In compliance with the Canadian Privacy Legislation some supporting forms may have been removed from this dissertation.

While these forms may be included in the document page count, their removal does not represent any loss of content from the dissertation.

## Sulfur Functionalized Cubane and

### **Related Derivatives**

A thesis submitted to the McGill University in partial fulfillment of the requirements of

the degree of Doctor of Philosophy

By

**Ronny Priefer** 

November

2002

Department of Chemistry

McGill University

Montreal, Quebec, Canