seconds of irradiation; d) image superimposing three snapshots of crystal motion. e) PXRD patterns for bulk *cis*-**3** at different irradiation times, demonstrating gradual conversion to *trans*-**3** 

The maximum observed crystal tip deflection was 5°. Similar to cis-1 and cis-2, irradiation of *cis*-**3** leads to *cis*-*trans* isomerization, confirmed through reaction monitoring by powder X-ray diffraction (PXRD, Figure 5.3e). Irradiation of bulk powder leads to disappearance of X-ray reflections of *cis*-3 and the appearance of new reflections, largely matched those for *trans*-3 which was separately prepared and characterized by X-ray single crystal diffraction.<sup>‡</sup> A tentative explanation for the unusual bending behaviour of cis-3 compared to cis-1 and cis-2 may lie in the relative densities of corresponding cis- and trans-compounds. Whereas the structures of trans-1 and -2 exhibit densities only  $\sim$ 3% higher than those of *cis*-isomers, the density of *trans*-3 is >5% higher than for cis-3 (see Table A4.3, Appendix 4). Consequently, it may be that during the photochemical transformation the density of irradiated material is first reduced due to transient amorphization, resulting in photo-expansion and bending away from the light source, as indeed observed for irradiated single crystals and cocrystals of *cis*-1 and -2.<sup>14</sup> Subsequent crystallization of the more dense *trans*-isomer exhibited a much weaker response to irradiation (Table A4.3, Appendix 4).<sup>‡</sup> Whereas the Kobatake group recently demonstrated how varying the radiation wavelength can alter the direction of photo-mechanical motion for diarylethylene crystals,<sup>22</sup> in our case the course of bending did not change upon irradiation at 405 nm, 488 nm and 532 nm.

#### 5.3.5 Halogen-Bonded Cocrystals Retain the Stacking Interaction

The stabilizing interaction of the fluorinated phenyl group with negatively charged rim of the iodine or bromine substituents (**Figure A4.3**, **A4.4**) leaves the azo…phenyl stacks in in *cis*-1 and *cis*-2 decorated with positively charged  $\sigma$ -holes potentially accessible for halogen bonding. Consequently, we tested if azo…phenyl stacking in *cis*-1 is retained upon halogen-bonded cocrystallization<sup>23,24</sup> with 1,4-diazabicyclo[2.2.2]octane (**dabco**), 1,4-dithiane and 4-vinylpyridine acceptors (**Figure 5.4a**). Cocrystallization of *cis*-1 with **dabco** from dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) gave needle-like crystals of (*cis*-1)(**dabco**), established to consist of antiparallel azo…phenyl stacks of *cis*-1 (stack repeat distance: 6.331(1) Å) laterally decorated by I…N halogen bonds to **dabco** molecules (I…N distance: 2.758(2) Å) that bridge neighboring stacks. Similarly, cocrystallization of *cis*-1 and dithiane from CH<sub>2</sub>Cl<sub>2</sub> provided long needles of (*cis*-2)(dithiane) cocrystals.



**Figure 5.4** a) Herein explored halogen bond acceptors. Fragments of crystal structures of cocrystals of *cis*-1 with: b) **dabco**; c) dithiane and d) 4-vinylpyridine, demonstrating halogen bond formation lateral to azo…phenyl stacking of *cis*-1. Molecular stacks are parallel to the long axis of the needle-shaped crystal.

Crystal structure analysis of (*cis*-1)(dithiane) revealed antiparallel stacks of *cis*-1 (stack repeat distance: 5.4079(4) Å), bridged by dithiane molecules connected *via* I···S halogen bonds (I···S distance: 3.2907(5) Å). Cocrystals of (*cis*-1)(4-vinylpyridine)<sub>2</sub> were obtained from a CH<sub>2</sub>Cl<sub>2</sub>/4-vinylpyridine mixture (90:10, v/v) by slow evaporation. Single crystal X-ray diffraction revealed antiparallel stacks of *cis*-1 (stack repeat: 5.4157(7) Å), laterally decorated by halogenbonded 4-vinylpyridine acceptors (I···N distance: 2.780(2) Å). Synthesis and structures of (*cis*-1)(dabco), (*cis*-1)(dithiane) and (*cis*-1)(4-vinylpyridine)<sub>2</sub> demonstrate that azo...phenyl stacking of fluorinated *cis*-azobenzenes may be a persistent motif for crystal engineering. Evaluation of

intermolecular potentials for structures of all three cocrystals revealed that azo…phenyl stacking again represents the most significant stabilizing interaction (see Appendix 4, **Figures A4.5-A4.13**). Azo…phenyl stacks are in all cases aligned with the long needle axis of the crystal.

### 5.4 Conclusions

In conclusion, we identified a new persistent supramolecular stacking motif based on fluorinated cis-azobenzene units. This azo...phenyl stacking motif has been observed for all herein described compounds, as well as all previously published structures of fluorinated *cis*-azobenzene crystals and cocrystals. Stacking persists upon varying the type and position of substituents (H, F, Br, I) on the fluorinated phenyl rings, and upon halogen-bonded cocrystallization, which permitted the organization of diverse molecules in a desirable, one-dimensional fashion.<sup>24</sup> All fluorinated cis-azobenzene crystals and cocrystals, explored herein or in previous work,<sup>14</sup> appeared as elongated needles, with azo...phenyl molecular stacks parallel to the crystal long axis. We therefore believe that azo...phenyl stacking of fluorinated cis-azobenzenes might allow both the predictable organization of these photo-mechanically active molecules into columnar 'pringle'like supramolecular architectures, as well as encourage the growth of the resultant crystals into needles, the ideal morphology for photo-mechanical effects and devices. Also described here is the unique observation of two distinct and opposite photo-mechanical regimes in the same crystal, resulting in bending either towards or away from visible light, controlled depending on the timescale of irradiation. We believe that azo...phenyl stacking of fluorinated *cis*-azobenzenes may be developed into a rational tool to simultaneously control the crystal structure and to permit ideal crystal morphologies for various applications.<sup>24</sup> In that context, we are now investigating photomechanical behaviour of the herein reported cocrystals.

# 5.5 Acknowledgements

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#### 5.6 Notes

<sup>‡</sup> As *cis-o*-fluoro-azobenzenes exhibit long thermal half-lives, all herein prepared azobenzenes were nearly quantitatively converted into the *cis*-form by 532 nm laser irradiation and then crystallized in the dark.<sup>25</sup> *trans*-isomers were also prepared and structurally characterized by single crystal X-ray diffraction. Crystallographic data for all new structures is summarized in the Appendix 4 and submitted in the CSD (CCDC codes 1431056-1431064). Change in orientation of molecules in *cis*-5 azo…phenyl stacks may be the result of C-H…N contacts in the stacks (**Figure A4.14**).

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# Appendix 4: Supporting Information for Chapter 5 1. Experimental

#### 1.1 Materials:

4,4'-diiodooctafluoroazobenzene (1) and 4,4'-dibromooctafluoroazobenzene (2) were synthesized according to the procedure outlined in our prior report.<sup>1</sup> Precursors such as 2-bromo-4,5,6-trifluoroaniline, and 2-bromo-3,4,6-trifluoroaniline were purchased from Santa Cruz Biotechnologies, 4-bromo-2,3,5,6-tetrafluoroaniline, 2,3,5,6-tetrafluoroaniline, pentafluoro-aniline, **dabco**, 4-vinylpyridine, dithiane, and HgO were obtained from Sigma-Aldrich Chemical Co. and used without purification.

#### 1.2 Syntheses:

*cis-bis*(pentafluorophenyl)diazene (*cis-3*) 300 mg of pentafluoroaniline was stirred overnight with freshly prepared activated manganese dioxide (6 g) in petroleum ether. The solution was filtered through celite, evaporated and purified by column chromatography on silicagel (50:50 DCM/hexanes). Yield 107 mg (35.7%) (*trans* and *cis* combined), MS m/z 363 C<sub>12</sub>N<sub>2</sub>F<sub>10</sub> (M + 1). Melting point (from hot-stage microscopy): 108 °C. <sup>13</sup>C NMR (126 MHz, toluene):  $\delta$  142.66 (s), 141.31 (s), 138.06 (s), 128.39 (s).

*cis-bis*(2-bromo-3H-4,5,6-trifluorophenyl)diazene (*cis-4*) 300 mg of 2-bromo-4,5,6-trifluoroaniline was stirred overnight with freshly prepared activated manganese dioxide (6 g) in petroleum ether. The solution was filtered through celite, evaporated and purified by column chromatography on silicagel (50:50 DCM/hexanes). Yield 82 mg (27.5%), (*trans* and *cis* combined), MS m/z 449 C<sub>12</sub>H<sub>2</sub>N<sub>2</sub>F<sub>6</sub>Br<sub>2</sub> (M+1). Melting point (from hot-stage microscopy): 99 °C. <sup>1</sup>H NMR (500 MHz, toluene), 6.43 (ddd, J = 8.8, 6.7, 1.9 Hz, 1H) (*cis-4*);  $\delta$  6.55 (ddd, J = 9.1, 7.0, 2.2 Hz, 1H) (*trans-4*). <sup>13</sup>C NMR (126 MHz, toluene)  $\delta$  152.16 (d, J = 6.4 Hz), 150.36 (t, J = 6.5 Hz), 142.20 (s), 139.46 (s), 116.87 (d, J = 194.3 Hz), 113.02 (s).

#### cis-bis(2-bromo-5H-3,4,6-trifluorophenyl)diazene (cis-5) 300 mg of 2-bromo-4,5,6-

trifluoroaniline was stirred overnight with freshly prepared activated manganese dioxide (6 g) in petroleum ether. The solution was filtered through celite, evaporated and purified by column chromatography on silicagel (50:50 DCM/hexanes). Yield 95 mg (31.8%),(*trans* and *cis* combined), MS *m*/*z* 449 C<sub>12</sub>H<sub>2</sub>N<sub>2</sub>F<sub>6</sub>Br<sub>2</sub> (M+1). Melting point (from hot-stage microscopy): 101 °C. <sup>1</sup>H NMR (500 MHz, toluene) 5.72 (td, J = 9.5, 6.3 Hz, 1H) (*cis*-**5**);  $\delta$  6.09 (td, J = 10.2, 6.7 Hz, 1H) (*trans*-**5**). <sup>13</sup>C NMR (126 MHz, toluene)  $\delta$  150.45 (d, J = 6.8 Hz), 147.90 (d, J = 6.7 Hz), 145.67 (s), 136.69 (d, J = 6.1 Hz), 112.01 (s), 105.83 (d, J = 169.7 Hz).

#### 1.3 Cocrystal Preparation

Cocrystals were prepared **in the dark** by mixing equimolar quantities of halogen bond donors and acceptors in dichloromethane (DCM). Single crystals were grown by slow evaporation of the solvent.

(*cis*-1)(dabco): 10.0 mg (0.017 mmol) of *cis*-1 was dissolved in 2.5 mL of DCM and added to the solution of 1.9 mg (0.017 mmol) of dabco in 2.5 ml of DCM. Resultant orange solution remained clear and small needle-shaped cocrystals were formed after solven evaporation.

(*cis*-1)(4-vinylpyridine): 300  $\mu$ L of 4-vinylpyridine (excess) was added to a solution of 10.0 mg (0.017 mmol) of 1 in 2.5 ml of DCM yielding long needle-like crystals upon solvent evaporation.

(*cis*-1)(dithiane): 10.0 mg (0.017 mmol) of *cis*-1 was dissolved in 2.5 mL of DCM and added to the solution of 4.7 mg (0.017 mmol) of dithiane in 2.5 ml of DCM resulting in yellow-orange needle-like crystals upon solvent evaporation.

# 2. Description of Single Crystal X-ray Diffraction Measurements and Crystallographic Summary

X-ray diffraction data was obtained on Bruker D8 single crystal X-ray diffractometer using a  $MoK_{\alpha}$  X-ray source and a graphite monochromator. Multi-scan absorption correction (SADABS) was applied and structures were solved by direct methods and refined using SHELX-97.<sup>2</sup> Complete table of crystallographic information and cif files can be obtained online at the RSC website.

Table A4.1 Comparison of calculated crystal packing densities of *cis* and *trans*-forms for *cis*-3, *cis*-4 and *cis*-5, and two of the best performing previously reported fluorinated *cis*-azobenzene photo-mechanical systems, *cis*-2 and (*cis*-1)(*cis*-*bis*(4-pyridyl)ethylene).

| Compound             | density of cis-         | density of <i>trans</i> - density |               | Direction of the overall |  |
|----------------------|-------------------------|-----------------------------------|---------------|--------------------------|--|
|                      | form, g/cm <sup>3</sup> | form g/cm <sup>3</sup>            | difference, % | photo-mechanical motion  |  |
| $(cis-1)(cis-bpe)^1$ | 2.006                   | 2.058                             | 2.6           | away                     |  |
| $cis-2^2$            | 2.373                   | 2.470                             | 4.1           | away                     |  |
| cis-3                | 2.008                   | 2.113                             | 5.2           | towards                  |  |
| cis-4                | 2.218                   | 2.276                             | 2.6           | away                     |  |
| cis-5                | 2.205                   | 2.385                             | 8.1           | towards                  |  |



Figure A4.1 Illustration of azo---phenyl stacking in crystals of cis-1 (left) cis-2 (right).



**Figure A4.2** Images of face-indexed crystals (left) and azo…phenyl stacking (right) in corresponding crystal structures of *cis*-1 (a and b); *cis*-3 (c and d) and *cis*-1:4-vinylpyridine (e and f), demonstrating preferrential growth of needle-like crystals along the direction of the azo…phenyl interaction. The (010) planes (shown in red) correspond to the capping faces of the needle crystals.

# 3. Theoretical Method for QM Calculations

QM software: GAMESS-US (v. 1 May 2013 (R1)),<sup>3, 4</sup>, NBO<sup>5</sup> and NCIplot<sup>6, 7</sup> Visualization software: MacMolPlt (v.7.4.4)<sup>8</sup>, Avogadro (v.1.1.1)<sup>9, 10</sup>, VMD <sup>11</sup> Functional : B3LYP, basis set : 6-31+G(d,p) XYZ coordinates of structures can be obtained online at the RSC website.

# 4. Calculated Molecular Electrostatic Potential & NCI Plots for cis-1 and cis-2



Figure A4.3 MEP plot iso = 0.007 (left) and NCI plot (right) of *cis*-1.



Figure A4.4 MEP plot iso = 0.007 (left) and NCI plot (right) of *cis*-2.

## 5. Calculations of Intermolecular Potentials

 Table A4.2 Three most negative calculated inter-molecular potentials for the crystal structure of *cis*-1 (CSD code DOCCOP)

| moll | mol2 | Distance, Å | Energy, kJ/mol |
|------|------|-------------|----------------|
| 0    | 1    | 5.3242      | -54.4191       |
| 0    | 2    | 6.41114     | -25.1655       |
| 0    | 3    | 6.56237     | -19.9726       |

Packing Energy:

- PE = -135.61 kJ/mol 40 interactions
- PE = -138.47 kJ/mol 120 interactions
- PE = -138.74 kJ/mol 160 interactions
- PE = -138.83 kJ/mol 180 interactions
- PE = -138.87 kJ/mol 190 interactions
- PE = -138.90 kJ/mol 200 interactions

Potential = A\*exp(-Br) - Cr(-6)

Table A4.3 Unified (UNI) pair-potential parameters:

| atom1 | code1 | atom2 | code2 | А         | В    | С       |
|-------|-------|-------|-------|-----------|------|---------|
| I1    | 15    | I1    | 15    | 1505374.0 | 3.11 | 26517.0 |
| I1    | 15    | F1    | 6     | 507240.7  | 3.67 | 3870.1  |
| I1    | 15    | N1    | 23    | 1302038.0 | 3.64 | 20663.5 |
| I1    | 15    | C1    | 3     | 583466.5  | 3.29 | 8007.4  |
| F1 | 6  | F1 | 6  | 170916.4 | 4.22 | 564.8  |
|----|----|----|----|----------|------|--------|
| F1 | 6  | N1 | 23 | 249858.9 | 3.93 | 1277.9 |
| F1 | 6  | C1 | 3  | 196600.9 | 3.84 | 1168.8 |
| N1 | 23 | N1 | 23 | 365263.0 | 3.65 | 2891.0 |
| N1 | 23 | C1 | 3  | 491494.0 | 3.86 | 2791.0 |
| C1 | 3  | C1 | 3  | 226145.2 | 3.47 | 2418.0 |



**Figure A4.5** Fragment of crystal structure of *cis*-1 (CSD code DOCCOP), displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo---phenyl is oriented vertically.

 Table A4.4 Three most negative calculated inter-molecular potentials for crystal structure

 of *cis*-2 (CSD code DOCCEF):

| mol1 | mol2 | distance | energy (kJ/mol) |
|------|------|----------|-----------------|
| 0    | 1    | 5.3155   | -49.628         |
| 0    | 2    | 6.33694  | -21.9495        |
| 0    | 3    | 6.4965   | -19.8855        |

Packing Energy:

PE = -129.39 kJ/mol 40 interactions

- PE = -131.85 kJ/mol 120 interactions
- PE = -132.10 kJ/mol 160 interactions
- PE = -132.18 kJ/mol 180 interactions
- PE = -132.22 kJ/mol 190 interactions
- PE = -132.25 kJ/mol 200 interactions

Potential =  $A^{*}exp(-Br) - Cr(-6)$ 

| Table A4.5 Unified (UNI) pair | r-potential parameters: |
|-------------------------------|-------------------------|
|-------------------------------|-------------------------|

| atom1 | code1 | atom2 | code2 | А         | В    | С       |
|-------|-------|-------|-------|-----------|------|---------|
| Br1   | 13    | Br1   | 13    | 2017608.0 | 3.57 | 10786.0 |
| Br1   | 13    | C1    | 3     | 675479.4  | 3.52 | 5106.9  |
| Br1   | 13    | F1    | 6     | 587232.7  | 3.89 | 2468.3  |
| Br1   | 13    | N1    | 23    | 651019.0  | 3.53 | 12358.4 |
| C1    | 3     | C1    | 3     | 226145.2  | 3.47 | 2418.0  |
| C1    | 3     | F1    | 6     | 196600.9  | 3.84 | 1168.8  |
| C1    | 3     | N1    | 23    | 491494.0  | 3.86 | 2791.0  |
| F1    | 6     | F1    | 6     | 170916.4  | 4.22 | 564.8   |
| F1    | 6     | N1    | 23    | 249858.9  | 3.93 | 1277.9  |
| N1    | 23    | N1    | 23    | 365263.0  | 3.65 | 2891.0  |



**Figure A4.6** Fragment of crystal structure of *cis*-2 (CSD code DOCCEF), displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo…phenyl interaction is oriented vertically.

 Table A4.6 Three most negative calculated inter-molecular potentials for the crystal structure of *cis*-2 (CSD code DOCCEF01):

| moll | mol2 | distance | energy (kJ/mol) |
|------|------|----------|-----------------|
| 0    | 1    | 5.597    | -43.5418        |
| 0    | 2    | 9.12777  | -22.137         |
| 0    | 3    | 7.40284  | -19.3471        |

Packing Energy:

PE = -129.47 kJ/mol 40 interactions

PE = -131.74 kJ/mol 120 interactions

PE = -131.99 kJ/mol 160 interactions

PE = -132.08 kJ/mol 180 interactions

PE = -132.11 kJ/mol 190 interactions

PE = -132.14 kJ/mol 200 interactions

Potential = A\*exp(-Br) - Cr(-6)

Table A4.7 Unified (UNI) pair-potential parameters:

| atom1 | code1 | atom2 | code2 | А         | В    | С       |
|-------|-------|-------|-------|-----------|------|---------|
| Br1   | 13    | Br1   | 13    | 2017608.0 | 3.57 | 10786.0 |
| Br1   | 13    | C1    | 3     | 675479.4  | 3.52 | 5106.9  |
| Br1   | 13    | F1    | 6     | 587232.7  | 3.89 | 2468.3  |
| Br1   | 13    | N1    | 23    | 651019.0  | 3.53 | 12358.4 |
| C1    | 3     | C1    | 3     | 226145.2  | 3.47 | 2418.0  |
| C1    | 3     | F1    | 6     | 196600.9  | 3.84 | 1168.8  |
| C1    | 3     | N1    | 23    | 491494.0  | 3.86 | 2791.0  |
| F1    | 6     | F1    | 6     | 170916.4  | 4.22 | 564.8   |
| F1    | 6     | N1    | 23    | 249858.9  | 3.93 | 1277.9  |
| N1    | 23    | N1    | 23    | 365263.0  | 3.65 | 2891.0  |



**Figure A4.7** Fragment of crystal structure of *cis*-2 (CSD code DOCCEF01), displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo---phenyl stacking is oriented vertically.

 Table A4.8 Three most negative calculated inter-molecular potentials for crystal structure of *cis*-3:

| mol1 | mol2 | distance | energy (kJ/mol) |
|------|------|----------|-----------------|
| 0    | 1    | 5.569    | -33.876         |
| 0    | 2    | 7.42675  | -15.9682        |
| 0    | 3    | 8.34309  | -12.882         |

Packing Energy:

PE = -108.13 kJ/mol 40 interactions

PE = -110.03 kJ/mol 120 interactions

PE = -110.24 kJ/mol 160 interactions

PE = -110.32 kJ/mol 180 interactions

PE = -110.34 kJ/mol 190 interactions

PE = -110.37 kJ/mol 200 interactions

Potential = A\*exp(-Br) - Cr(-6)

| atom1 | code1 | atom2 | code2 | А        | В    | С      |
|-------|-------|-------|-------|----------|------|--------|
| F1    | 6     | F1    | 6     | 170916.4 | 4.22 | 564.8  |
| F1    | 6     | N1    | 23    | 249858.9 | 3.93 | 1277.9 |
| F1    | 6     | C1    | 3     | 196600.9 | 3.84 | 1168.8 |
| N1    | 23    | N1    | 23    | 365263.0 | 3.65 | 2891.0 |
| N1    | 23    | C1    | 3     | 491494.0 | 3.86 | 2791.0 |
| C1    | 3     | C1    | 3     | 226145.2 | 3.47 | 2418.0 |

Table A4.9 Unified (UNI) pair-potential parameters:



**Figure A4.8** Fragment of crystal structure of *cis*-3, displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo...phenyl stacking is oriented vertically.

 Table A4.10 Three most negative calculated inter-molecular potentials for the crystal structure of *cis*-4:

| mol1 | mol2 | distance | energy(kJ/mol) |
|------|------|----------|----------------|
| 0    | 1    | 5.6611   | -40.3024       |
| 0    | 2    | 7.74331  | -20.4451       |
| 0    | 3    | 7.45     | -15.2718       |

Packing Energy:

- PE = -115.55 kJ/mol 40 interactions
- PE = -117.67 kJ/mol 120 interactions
- PE = -117.90 kJ/mol 160 interactions
- PE = -117.97 kJ/mol 180 interactions
- PE = -118.00 kJ/mol 190 interactions
- PE = -118.03 kJ/mol 200 interactions

Potential = A\*exp(-Br) - Cr(-6)

| atom1 | code1 | atom2 | code2 | А         | В    | С       |
|-------|-------|-------|-------|-----------|------|---------|
| Br1   | 13    | Br1   | 13    | 2017608.0 | 3.57 | 10786.0 |
| Br1   | 13    | C1    | 3     | 675479.4  | 3.52 | 5106.9  |
| Br1   | 13    | H1    | 1     | 220774.5  | 3.79 | 1085.3  |
| Br1   | 13    | F1    | 6     | 587232.7  | 3.89 | 2468.3  |
| Br1   | 13    | N1    | 23    | 651019.0  | 3.53 | 12358.4 |
| C1    | 3     | C1    | 3     | 226145.2  | 3.47 | 2418.0  |
| C1    | 3     | H1    | 1     | 120792.1  | 4.10 | 472.8   |
| C1    | 3     | F1    | 6     | 196600.9  | 3.84 | 1168.8  |
| C1    | 3     | N1    | 23    | 491494.0  | 3.86 | 2791.0  |
| H1    | 1     | H1    | 1     | 24158.0   | 4.01 | 109.2   |
| H1    | 1     | F1    | 6     | 64257.8   | 4.11 | 248.4   |
| H1    | 1     | N1    | 23    | 228279.0  | 4.52 | 502.1   |
| F1    | 6     | F1    | 6     | 170916.4  | 4.22 | 564.8   |
| F1    | 6     | N1    | 23    | 249858.9  | 3.93 | 1277.9  |
| N1    | 23    | N1    | 23    | 365263.0  | 3.65 | 2891.0  |

Table A4.11 Unified (UNI) pair-potential parameters:



**Figure A4.9** Fragment of crystal structure of *cis*-4, displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo…phenyl stacking is oriented vertically.

 Table A4.12 Three most negative calculated inter-molecular potentials for the crystal structure of *cis*-5:

| mol1 | mol2 | distance | energy(kJ/mol) |
|------|------|----------|----------------|
| 0    | 1    | 5.88969  | -34.3962       |
| 0    | 2    | 8.37817  | -28.3839       |
| 0    | 3    | 8.96892  | -22.8244       |

Packing Energy:

PE = -113.75 kJ/mol 40 interactions

PE = -115.80 kJ/mol 120 interactions

- PE = -116.02 kJ/mol 160 interactions
- PE = -116.09 kJ/mol 180 interactions
- PE = -116.12 kJ/mol 190 interactions
- PE = -116.14 kJ/mol 200 interactions

Potential =  $A^{*}exp(-Br) - Cr(-6)$ 

| atom1 | code1 | atom2 | code2 | А         | В    | С       |
|-------|-------|-------|-------|-----------|------|---------|
| Br1   | 13    | Br1   | 13    | 2017608.0 | 3.57 | 10786.0 |
| Br1   | 13    | F1    | 6     | 587232.7  | 3.89 | 2468.3  |
| Br1   | 13    | N1    | 23    | 651019.0  | 3.53 | 12358.4 |
| Br1   | 13    | C1    | 3     | 675479.4  | 3.52 | 5106.9  |
| Br1   | 13    | H2    | 1     | 220774.5  | 3.79 | 1085.3  |
| F1    | 6     | F1    | 6     | 170916.4  | 4.22 | 564.8   |
| F1    | 6     | N1    | 23    | 249858.9  | 3.93 | 1277.9  |
| F1    | 6     | C1    | 3     | 196600.9  | 3.84 | 1168.8  |
| F1    | 6     | H2    | 1     | 64257.8   | 4.11 | 248.4   |
| N1    | 23    | N1    | 23    | 365263.0  | 3.65 | 2891.0  |
| N1    | 23    | C1    | 3     | 491494.0  | 3.86 | 2791.0  |
| N1    | 23    | H2    | 1     | 228279.0  | 4.52 | 502.1   |
| C1    | 3     | C1    | 3     | 226145.2  | 3.47 | 2418.0  |
| C1    | 3     | H2    | 1     | 120792.1  | 4.10 | 472.8   |
| H2    | 1     | H2    | 1     | 24158.0   | 4.01 | 109.2   |

Table A4.13 Unified (UNI) pair-potential parameters:



**Figure A4.10** Fragment of crystal structure of *cis*-**5**, displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo…phenyl stacking is vertical.

 Table A4.14 Four most negative calculated inter-molecular potentials for the crystal structure of (*cis*-1)(dabco) cocrystal:

| mol1 | mol2 | distance | energy (kJ/mol) |
|------|------|----------|-----------------|
| 0    | 1    | 6.3311   | -38.6093        |
| 2    | 3    | 6.3311   | -37.5472        |
| 2    | 4    | 8.84633  | -17.9562        |
| 2    | 5    | 5.71033  | -17.5944        |

Packing Energy:

Cluster 1 PE = -41.76 kJ/mol 440 interactions

PE = -41.77 kJ/mol 520 interactions

PE = -41.78 kJ/mol 560 interactions

PE = -41.78 kJ/mol 580 interactions

PE = -41.78 kJ/mol 590 interactions

PE = -41.78 kJ/mol 600 interactions

- Cluster 2 PE = -119.29 kJ/mol 440 interactions PE = -119.33 kJ/mol 520 interactions PE = -119.34 kJ/mol 560 interactions PE = -119.34 kJ/mol 580 interactions PE = -119.35 kJ/mol 590 interactions PE = -119.35 kJ/mol 600 interactions PE = -116.32 kJ/mol 440 interactions PE = -116.36 kJ/mol 520 interactions PE = -116.37 kJ/mol 560 interactions PE = -116.37 kJ/mol 580 interactions PE = -116.37 kJ/mol 580 interactions
  - PE = -116.37 kJ/mol 590 interactions
  - PE = -116.37 kJ/mol 600 interactions

Total packing energy = -277.5 kJ/mol

Inter-fragment energy (1-2): -17.6 kJ/mol

Inter-fragment energy (1-3): -7.73 kJ/mol

Inter-fragment energy (2-3): -0.717 kJ/mol

Potential = A\*exp(-Br) - Cr(-6)

| atom1 | code1 | atom2 | code2 | А         | В    | С       |
|-------|-------|-------|-------|-----------|------|---------|
| C1    | 3     | C1    | 3     | 226145.2  | 3.47 | 2418.0  |
| C1    | 3     | H4    | 1     | 120792.1  | 4.10 | 472.8   |
| C1    | 3     | N1    | 23    | 491494.0  | 3.86 | 2791.0  |
| C1    | 3     | F1    | 6     | 196600.9  | 3.84 | 1168.8  |
| C1    | 3     | I1    | 15    | 583466.5  | 3.29 | 8007.4  |
| H4    | 1     | H4    | 1     | 24158.0   | 4.01 | 109.2   |
| H4    | 1     | N1    | 23    | 228279.0  | 4.52 | 502.1   |
| H4    | 1     | F1    | 6     | 64257.8   | 4.11 | 248.4   |
| H4    | 1     | I1    | 15    | 190700.9  | 3.56 | 1701.7  |
| N1    | 23    | N1    | 23    | 365263.0  | 3.65 | 2891.0  |
| N1    | 23    | F1    | 6     | 249858.9  | 3.93 | 1277.9  |
| N1    | 23    | I1    | 15    | 1302038.0 | 3.64 | 20663.5 |
| F1    | 6     | F1    | 6     | 170916.4  | 4.22 | 564.8   |
| F1    | 6     | I1    | 15    | 507240.7  | 3.67 | 3870.1  |
| I1    | 15    | I1    | 15    | 1505374.0 | 3.11 | 26517.0 |

 Table A4.15 Unified (UNI) pair-potential parameters:



**Figure A4.11** Fragment of crystal structure of (*cis*-1)(**dabco**) cocrystal, displaying the directions and magnitudes (in kJ mol<sup>-1</sup>) of three most negative intermolecular potentials. For clarity, the direction of the azo…phenyl stacking is always vertical. The structure contains two symmetrically independent molecular stacks, hence two values for the intermolecular potential in the azo…phenyl stacking direction

 Table A4.16 Three most negative calculated inter-molecular potentials for (*cis*-1)(dithiane):

| mol1 | mol2 | distance | energy (kJ/mol) |
|------|------|----------|-----------------|
| 0    | 1    | 5.4079   | -51.0623        |
| 0    | 2    | 6.22387  | -26.0184        |
| 0    | 3    | 6.37657  | -21.9186        |

Packing Energy:

Cluster 1 PE = -51.27 kJ/mol 240 interactions

PE = -51.33 kJ/mol 320 interactions

PE = -51.34 kJ/mol 360 interactions

PE = -51.35 kJ/mol 380 interactions

PE = -51.35 kJ/mol 390 interactions

PE = -51.35 kJ/mol 400 interactions

Cluster 2 PE = -133.96 kJ/mol 240 interactions

PE = -134.10 kJ/mol 320 interactions

PE = -134.14 kJ/mol 360 interactionsPE = -134.15 kJ/mol 380 interactionsPE = -134.15 kJ/mol 390 interactionsPE = -134.15 kJ/mol 400 interactions

Total packing energy = -185.5 kJ/mol

Inter-fragment energy (1-2): -0.41 kJ/mol

| atom1 | code1 | atom2 | code2 | А         | В    | С       |
|-------|-------|-------|-------|-----------|------|---------|
| I1    | 15    | I1    | 15    | 1505374.0 | 3.11 | 26517.0 |
| I1    | 15    | C1    | 3     | 583466.5  | 3.29 | 8007.4  |
| I1    | 15    | F1    | 6     | 507240.7  | 3.67 | 3870.1  |
| I1    | 15    | N1    | 23    | 1302038.0 | 3.64 | 20663.5 |
| I1    | 15    | H7A   | 1     | 190700.9  | 3.56 | 1701.7  |
| I1    | 15    | S1    | 9     | 1279591.6 | 3.31 | 16889.2 |
| C1    | 3     | C1    | 3     | 226145.2  | 3.47 | 2418.0  |
| C1    | 3     | F1    | 6     | 196600.9  | 3.84 | 1168.8  |
| C1    | 3     | N1    | 23    | 491494.0  | 3.86 | 2791.0  |
| C1    | 3     | H7A   | 1     | 120792.1  | 4.10 | 472.8   |
| C1    | 3     | S1    | 9     | 529108.6  | 3.41 | 6292.7  |
| F1    | 6     | F1    | 6     | 170916.4  | 4.22 | 564.8   |
| F1    | 6     | N1    | 23    | 249858.9  | 3.93 | 1277.9  |
| F1    | 6     | H7A   | 1     | 64257.8   | 4.11 | 248.4   |
| F1    | 6     | S1    | 9     | 431162.5  | 3.87 | 2465.0  |
| N1    | 23    | N1    | 23    | 365263.0  | 3.65 | 2891.0  |
| N1    | 23    | H7A   | 1     | 228279.0  | 4.52 | 502.1   |
| N1    | 23    | S1    | 9     | 630306.9  | 3.59 | 5576.8  |
| H7A   | 1     | H7A   | 1     | 24158.0   | 4.01 | 109.2   |
| H7A   | 1     | S1    | 9     | 268571.0  | 4.03 | 1167.3  |
| S1    | 9     | S1    | 9     | 1087673.0 | 3.52 | 10757.1 |

**Table A4.17** Unified (UNI) pair-potential parameters, Potential = A\*exp(-Br) - Cr(-6):



**Figure A4.12** Fragment of crystal structure of (*cis*-1)(dithiane) cocrystal, displaying the directions and magnitudes (in kJ mol<sup>-1</sup>) of three most negative intermolecular potentials. For clarity, the direction of the azo…phenyl stacking is always vertical.

**Table A4.18** Three most negative calculated inter-molecular potentials for the crystal structure of the (*cis*-1)(4-vinylpyridine)<sub>2</sub> cocrystal:

| mol1 | mol2 | distance | energy(kJ/mol) |
|------|------|----------|----------------|
| 0    | 1    | 5.4157   | -52.6147       |
| 0    | 2    | 9.07845  | -19.3498       |
| 3    | 4    | 6.13737  | -13.3963       |

Packing Energy:

Cluster 1 PE = -130.56 kJ/mol 240 interactions

- PE = -130.72 kJ/mol 320 interactions
- PE = -130.76 kJ/mol 360 interactions
- PE = -130.78 kJ/mol 380 interactions
- PE = -130.78 kJ/mol 390 interactions
- PE = -130.79 kJ/mol 400 interactions

Cluster 2 PE = -54.39 kJ/mol 240 interactions PE = -54.44 kJ/mol 320 interactions PE = -54.46 kJ/mol 360 interactions PE = -54.46 kJ/mol 380 interactions PE = -54.46 kJ/mol 390 interactionsPE = -54.46 kJ/mol 400 interactions

Total packing energy = -185.3 kJ/mol

Inter-fragment energy (1-2): -5.41 kJ/mol

| atom1 | code1 | atom2 | code2 | А         | В    | С       |
|-------|-------|-------|-------|-----------|------|---------|
| I1    | 15    | I1    | 15    | 1505374.0 | 3.11 | 26517.0 |
| I1    | 15    | F1    | 6     | 507240.7  | 3.67 | 3870.1  |
| I1    | 15    | N2    | 23    | 1302038.0 | 3.64 | 20663.5 |
| I1    | 15    | C8    | 3     | 583466.5  | 3.29 | 8007.4  |
| I1    | 15    | H1    | 1     | 190700.9  | 3.56 | 1701.7  |
| F1    | 6     | F1    | 6     | 170916.4  | 4.22 | 564.8   |
| F1    | 6     | N2    | 23    | 249858.9  | 3.93 | 1277.9  |
| F1    | 6     | C8    | 3     | 196600.9  | 3.84 | 1168.8  |
| F1    | 6     | H1    | 1     | 64257.8   | 4.11 | 248.4   |
| N2    | 23    | N2    | 23    | 365263.0  | 3.65 | 2891.0  |
| N2    | 23    | C8    | 3     | 491494.0  | 3.86 | 2791.0  |
| N2    | 23    | H1    | 1     | 228279.0  | 4.52 | 502.1   |
| C8    | 3     | C8    | 3     | 226145.2  | 3.47 | 2418.0  |
| C8    | 3     | H1    | 1     | 120792.1  | 4.10 | 472.8   |
| H1    | 1     | H1    | 1     | 24158.0   | 4.01 | 109.2   |

**Table A4.19** Unified (UNI) pair-potential parameters, Potential = A\*exp(-Br) - Cr(-6):



**Figure A4.13** Fragment of crystal structure of (cis-1)(4-vinylpyridine)<sub>2</sub> cocrystal, displaying the directions and magnitudes (in kJ mol<sup>-1</sup>) of three most negative intermolecular potentials. For clarity, the direction of the azo---phenyl stacking is always vertical.



**Figure A4.14** View of a fragment of a single azo…phenyl stack in the crystal structure of *cis-5*, highlighting the C-H…N interactions that might be responsible for directing the orientation of nearest-neighbour molecules in the stack. The C…N distance is 3.22 Å, the C-H…N angle 116°.



6. Fourier-Transform Attenuated Total Reflectance (FTIR-ATR) Spectroscopy

Figure A4.15 FTIR-ATR spectrum of *cis-bis*(pentafluorophenyl)diazene (3).



Figure A4.16 FTIR-ATR spectrum of *cis-bis*(2-bromo-3H-4,5,6-trifluorophenyl)diazene (4).



Figure A4.17 FTIR-ATR spectrum of *cis-bis*(2-bromo-5H-3,4,6-trifluorophenyl)diazene (5).



Figure A4.18 FTIR-ATR spectrum of *cis*-1:dabco cocrystal.



Figure A4.19 FTIR-ATR spectrum of *cis*-1:4-vinylpyridine cocrystal.



Figure A4.20 FTIR-ATR spectrum of *cis*-1:dithiane cocrystal.

## 7. Mass Spectrometry



Figure A4.21 High Resolution Mass spectrum for compound *cis*-3.



Figure A4.22 High Resolution Mass spectrum for compound cis-4.



Figure A4.23 High Resolution Mass spectrum for compound cis-5.

# 8. UV-Vis Spectroscopy

UV-Vis spectroscopy studies of compounds **3-5** were performed on a Cary 300 Bio UV-Vis spectrometer in hexane solution.



**Figure A4.24** UV-Vis absorption spectra of *cis* and *trans*-isomers of compound **3** (a, b) **4** (c, d) **5** (e, f) in hexanes. In all figures red line denotes the *cis*-isomer and black line the *trans*-isomer.

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## Rationale for Chapter 6: Controlling Dichroism of Molecular Crystals by Cocrystallization

Control of physical properties of crystals by cocrystallization which was reported in Chapters 4 and 5 highlighted the possibility of drastically improving a property by a careful choice of a cocrystal partner. Azobenzenes are generally preferred in materials chemistry applications because of their superior optical properties. In particular, linear and rigid rod-shaped azobenzene chromophores are strongly dichroic. In the next Chapter a methodology is given which allows one to predict and dictate a strong dichroic behaviour in the cocrystals of various azobenzenes. The contribution 'Controlling Dichroism of Molecular Crystals by Cocrystallization' was published in *Crystal Growth & Design*.



### **Chapter 6: Controlling Dichroism of Molecular Crystals by Cocrystallization**

## 6.1 Abstract

A combined crystallographic and optical properties study offers a simple model for the dichroic behaviour of crystalline azobenzene chromophores, leading to a cocrystallization strategy to manipulate their solid-state arrangement and, therewith, dichroic behaviour. This supramolecular strategy represents the first entry of crystal engineering into the design of dichroism in organic crystals.

#### 6.2 Introduction

The understanding and control of light-matter interactions are central to modern materials chemistry,<sup>1-6</sup> directed towards developing new materials for manipulating light, such as waveguides,<sup>7</sup> switches,<sup>8,9</sup> light-harvesting<sup>10-13</sup> and non-linear optics applications,<sup>14</sup> or for conducting photochemical reactions.<sup>15,16</sup> Cocrystallization, *i.e.* the formation of solid-state molecular complexes through designs based on well-defined supramolecular interactions,<sup>17,18</sup> has been particularly successful in making new organic solids with improved physicochemical properties.<sup>19,20</sup> In the context of light-matter interactions, particularly successful uses of cocrystallization have been in directing photochemical [2+2] photodimerization of olefins<sup>21-23</sup> and polymerization of di- and triacetylenes.<sup>24,25</sup> Besides these applications there has been surprisingly little exploration of how cocrystallization can be used to manipulate optical properties of organic solids,<sup>26-32</sup> considering that one of the first applications of cocrystallization was for generating organic crystals with advanced optical properties.<sup>33,34</sup>

Focusing on visible light, and using azobenzene (azo) model chromophores, we now demonstrate a cocrystallization-based approach to control dichroism, *i.e.* difference in absorption of polarized light dependent on the orientation of its polarization, in organic crystals.<sup>35-37</sup> Although optical dichroism has been known for a long time in organic crystals,<sup>38,39</sup> and was recently utilized to design photo-switchable microporous materials and investigate molecular assembly on surfaces,<sup>40,41</sup> a strategy to control dichroic behaviour of crystals by manipulating their structure has not yet been reported. The herein presented strategy permits crystal engineering<sup>42-44</sup> of optically dichroic crystals by using well-defined supramolecular interactions, such as halogen bonding, to direct the alignment of light-absorbing chromophores.<sup>45-48</sup>

## 6.3 **Results and Discussion**

## 6.3.1 Crystal Packing and Dichroic Behaviour of Perhalogenated Azobenzenes

As our first entry into investigation of dichroism in azo crystals we noted that single of crystals two chemically similar azobenzenes, trans-bis(4-bromo-2,3,5,6tetrafluorophenyl)diazene and iodo-analogue trans-bis(4-iodo-2,3,5,6-(trans-1) its tetrafluorophenyl)diazene (trans-2) (Figure 6.1a),<sup>49</sup> exhibit very different optical properties if observed in plane-polarized light under a transmission optical microscope. Single crystals of trans-1 exhibit strong dichroism (Figure 6.1b,c): in one orientation of the polarizer the crystals appear dark orange, but turn almost colourless upon 90° rotation. Importantly, this observation was found not to depend on the crystal face being observed. In contrast, the perceived colour of a *trans*-2 single crystal changes much less upon polarizer rotation, (Figure 6.1d,e).

The difference in dichroism of *trans*-1 and -2 crystals cannot be explained by differences in chemical structure or conformation, as both molecules are rigid and structurally similar. Therefore, we turned to differences in crystal structures. In their respective single crystals, the compounds exhibit very different alignments of azo chromophores. In the highly dichroic *trans*-1, molecules are arranged with their longest molecular axes aligned in parallel, while in *trans*-2 they adopt a herringbone orientation (**Figure 6.1f,g**). These differences offer an explanation for dichroic behaviour.



**Figure 6.1** (a) Azobenzenes and cocrystal formers used in this study. Images of single crystals of: (b) and (c) *trans*-1; and (d) and (e) *trans*-2, each viewed in plane-polarized light with two perpendicular orientations of the polarizer. Molecular packing motifs in crystals of: (f) *trans*-1 and (g) *trans*-2, responsible for strong and weak dichroic behaviour, respectively. (h) Schematic representation of the azo chromophore transition dipole moment, with arrow length representing its magnitude.

Namely, the absorption of light by the azo group depends on the orientation of its transition dipole moment, whose magnitude is related to molecular dimensions: the longest molecular axis roughly approximates the direction of the largest transition dipole moment (**Figure 6.1h**).<sup>50,51</sup> Plane-polarized light is expected to be most strongly absorbed by the azo chromophore if the direction of polarization coincides with the longest molecular axis.<sup>52,53</sup> It follows that a crystal structure in which the longest axes of all chromophores are aligned in parallel would make the absorption of plane-polarized light highly dependent on the orientation of the plane of light polarization with respect to the crystal.<sup>40,41</sup> It is important to distinguish that with such an arrangement dichroism should be observed *regardless of the crystal face being observed*. The behaviour and crystal structure of *trans*-1 are consistent with this expectation. Conversely, a crystal structure with a non-parallel orientation of neighboring molecular dipoles should almost always allow strong interaction between chromophores and plane-polarized light, regardless of the direction of polarization. (**Figure A4.1**, Appendix 5) Therefore, a herringbone-type structure is expected to be weakly dichroic or not at all, as indeed is observed for *trans*-2.

## 6.3.2 Circumventing Herringbone Packing by Cocrystallization

The above rationalization implies that inducing solid-state dichroism in crystalline organic solids is a question of circumventing herringbone arrangements, which is a problem already encountered in crystal engineering, *e.g.* in the design of organic semiconductors.<sup>54-59</sup> This suggests a means to manipulate dichroism of azo crystals by adjusting the spatial alignment of chromophores through cocrystal formation.<sup>60-64</sup> The azo chromophore is a suitable model for this purpose due to its rigid and linear shape. To verify the above hypothesis, we first turned to optical poperties of the recently reported<sup>65</sup> cocrystals of *trans*-1 and -2 with *trans*-azopyridine (**apy**). The cocrystals (*trans*-1)(**apy**) and (*trans*-2)(**apy**) are reported to consist of linearly aligned halogenbonded chains held together by Br…N and I…N interactions.<sup>65-68</sup> Therefore, both cocrystals should exhibit notable dichroism which is, indeed, observed (**Figure A5.2**, Appendix 5).

Next, we prepared two azo compounds anticipated to form similarly structured cocrystals as **apy**: *trans*-4,4'-dinitroazobenzene (**nab**) and *trans*-4,4'-dicyanoazobenzene (**cab**) (**Figure 6.1a**). Crystal structure analysis of pure **nab** and **cab** reveals a herringbone arrangement of azo groups (**Figure A5.3**, Appendix 5) and, consequently, neither compound exhibits notable dichroism (Figures 6.2a and A5.2). Cocrystallization of cab with *trans*-2 yields (*trans*-2)(cab), based on chains held by cyano…iodo halogen bonds (I…N distance: 2.973(2) Å), Figures A5.3, A5.4 Appendix 5).<sup>69</sup> As in apy cocrystals, the halogen-bonded chains pack to form a structure that contains all azo groups aligned in parallel. Consistent with such a structure, the cocrystals are strongly dichroic, which is clearly seen for the (001) face of (*trans*-2)(cab), compared to the (011) face of cab (Figures 6.2b, A5.4), which demonstrates the ability to generate a highly dichroic material from otherwise poorly dichroic components. A comparison of polarized light transmission for these two sets of faces with respect to crystal orientation is given in the Appendix 5 Figure A5.5. Similar behaviour is observed for (*trans*-2)(nab) cocrystals, composed of linear halogenbonded chains, based on I…O halogen bonds involving nitro groups<sup>69,70</sup> as acceptors (I…O distances: 3.114(2) Å and 3.411(2) Å, Figure A5.3, Appendix 5). Again, the chains are arranged in parallel, enabling highly dichroic behaviour (Figures A5.2 and A5.3).

In order to enhance dichroism by using cocrystal formers that are not azobenzenes, we explored cocrystallization of *trans*-2 with 4-cyano-4'-n-pentylbiphenyl (cpb). In addition to the nitrile group as a halogen bond acceptor, cpb also offers an aliphatic chain that should encourage the formation of layers in which the azo groups are aligned in parallel *via* halogen bonds and alkyl chain interdigitation.<sup>71,72</sup> Crystal structure analysis of  $(trans-2)(cpb)_2$  reveals the expected layers containing parallel-aligned *trans-2* molecules, held together by cyano...iodo interactions (I...N distance: 3.08(2) Å) and alkyl group interdigitation. As a result, (*trans-2*)(cpb)<sub>2</sub> is strongly dichroic, demonstrating the rational formation of an organic dichroic material from one poorly dichroic and one optically transparent component. (Figure 6.2c and A5.4). We also tested the (trans-2)(nab) cocrystal as a single wavelength dichroic filter. Consistent with the UV-VIS absorption spectra of individual *trans-2* and **nab**, the cocrystal exhibits efficient dichroism up to 633 nm, after which nearly all light intensity is transmitted, regardless of crystal orientation (Figures 6.2d,e). It is important to stress that the linear arrangement of chromophores results in the strongly dichroic crystals regardless of the face being examined. This behaviour can be illustrated by a batch of (*trans-2*)(cpb)<sub>2</sub> or (*trans-2*)(cab) crystals exposing a variety of crystal faces. All of the crystals are strongly dichroic and change colour from orange-red to colourless upon polarizer rotation (Figure 6.3).



**Figure 6.2** A single crystal, viewed in plane-polarized light with two mutually perpendicular orientations of the polarizer, and a general view of the solid-state packing of azo chromophores for: (a) the (011) face of **cab**; (b) the (001) face of (*trans-2*)(**cab**); (c) the (001) face of (trans-2)(**cpb**)<sub>2</sub>. The actual orientation of azo chromophores for the (011) face of **cab** and (001) face of (*trans-2*)(**cab**) is given in Figure A5.4. (d) and (e) Transmission images of a single crystal of (*trans-2*)(**nab**) taken using single-wavelength radiation, with two mutually perpendicular polarizer orientations.



**Figure 6.3** Views of a batch of crystal of (trans-2)(cab) (a) and  $(trans-2)(cpb)_2$  (b) in plane-polarized light in mutually perpendicularly orientations. The few crystals that seem to not change colour are also dichroic, but have transition dipole moment axis not coinciding with either of the two selected polarizer orientations.

#### 6.3.3 Dichroism at Different Faces of Herringbone-Packed Crystals

An excellent verification of the proposed model of dichroism in azo crystals is given by the cocrystal of *trans*-1 with 1,10-phenanthroline (**phen**). In contrast to *trans*-1, whose single crystals are highly dichroic regardless of the crystal face being observed, the dichroism of (*trans*-1)(**phen**) is highly dependent on the crystal face being inspected. Observation normal to the (0-11) face reveals only very weak dichroism (**Figure 6.4a**) but, if viewed normal to the (310) face, the cocrystal appears highly dichroic (**Figure 6.4b**). Variation in the intensity of transmitted light with respect to crystal orientation is roughly ten times higher for the (310) face compared to the (0-11)

face. This is remarkable, as crystal thickness along the (310) direction is double that along the (0-11) direction (**Figure 6.4c**).



**Figure 6.4** Views of a single crystal of (*trans*-1)(**phen**) in plane-polarized light, each with two perpendicular orientations of the polarizer: (a) perpendicular to (0-11) face (b) perpendicular to (310) face. (c) Difference in transmission of polarized light by a (trans-1)(phen) cocrystal at (310) and (0-11) crystal faces (d) Azobenzene chromophore orientations for the highly dichroic (310) face (left) and the weakly dichroic (0-11) face (right), phen molecules were omitted for clarity.

The dichroic properties of (trans-1)(**phen**) are readily explained by its crystal structure which consists of  $\pi$ -stacked layers of **phen** and *trans-1* (Figure 6.4d) parallel to the crystallographic *ab*-plane. In each layer, **phen** molecules are connected by C-H…N hydrogen bonds (C…N distances 3.501(3) Å and 3.410(3) Å, Figure A5.3), while *trans-1* molecules mutually associate *via* Br…Br interactions (Br…Br distance 3.824(1) Å, Figure A5.3). Whereas the azo chromophores are aligned in parallel in each *trans-1* layer, molecules in consecutive layers of
*trans*-1 are mutually rotated by 45°. Consecutive layers of *trans*-1 therefore function as inherent crossed polarizers, which results in only slight dichroism along the (0-11) direction (**Figure 6.4d**). Along the (310) direction, however, all azo groups in (*trans*-1)(**phen**) appear aligned, leading to strong dichroic behaviour.

#### 6.4 Conclusions

In summary, we have described a methodology to control optical dichroic properties of crystals of azobenzene chromophores by cocrystallization. Parallel assembly of azo building blocks was identified as a prerequisite to obtain highly dichroic crystals, which was achieved by utilizing strongly directional interactions, such as halogen bonds. In this way, it was possible to generate highly dichroic materials from organic building blocks which, on their own, do not exhibit solid-state dichroism. Conversely, the herringbone packing is conducive of non-discriminative light absorption, leading to nearly perfect isotropic optical properties at certain crystal faces. We believe that the presented work provides an important step forward in the understanding and design of optical properties of crystalline organic solids,<sup>73-80</sup> with specific applications as optical filters and polarizers.

#### 6.5 Acknowledgements

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#### 6.6 Notes

Details of synthesis and cocrystallisation experiments, images of selected cocrystals in polarised light, detailed images of crystal structures of herein reported cocrystals, selected Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectra, thermal analysis data and crystallographic data in CIF format (deposition codes CCDC 1400996-1401001) can be found in Appendix 5. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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#### **Appendix 5: Supporting Information for Chapter 6**

#### 1. Experimental

#### 1.1 Materials

4,4'-dibromooctafluoroazobenzene (*trans*-1) and 4,4'-diiodooctafluoroazobenzene (*trans*-2) were synthesized according to the procedure outlined in our prior report.<sup>1</sup> Precursors such as 4-bromo-2,3,5,6-tetrafluoroaniline, 2,3,5,6-tetrafluoroaniline, nitroaniline, 4-aminobenzonitrile, 1,10-phenanthroline, and mercury oxide were obtained from Sigma Aldrich and used without purification.

#### 1.2 Syntheses

(nab) 4,4'-dinitroazobenzene: To an aqueous slurry of 0.25 g of 4-nitroaniline solution of 0.30 g of Oxone in 5 ml of water was added at 0 °C and left stirring overnight. Yellowish precipitate was filtered and without purification dissolved in 2.5 ml of AcOH, 0.25 g of 4-nitroaniline was added and left stirring for 24 hours resulting in orange slurry. The product was evaporated and extracted with dichloromethane and purified on silica column (30% EtAc in hexane). Yield 236 mg (48%). IR: IR (ATR) 1605, 1533, 1477, 1346, 1319, 1210, 1105, 1003, 861, 805, 758, 688, 496 cm<sup>-1</sup>.

(cab) 4,4'-dicyanoazobenzene: To an aqueous slurry of 0.50 g of 4-aminobenzonitrile solution of 0.65 g of Oxone in 5 ml of water was added at 0 °C and left stirring overnight. Off-yellow precipitate was filtered and without purification dissolved in 2.5 ml of AcOH, 0.50 g of 4-aminobenzonitrile was added and left stirring for 72 hours resulting in pale orange slurry. The product was evaporated and extracted with dichloromethane and purified on silica column (30% EtOAc in hexane). Yield 450 mg (38%). IR (ATR) 2227, 1490, 1463, 1406, 1294, 1098, 1010, 850, 563, 503, 416 cm<sup>-1</sup>.

#### **1.3 Cocrystal Preparation**

Cocrystals were prepared by mixing equimolar quantities of halogen bond donors and acceptors in dichloromethane (DCM). Single crystals were grown by slow evaporation of the solvent.

(trans-1)(phen): 10.0 mg (0.0207 mmol) of 1 was dissolved in 2.5 ml of DCM and added to the solution of 3.7 mg (0.0207 mmol) of 1,10-phenanthroline in 2.5 ml of DCM. Resultant orange solution remained clear and large block-shaped cocrystals precipitated when the solvent evaporation was nearly completed.

(*trans-2*)(nab): 10.0 mg (0.0173 mmol) of **2** was dissolved in 2.5 ml of DCM and added to the solution of 4.7 mg (0.0173 mmol) of dinitroazobenzene in 2.5 ml of DCM. Dark red highly dichroic cocrystals precipitated towards the end of solvent evaporation.

(*trans-2*)(cab): 10.0 mg (0.0173 mmol) of **2** was dissolved in 2.5 ml of DCM and added to the solution of 4.0 mg (0.0173 mmol) of dicyanoazobenzene in 2.5 ml of DCM. Dark orange highly dichroic cocrystals precipitated towards the end of solvent evaporation.

(*trans-2*)(5-cpb): 10.0 mg (0.0173 mmol) of 2 was dissolved in 2 ml of DCM and several drops (ca. 50 mg) of 5-cpb was added to that solution. Upon evaporation of DCM dark orange-red block crystals of (*trans-2*)(5-cpb) were collected. Note: Excess of 5-cpb is important to avoid growth of *trans-2* crystals upon solvent evaporation.

2. Collinear Crystal Packing of trans-1 Viewed along Principal Dimensions of the Molecule



**Figure A5.1** (a) Schematic representation of the azo chromophore transition dipole moment, with arrow length representing its magnitude. (b-d) Three different views of the crystal packing of *trans*-1 molecules in the solid state, viewed along principal dimensions of the molecule, highlighting persistently linear chromophore arrangement.

## 3. Photographs of Selected Crystals Taken in Polarized Light



Figure A5.2 Photographs of selected crystals, viewed in polarized light in mutually perpendicular polarizer orientations: (a) (*trans*-1)(apy) cocrystal; (b) pure **nab** solid; (c) (*trans*-2)(**nab**) cocrystal.



4. Single Crystal X-ray Diffraction Measurements and Crystallographic Summary

**Figure A5.3** Views of crystal structures of: (a) **cab**, with hydrogen atoms omitted for clarity; (b) **nab**, with hydrogen atoms omitted for clarity. (c) Three parallel aligned halogenbonded chains in (trans-2)(nab). (d) Three parallel aligned halogen-bonded chains in (trans-2)(cab). (e) Fragment of a layer in (trans-2)(cpb), based on I···N halogen bonds and *n*-pentyl chain interdigitation. (f) Layers of *trans*-1 and (g) **phen** in the (trans-1)(phen) cocrystal, each parallel to the crystallographic *ab*-plane, with selected C-H···N and Br···Br interactions highlighted.



**Figure A5.4** Photographs of crystals viewed in polarized light, in mutually perpendicular polarizer orientations: (a) (*trans-2*)(**cab**) cocrystal: view of the (001) crystal face and the corresponding orientation of molecules; (b) (*trans-2*)(**cpb**)<sub>2</sub> cocrystal: view of (001) crystal face and the corresponding orientation of molecules.



**Figure A5.5** (a) View of the (011) face for two orientations of a crystal of **cab** in polarized light; (b) view of the (001) face for two orientations of a crystal of (*trans-2*)(**cab**) in polarized light; (c) view of the crystal packing of **cab** perpendicular to the (011) crystal face; (d) view of the crystal packing of (*trans-2*)(**cab**) perpendicular to the (001) crystal face. (e) Transmission of polarized right with respect to crystal orientation, viewed normal to the (011) face of a **cab** crystal (blue) and viewed normal to the (001) face of (*trans-2*)(**cab**) (red).

### 5. Thermal Analysis Data



**Figure A5.6** Thermal analysis for the (*trans-2*)(**cab**) cocrystal: (top) thermogravimetric measurement and (bottom) differential scanning calorimetry.



**Figure A5.7** Thermal analysis for the (*trans-2*)(**nab**) cocrystal: (top) thermogravimetric measurement and (bottom) differential scanning calorimetry.



**Figure A5.8** Thermal analysis for 4,4'-dicyanoazobenzene (**cab**): (top) thermogravimetric measurement and (bottom) differential scanning calorimetry.



**Figure A5.9** Thermal analysis for 4,4'-dinitroazobenzene (**nab**): (top) thermogravimetric measurement and (bottom) differential scanning calorimetry.



**Figure A5.10** Thermal analysis for (*trans-2*)(**5-cpb**): (top) thermogravimetric measurement and (bottom) differential scanning calorimetry.



**Figure A5.11** Thermal analysis for (*trans*-1)(**phen**): (top) thermogravimetric measurement and (bottom) differential scanning calorimetry.



6. Fourier-Transform Infrared Attenuated Total Reflectance (FTIR-ATR) Spectroscopy

Figure A5.12 FTIR-ATR spectrum of 4,4'-dinitroazobenzene.



Figure A5.13 FTIR-ATR spectrum of 4,4'-dicyanoazobenzene.







Figure A5.15 FTIR-ATR spectrum of (*trans-2*)(cab) cocrystals.



Figure A5.16 FTIR-ATR spectrum of (*trans-2*)(5-cpb) cocrystals.



Figure A5.17 FTIR-ATR spectrum of (*trans*-1)(phen) cocrystals.

# Rationale for Chapter 7: Fluorinated Azobenzenes with Highly Strained Geometries for Halogen Bond-Driven Self-Assembly

Perhalogenated azobenzenes activated for halogen bond formation described in Chapters 3-6 proved useful for preparation of crystals with various optical and photo-mechanical properties. Chapter 7 presents a facile route for room temperature chemical modification of fluorinated azobenzenes, which allows to prepare ever more sophisticated self-assembled structures. The contribution 'Fluorinated Azobenzenes with Highly Strained Geometries for Halogen Bond-Driven Self-Assembly' that was published in *CrystEngComm* demonstrates how replacement of *ortho*-fluorine substituents on fluorinated azobenzenes with morpholine groups provides conformationally unusual molecules acting as halogen bond donors and acceptors.



## Chapter 7: Fluorinated Azobenzenes with Highly Strained Geometries for Halogen Bond-Driven Self-Assembly

#### 7.1 Abstract

Attempted cocrystallisation of brominated and iodinated octafluoroazobenzene derivatives with morpholine led to the unexpected and exhaustive replacement of fluorine substituents in *ortho*-positions to the azobenzene with sterically demanding morpholine groups. The resulting molecules exhibit a highly unusual strained conformation of the azobenzene unit, in which the terminal phenyl rings adopt a mutually nearly completely orthogonal orientation. Substitution of *ortho*-fluorine groups with N-morpholine fragments provides the resulting molecules with active halogen bond donor and acceptor sites that guide the molecular self-assembly in the solid state towards the formation of polymeric halogen-bonded chains.

#### 7.2 Introduction

Azobenzene (azo) compounds are a family of molecules that is ubiquitous in the design of photo-switchable materials, i.e. materials whose properties can be changed upon irradiation with light.<sup>1</sup> The photo-switchable behaviour of azobenzene-based materials is based on a change of molecular geometry upon light-induced reversible *trans-cis* azo isomerization.<sup>2</sup> Owing to the large stereochemical change involved in the isomerization, incorporation of azo molecules within polymers,<sup>3</sup> liquid crystals<sup>4</sup> and even crystalline metal-organic frameworks,<sup>5</sup> has been utilized to create solid materials displaying the photo-mechanical effect, *i.e.* the direct conversion of light into mechanical energy.<sup>6</sup> Very recently, however, it was demonstrated that crystalline solid azobenzenes can exhibit reversible<sup>7</sup> or irreversible<sup>8</sup> photo-mechanical behaviour, inspiring interest and activity in structural characterization of azobenzene solids. In that context, we have recently demonstrated irreversible solid-state *cis-trans* isomerization in crystals of *cis*-4,4'-di(bromo)perfluoroazobenzene (*cis*-1) and its iodo analogue (*cis*-2).<sup>8</sup> The solid-state isomerization allowed the controllable and permanent modification in shape of the crystalline solids through irreversible photo-mechanical transformation. More recently, Saccone and co-workers have demonstrated the synthesis of two-component cocrystals using *trans*-2 as the halogen bond donor

in combination with nitrogen-based halogen bond<sup>9</sup> acceptors,<sup>10</sup> and our group has demonstrated irreversible photo-mechanical bending induced by visible light irradiation of halogen-bonded cocrystals of *cis*-1 and *cis*-2.<sup>11</sup>

We now describe the crystal structures of three substituted derivatives of azobenzenes 1 and 2 that were serendipitously obtained as a result of attempted halogen bond-driven cocrystallisation with morpholine. In particular, recrystallisation of either *cis*-1 or *trans*-1 from liquid morpholine at room temperature produced, instead of the desired halogen-bonded cocrystals with morpholine, compounds 3 and 4 in which three or four of the fluorine substituents in *ortho*-position to the azo group are substituted by N-morpholine residues (Scheme 1), respectively. Similarly, attempted recrystallisation of *trans*-2 or *cis*-2 from morpholine gave compound 5 in which all fluorine groups *ortho* to the azo moiety are replaced by N-morpholine substituents.



Scheme 1. The preparation of herein investigated compounds 3-5.

The herein described crystal structures of compounds 3-5 are remarkable in terms of molecular structure, as the bulkiness of juxtapositioned N-morpholine substituents imposes a

highly unusual stereochemistry of the azo moiety, as well as in terms of crystal packing due to the presence of strong halogen bond donor and acceptor sites on each molecule.

#### 7.3 Experimental

The trans- and cis-forms of the precursors 1 and 2 were synthesised using previously described procedures.<sup>8</sup> Compounds 3-5 were prepared by dissolving 50 mg *cis*- or *trans*-1 or -2 in morpholine at room temperature. Reaction mixture immediately turned red and colour rapidly became deeper, reaching almost black within 15 minutes. The formation of fluoride ions in the reaction was confirmed by recording an <sup>19</sup>F NMR spectrum of the reaction mixture involving *cis*-1, which revealed the appearance of a signal at 146 ppm, consistent with the shift of a fluoride ion in a separately prepared sample of morpholinium fluoride (see Appendix 6). After 12 hours, the solvent was removed on a rotary evaporator and samples we purified using an automated CombiFlash column equipped with a 4 g silica cartridge and a mixture of hexanes and ethyl acetate as the mobile phase. The identity of products 3-5 was confirmed by X-ray analysis, mass spectrometry (MS), <sup>1</sup>H NMR and elemental analysis. **3**: 4 mg (5.6%) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.59-3.55 (comp, 8H), δ 3.15-3.06 (comp, 8H), MS m/z 686.02 C<sub>24</sub>H<sub>24</sub>Br<sub>2</sub>F<sub>5</sub>N<sub>5</sub>O<sub>3</sub> (M+1), decomposes without melting at 171°C; calculated for 3: N (10.22%) C (42.06%) H (3.53%), determined for **3**: N (10.08%) C (42.33%) H (3.42%); **4**: 41 mg (53% yield), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.51-3.49 (t, J = 3.0 Hz, 8H) v  $\delta$  3.11-3.09 (t, J = 3.0 Hz, 8H), MS m/z 753.08 C<sub>28</sub>H<sub>32</sub>Br<sub>2</sub>F<sub>4</sub>N<sub>6</sub>O<sub>4</sub> (M+1), decomposes without melting at 175°C; calculated for 4 morpholine: N (11.68%) C (45.78%) H (4.92%), determined for 4 morpholine: N (11.55%) C (46.18%) H (5.03%); 5: 43 mg (58%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.51-3.49 (t, J = 3.0 Hz, 8H),  $\delta$  3.08 (app. s, 8H), MS m/z 847.05 C<sub>28</sub>H<sub>32</sub>I<sub>2</sub>F<sub>4</sub>N<sub>6</sub>O<sub>4</sub> (M+1), decomposes without melting at 175°C; calculated for 5 · morpholine: N (10.50%) C (41.17%) H (3.43%), determined for 5 · morpholine: N (10.00%) C (41.35%) H (4.34%);

Single crystals were prepared by recrystallisation of ca. 10 mg of the corresponding precursors 1 or 2 from excess morpholine. Using this methodology, single crystals of 3 were always obtained in small amounts along with the crystals of the main product 4 morpholine. Single crystal X-ray diffraction experiments (Table 7.1) were performed on a Bruker D8 single crystal diffractometer at 100 K or 150 K. Crystal structure refinement was conducted using SHELXL-

2014/3 implemented within the WinGX 2013.3 integrated program system.<sup>12,13</sup> Solution UV-Vis measurements were performed on a Cary 300 Bio spectrometer using THF and DCM and cyclohexane as solvents. In all solvents we found that solutions of **4** and **5** exhibit nearly identical spectra, including a shoulder at 500 nm of coalescing  $\pi$ - $\pi$ \* and n- $\pi$ \* transitions (see Appendix 6, **Figure A6.1**). Cambridge Structural Database (CSD) searches were performed using the CSD version 5.35, November 2013 update.

Density Functional Theory (DFT) calculations were performed using the Gaussian09 package of programs.<sup>14</sup> Geometrical optimizations were carried out using the popular Becke's three parameter functional<sup>15</sup> with the nonlocal Lee-Yang-Parr correlation functional<sup>16</sup> (B3LYP) theory. LANL2DZ basis set including double- $\zeta$  valence basis set with the Hay and Wadt effective core potential<sup>17</sup> (ECP) was used for the heavy Br and I atoms, while the 6-31+G(d,p) Pople basis set<sup>18</sup> was used for the rest of the atoms.

#### 7.4 **Results and Discussion**

#### 7.4.1 Molecular and Crystal Structures of 3 and 4 Morpholine

Crystallisation of 1 from morpholine gave rise to two distinct types of crystals: a small number of carmine red plates and much more abundant burgundy red needles. Crystal structure analysis by single crystal X-ray diffraction (**Table 7.1**) revealed that the plates consist of molecules (**3**) in which three out of four fluorine substituents *ortho* to the azo moiety of *trans*-1 have been replaced by nitrogen-bound morpholine units (**Figure 7.1a**). Due to steric crowding around the azo group, the molecules of **3** adopt a conformation that is very different from that found in the parent *trans*-1. Specifically, the *trans*-azo group, defined by the two nitrogen atoms and the two adjacent carbon atoms, is no longer planar but exhibits a significant torsional angle ( $\tau$ ) of 15(1)°. Moreover, the phenyl ring substituents that are coplanar in the crystals of *trans*-1 starting material are now found to be almost completely perpendicular, with an angle ( $\pi$ ) of 88.8(3)° between the best planes drawn through the carbon atoms of each phenyl ring (**Figure 7.1b,c**). In the crystal, the molecules of **3** are associated by relatively long<sup>19</sup> Br···O interactions of 3.272(8) Å into discrete halogen-bonded dimers. Consistent with their length, these halogen-bonding interactions show a significant deviation from linearity,<sup>20</sup> expressed by the C-Br···O angle of 168.8(3)°. No specific

interactions are observed between the dimers, except a pair of long C-H $\cdots$ O<sup>21</sup> interactions (C $\cdots$ O distance 3.59(1) Å).

| Compound                             | 3                           | 4·morpholine                | 5-morpholine  |
|--------------------------------------|-----------------------------|-----------------------------|---|
| Formula                              | $C_{24}H_{24}Br_2F_5N_5O_3$ | $C_{32}H_{41}Br_2F_4N_7O_5$ | C <sub>32</sub> H <sub>41</sub> F <sub>4</sub> I <sub>2</sub> N <sub>7</sub> O <sub>5</sub> |
| Mr                                   |                             |                             |   |
| Crystal system                       | monoclinic                  | orthorhombic                | orthorhombic  |
| Space group                          | $P2_{1}/c$                  | $Pna2_1$                    | $Pna2_1$  |
| <i>a</i> / Å                         | 14.052(3)                   | 19.414(2)                   | 19.680(1)   |
| <i>b</i> / Å                         | 10.029(3)                   | 17.370(1)                   | 17.411(1)   |
| <i>c</i> / Å                         | 18.994(5)                   | 10.4512(8)                  | 10.6952(7)  |
| β/°                                  | 101.069(3)                  | 90                          | 90  |
| V / Å <sup>3</sup>                   | 2627(1)                     | 3524.3(5)                   | 3664.7(4)   |
| Ζ                                    | 4                           | 4                           | 4   |
| <i>T /</i> K                         | 150(2)                      | 150(2)                      | 100(2)  |
| $ ho_{ m calc}$ / g cm <sup>-3</sup> | 1.73                        | 1.58                        | 1.69  |
| no. data                             | 4628                        | 8163                        | 8076  |
| no. data with $I \ge 2\sigma_I$      | 1910                        | 5730                        | 6845  |
| no. parameters                       | 352                         | 452                         | 451   |
| R <sub>int</sub>                     | 0.187 <sup>a</sup>          | 0.086                       | 0.066   |
| F(000)                               | 1368                        | 1712                        | 1856  |
| R(all data)                          | 0.199                       | 0.091                       | 0.054   |
| $R(I \ge 2\sigma_I)$                 | 0.069                       | 0.049                       | 0.039   |
| w $R_2$ (all data)                   | 0.180                       | 0.101                       | 0.074   |
| $\mathbf{w}R_2 \ (I \geq 2\sigma_I)$ | 0.148                       | 0.088                       | 0.069   |
| S                                    | 0.925                       | 1.023                       | 1.015   |

 Table 7.1 Crystallographic and general data for the crystal structures of 3, 4·morpholine

 and 5·morpholine.

a) the crystal diffracted poorly past  $2\theta = 45^{\circ}$ .



Figure 7.1 (a) Thermal ellipsoid plot of a single molecule of 3 as found in the crystal structure, thermal ellipsoids are shown at 25% probability level. Overlay of the solid-state conformations of 3 (green) to that of *trans*-1 (red) viewed: along (b) and perpendicular (c) to the molecular plane of *trans*-1. For clarity all phenyl ring substituents except bromine atoms have been removed in the overlay figures (b) and (c); (d) the assembly of two molecules of 3 in the solid state, based on a pair of Br…O interactions.

Crystallographic analysis of burgundy red needles that are the major product of recrystallizing *trans*- or *cis*-1 from morpholine revealed a morpholine solvate of an even more sterically hindered molecule (4), in which all four fluorine substituents *ortho* to the azo moiety have been replaced by N-morpholine residues (Figure 7.2a).



**Figure 7.2** Thermal ellipsoid plot of a single molecule of **4** as found in the crystal structure, with thermal elliposids shown at 25% probability level. Overlay of the solid-state conformations of one molecule of **4** (green) to that of *trans*-**1** (red) viewed: (b) along and (c) perpendicular to the molecular plane of *trans*-**1**. For clarity all phenyl ring substituents except the bromine atoms have been removed in the overlay figures (b) and (c).

Similar to **3**, the *trans*-azo group in **4** is no longer planar but exhibits a torsional angle  $\tau$ =14.6(5)°, and the phenyl groups are mutually perpendicular with the angle  $\pi$ =87.5(2)° between the planes drawn through carbon atoms of each ring (**Figure 7.2b,c**). In a crystal of **4** ·morpholine, molecules of **4** are associated into one-dimensional halogen-bonded polymers held together by Br...O interactions and propagating in the crystallographic (011) direction (**Figure 7.2d**). Each molecule of **4** is involved in two shorter and two longer halogen bonds, simultaneously acting as a two-fold halogen bond donor and a two-fold halogen bond acceptor. Two of the halogen bonds to each molecule are significantly shorter (Br...O distance 2.923(5) Å) than those observed in the crystal structure of **3**, while the other two are of comparable length (Br...O distance 3.324(5) Å).

Consistent with previous studies, the shorter halogen bonds exhibit a higher degree of linearity (C-Br···O angle of  $176.0(2)^{\circ}$ ) than the longer ones (C-Br···O angle of  $165.6(2)^{\circ}$ ). The additional molecules of morpholine in the crystal structure are associated with the halogen-bonded chains of **4** by way of long N-H···O hydrogen bonds (N···O distance 3.33(1) Å, **Figure 7.2d**).

#### 7.4.2 Crystal and Molecular Structure of 5. Morpholine

Molecular structures of **3** and **4** are remarkable not only because of their highly unusual stereochemistry, but also in the context of supramolecular chemistry. These serendipitously obtained molecules contain both a strong halogen bond donor site, in the form of an electron-deficient bromine atom attached on a fluorinated benzene ring, as well as a potential halogen bond acceptor site in the form of the ether oxygen<sup>22</sup> of the N-morpholine substituents (**Figure 7.3a**).

Whereas the intense exploration of halogen bonding in the solid state has strongly focused on the formation of cocrystals between halogen bond donors and acceptors, there has been much less exploration of molecular building blocks designed to form self-assembled halogen-bonded structures in single-component crystals.<sup>23</sup> The facile transformation of *trans*- or *cis*-1 into 3 or 4 upon recrystallization from morpholine offers a simple means to create such mixed donor and acceptor building blocks. As the first step in that direction, we attempted the analogous replacement of fluorine atoms in 2, the iodinated analogue of 1. Indeed, recrystallization of either *trans*-2 or *cis*-2 from morpholine gave crystals whose unit cell parameters were found to be almost identical to those of 4 morpholine.



Figure 7.3 (a) Electrostatic potential plot of a single molecule of 4, revealing well-defined areas of negative and positive potential located on the oxygen and bromine atoms, respectively; (b) a thermal ellipsoid plot of a single molecule of 5 as found in the crystal structure of  $5 \cdot \text{morpholine}$ , with thermal ellipsoids shown at 25% probability level; (c) (a) electrostatic potential plot of a single molecule of 5 and (d) overlay of the molecular geometries of 4 (blue) and 5 (red) as found in solid-state solvates with morpholine. For clarity, hydrogen atoms are omitted.

Crystal structure determination revealed that the crystal consists of molecules of **5**, an iodine-based analogue of **4**, and morpholine solvent in a 1:1 stoichiometric ratio. The crystal of **5**•morpholine is isostructural to that of **4**•morpholine, with **5** adopting a molecular conformation almost identical to that observed for **4** (**Figure 7.3b-d**). Like in **4**•morpholine, the molecules of **5** 

in the structure of **5**·morpholine are associated into infinite halogen-bonded chains, propagating in the crystallographic (011) direction and held together by I···O halogen bonds (Figure 7.3e). In the chain, molecules of 5 act as a two-fold halogen bond donors and two-fold acceptors. Each molecule forms one pair of shorter (I···O distance 2.923(5) Å) and one pair of longer (3.140(5)Å) I···O halogen bonding interactions. The shorter ones are highly linear (C-I···O angle 175.1(2)°) and comparable to the analogous interactions in 4 morpholine (Figure 7.3e). The set of longer I···O halogen bonds are considerably shorter and more linear (C-I···O angle of 172.2(2)°) than their Br…O counterparts in 4 morpholine, consistent with the greater strength and linearity of halogen bonds involving iodine donors<sup>24,25</sup> compared to those based on bromine. The molecules of morpholine in the crystal structure of 5. morpholine are associated with halogen-bonded chains of 5 through long N-H···O interactions whose length (3.25(1) Å) and geometry resemble those found in 4-morpholine (Figure 7.3e). The similarity of crystal structures of 4-morpholine and 5.morpholine is consistent with the previously described isostructurality of halogen-bonded structures based on iodine and bromine.<sup>19b,25</sup> Another view of the crystal structures of 4.morpholine and 5.morpholine is as lattice inclusion compounds involving halogen-bonded chains of 5 as the host and morpholine molecules as guests. In such a view, the lattice host is formed from halogen-bonded chains which stack in the crystallographic bc-plane to form layers. The assembly of neighbouring layers into a stacked log pattern which creates cavities that host morpholine guests (Figures 7.4a,b).



**Figure 7.4** (a) Formation of cavities by the assembly of halogen-bonded chains in **5**·morpholine, with morpholine molecules occupying the cavities omitted and (b) the "log stack" assembly of layers of parallel halogen-bonded chains of **5**. For clarity, different layers are coloured red and blue.

#### 7.4.3 Database Analysis

Analysis of the Cambridge Structural Database (CSD) reveals that the geometry of the azo moiety in **3** and **4** is among the most distorted ones reported so far in *trans*-azobenzenes. The database search focused on the distribution of the torsion angle around the azo moiety ( $\tau$ , **Figure 7.5a**) and  $\pi$ , the angle between the planes of the two azobenzene phenyl substituents. Most reported *trans*-azobenzene structures exhibit highly planar molecular conformations, reflected by a  $\pi$  angle of no more than 50°, with the torsion angle  $\tau$  deviating no more than ±10° from 180°. A limited number of structures exhibit a perpendicular orientation of phenyl substituents which, upon individual inspection, appears to be largely associated with the presence of sterically highly demanding substituents in *ortho*-positions to the azo group (*e.g.* in BRBUAB,  $\tau$ =3.2°,  $\pi$ =87.3° or HNIABZ21  $\tau$ =1.5°,  $\pi$ =85.2°).<sup>26</sup> The distortion of the torsion angle  $\tau$  is encountered much more rarely and appears to be associated with strained structures, *e.g.* with the azobenzene group being a part of a cyclophane ring (*e.g.* in JEMLIX,  $\tau$ =15.3°,  $\pi$ =84.0°)<sup>27</sup> or highly sterically encumbered systems, such as 2,2',4,4',6,6'-hexakis(*tert*-butyl)azobenzene (CSD KEBYAT,  $\tau = 10.1^{\circ}$ ,  $\pi =$ 83.0°).<sup>28</sup> The combination of unusual  $\tau$ - and  $\pi$ -values places the conformations of **3** and **4** among the most extreme distortions of the *trans*-azobenzene moiety reported in a crystalline solid.



Figure 7.5 (a) Schematic representation of the C-N=N-C torsion angle ( $\tau$ ) around the azo moiety, used in the CSD search. (b) Scatterplot of the absolute value of  $\tau$  against the phenyl-phenyl interplanar angle ( $\pi$ ), based on azobenzene structures deposited in the CSD. Molecular geometries of **3** and **4** are highlighted in red. The highly populated region at  $\tau$ =180° corresponds to *trans*-azobenzene structures, while the poorly populated region around  $\tau$ =0° corresponds to structures of *cis*-azobenzenes.

#### 7.4.4 Computational Studies

In order to evaluate the degree of distortion of the azobenzene moiety imposed by introducing the four bulky substituents in compound **4**, we have compared the calculated molecular energies for azobenzene, perfluoroazobenzene and compound **1** in three different conformations: the idealised planar arrangement found in crystal structures of all three compounds,<sup>8,29-31</sup> the minimum energy gas-phase conformation calculated at the B3LYP level and the orthogonal conformation corresponding to that of the azobenzene skeleton in the crystal structure of **4**.

Gas-phase energy minimisation confirmed the planar conformation is the most stable one for azobenzene. However, calculations on perfluoroazobenzene and **1** revealed that these molecules can access a twisted conformation ca. 2 kcal mol<sup>-1</sup> lower than the planar conformations found in crystal structures. Comparison of the molecular energies calculated for all three conformations indicated that the orthogonal conformation adopted by molecules of **4** is up to 40 kcal mol<sup>-1</sup> higher than the energy of the lowest energy conformation (**Table 7.2**). The orthogonal geometries were first obtained from the crystal structures of compound **4**·**morpholine** by replacing the *ortho* morpholine moieties with fluorine atoms and subsequently freezing the core Ph-N=N-Ph atoms while the other peripheral atoms were allowed to relax. Although the constraints required to impose this particular geometry imply that the calculated energies should be taken with caution, the obtained values clearly indicate a high degree of strain in the azobenzene skeleton of **4**.

|                     | planar | gas-phase minimum | orthogonal |
|---------------------|--------|-------------------|------------|
| azobenzene          | 0.0    | -                 | +31.5      |
| perfluoroazobenzene | 0.0    | -1.9              | +38.3      |
| 1                   | 0.0    | -2.0              | +39.7      |

**Table 7.2** Calculated molecular energies (kcal mol<sup>-1</sup>), at the B3LYP level, for azobenzene, perfluorobenzene and **1** in three different conformations

It is surprising that the azobenzene skeleton can be twisted into a high-energy conformation *via* a simple and mild room-temperature procedure. Presumably, compounds **3-5** result from an electrophillic substitution of fluorine atoms ortho to an azo group, resulting in the formation of a

new carbon-nitrogen bond and morpholinium fluoride byproduct. This pathway is confirmed by the <sup>19</sup>F NMR spectrum of the reaction mixture involving *cis*-1, which revealed the formation of a signal at 137.5 ppm, consistent with that for a separately prepared sample of morpholinium fluoride (139 ppm, see Appendix 6). We computationally confirmed the likelihood of such a reaction by evaluating the free energy change for the transformation of compound 1 into 4 in the gas phase (**Figure 7.6**). Calculated at the B3LYP level, the free energy change for this reaction is *ca.* -8 kcal mol<sup>-1</sup>. The calculations also revealed the LUMO levels of 1 are largely localised on azo nitrogen atoms, as well as the carbon atoms in *ortho*- and *para*-positions to the azo group (**Figure 7.6**).



**Figure 7.6** Computationally evaluated gas-phase transformation of 1 into 4 (top) and plot of the LUMO level for a molecule of 1, calculated at the B3LYP level (bottom).

Such LUMO distribution is consistent with the observed facile nucleophilic substitution of fluorine atoms *ortho* to the azo moiety. The calculations revealed a similar organisation of the LUMO levels for perfluoroazobenzene, indicating that the observed reactivity is not associated with the presence of the heavy halogen substituent in the *para*-position. A similar result was obtained by the Hecht group<sup>32</sup> in their study of the electronic structure of *trans*-

perfluoroazobenzene, supporting the validity of our results. The distribution of LUMO levels in compound **1** is not significantly different between the idealised planar conformation and the calculated lowest-energy conformation, indicating that the observed nucleophilic substitution reactions are not significantly affected by molecular conformation.<sup>33</sup>

#### 7.5 Conclusions

In summary, we have recognised a simple room-temperature reaction which allows extensive substitution of all four sites ortho to the azo group in perhalogenated azobenzenes. The resulting azobenzenes are highly sterically hindered and exhibit two halogen bond donor and three or four halogen bond acceptor sites. Such distribution of substituents allows for the formation of self-assembled halogen-bonded chain structures in the solid state. Whereas the exploration of molecules capable of self-assembling by way of strong halogen bonds is still in its infancy, the herein presented molecules illustrate an opportunity to expand such studies towards potentially photo-dynamic systems involving the azo chromophore. The ability to readily generate new potentially functional systems capable of halogen bonding is, we believe, one of the most important requirements for the further development of halogen bonding as a concept relevant to a wide range of research areas, including functional materials science, pharmaceuticals and biomolecular studies.<sup>9,34</sup> In contrast to conventional methods<sup>33</sup> for making substituted perfluorobenzene halogen bond donors, which focus on modifying the substituent para to the halogen bond donor atom, the herein observed reactivity leads to the modification of substituents in meta-positions to the halogen bond donor. We are now exploring the synthetic scope of this facile method for derivatising fluorinated azobenzenes.

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#### 7.7 Notes

Experimental details, UV-Vis spectra of 4 and 5 in tetrahydrofuran solution, FTIR spectra, results of thermal and mass spectroscopy and selected <sup>19</sup>F spectra are presented in Appendix 6. Crystallographic data for 3, 4·morpholine and 5·morpholine in CIF format (respective CCDC deposition numbers 1007719-1007721) is available from Cambridge Structural Database.

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## **Appendix 6: Supporting Information for Chapter 7**

### 1. X-ray Diffraction Studies

Single crystals of compounds 3-5 were grown from solutions of either *cis*- or *trans*-1 or -2 in morpholine by slow evaporation. X-ray single crystal diffraction data was obtained on Bruker D8 single-crystal X-ray diffractometer equipped with a Mo $K_{\alpha}$  X-ray source and a graphite monochromator. In all cases multi-scan absorption correction (SADABS) was applied. Structures were solved by direct methods and refined using SHELXL-2014/3 implemented within the WinGX 2013.3 integrated program system. Crystallographic data for all prepared cocrystals has been deposited with the Cambridge Structural Database CCDC deposition numbers 1007719-1007721.

# 2. Infrared Spectroscopy



Figure A6.1 Fourier-transform infrared (FTIR) spectra for: (top) compound 3; (middle) compound 4 and (bottom) compound 5.



3. Combined Thermal (TGA and DSC) Analyses

Figure A6.2 Combined TGA and DSC plots of: (top) compound 3; (middle) 4 · morpholine and (bottom) 5 · morpholine.

### 4. Mass Spectrometry





## 5. UV-Vis Spectroscopy

UV-Vis studies of compounds **4** and **5** were performed on a Cary 300 Bio UV-Vis spectrometer in THF solution at 0.078 ML<sup>-1</sup> for compound **4** 0.065 ML<sup>-1</sup> for compound **5**. Both compounds exhibit nearly identical spectra including a shoulder at 500 nm of coalescing  $\pi$ - $\pi$ \* and n- $\pi$ \* transitions. Nearly identical behaviour was observed in CH<sub>2</sub>Cl<sub>2</sub> and in cyclohexane solutions, indicating the absence of solvatochromism.



Figure A6.4 UV-Vis profiles of: (left) compound 4 and (right ) compound 5 in THF.

## 6. <sup>19</sup>F NMR Spectroscopy

The <sup>19</sup>F NMR spectrum for the reaction between *trans*-1 and morpholine was recorded in a 6:4 respective mixture of morpholine and  $(CD_3)_2CO$ . Spectra of pure compounds 3, 4 and 5 were recorded in CDCl<sub>3</sub> due to solubility limitations.



Figure A6.5 <sup>19</sup>F NMR spectrum of compound 5 in CDCl<sub>3</sub>.



**Figure A6.6** <sup>19</sup>F NMR spectra for the reaction of *trans*-1 and morpholine: (a) solution of morpholinium fluoride in  $(CD_3)_2CO$ ; (b) solution of *trans*-1 in a 6:4 mixture of morpholine and  $(CD_3)_2CO$  after 20 minutes at room temperature and (c) compound 3 in CDCl<sub>3</sub>.



Figure A6.7 <sup>19</sup>F NMR spectrum of compound 5 in CDCl<sub>3</sub>.

#### **Chapter 8: Conclusions and Outlook**

This thesis describes some optical and mechanical behaviour of azobenzene chromophores in crystals. While Chapters 2 and 3 deal with the observation of reversible and irreversible photomechanical effects in azobenzene crystals, the focus gradually shifts towards the design and engineering of crystals with properties optimal for these effects. The results of Chapters 4 and 5 offer a route to better photo-mechanical crystals through cocrystallization-based control of physical properties, crystal packing and morphology. Finally Chapters 6 and 7 reach beyond the initial photo-mechanical efforts and open up new opportunities in the design of dichroic organic cocrystals based on azobenzenes and highlight the unanticipated reactivity of halogenated azobenzenes.

A few key conclusions that rise from the presented contributions are worth reiterating. First and foremost, the results of Chapters 2 and 3 unambiguously demonstrate for the first time the possibility of reversible and irreversible transformations of *trans*- and *cis*-azobenzenes in the crystalline state. This phenomenon was not a straightforward one to predict, as molecules in the crystal lattice are arranged under tight constraints and require a lot of free space to proceed through the sterically demanding isomerization.

Chapter 4 sheds light on this seeming controversy: how could tightly-packed molecules move in a highly constrained environment? A possible answer is by making it less constrained in a process of amorphization. Instead of proceeding through a concerted isomerization of planes of molecules in a single-crystal-to-single-crystal fashion, irradiation by light and isomerization of just some of the chromophores breaks down the crystal lattice and amorphizes the sample. Possessing more free space in the amorphous mixture, other molecules then become free to isomerize, and do so. Differences in density between the crystalline and amorphous states are thus responsible for the bending away from light in photo-mechanical azobenzene crystals. Importantly, the extent of the photo-mechanical motion as well as the required irradiation power can both be controlled by cocrystallization. A choice of the cocrystal partner that will yield the lowest possible crystallographic density to the sample will result in a malleable cocrystal that could be easily shaped by light orders of magnitude less intense than that utilized in the prior investigations. In fact, the crystals move in light of power equivalent to that delivered by a band of just a few tens

of nanometers of the solar spectrum. It is truly remarkable and means that despite their overall modest efficiency, azobenzene photo-mechanical solids can indeed be powered by sunlight.

The results described in Chapter 5 examining photo-mechanical crystals of azobenzene are perhaps of broader interest to the field of crystal engineering than photochemistry. Having recognized a strong supramolecular interaction in crystals of fluorinated *cis*-azobenzenes, we have demonstrated that both crystal structure and morphology for these chromophores could be controlled simultaneously. A strong azo…phenyl stacking permits one to organize such chromophores into 'pringle chip'-like columns ideal for photo-mechanical crystals. Moreover, the activation towards halogen bonding of fluorinated azobenzenes allowed us to organize diverse molecules into defined stacks with control over supramolecular interactions in two out of three dimensions. The utilization of such crystal engineering interactions greatly contributed to the study of photo-mechanical crystals of fluorinated azobenzenes, but its utility should not be limited to this investigation and might find application in the diverse fields of rational design of molecular crystals.

Chapter 6 builds on prior investigations of optical properties of the azobenzene chromophore and transfers it to the crystalline state in a simple and efficient manner. Azobenzene chromophores are highly linearly dichroic, and this property was utilized in a myriad of studies of amorphous and liquid-crystalline materials. Predictable linear organization of azobenzene chromophores in a crystal should thus deliver strongly dichroic single crystals. Using the principles of crystal engineering we demonstrated that using halogen bonding as a supramolecular director. The resulting cocrystals were, as predicted, beautifully dichroic proving the hypothesis. This was the first demonstration of control over optical properties of a crystalline material, a surprising result, considering that some of the first goals of crystal engineering upon its advent over a quarter of a century ago was precisely such control over optical properties of crystals.

Chapter 7 reports the unexpected formation of highly strained morpholine-substituted azobenzene derivatives *via* a mild room temperature reaction. The resulting molecules are bulky, strained, coloured and activated for halogen bonding. So much so, in fact, that the molecules self-assemble into infinite halogen-bonded strings in a single crystal. The reaction allowed for the formation of molecules which are simultaneously halogen bond donors and acceptors, which is a

fairly unusual supramolecular synthon. Moreover, this simple substitution reaction offers a route to preparing families of new azobenzene molecules with a wide range of functionality. In the context of crystal engineering efforts started in Chapters 5 and 6 it could prove a highly useful reaction pathway.

The work described in Chapter 2-7 should no doubt continue. While the significance of most of the described contributions is of rather fundamental character, and as such it is hard to predict specifically what advances will be made in the field of crystal engineering, the photomechanical field is ripe for the next stage — the development of devices. The application for photo-mechanical crystals may come in the field of microfluidics as remotely switchable gates, micro switches in robotic devices or propellers. The possibility of remote actuation by laser light and the absence of electrical components makes photo-mechanical materials ideal for work under water or in biological environments. Fast photo-mechanical motion achievable by some elastomeric materials may someday allow them to hover powered by intermittent irradiation, which will allow for construction of light-powered micrometer-sized drones. Further research of the materials may eventually lead towards the development of ultra-robust samples capable of withstanding hundreds of thousands of switching cycles, comparing to the hundreds of cycles with currently studied materials. While crystals are ideal as study systems, no doubt for most practical applications polymeric or liquid crystalline materials will likely prevail. However, with further advances of crystal engineering completely new and currently unimaginable applications for photo-mechanical crystals may soon spring to light.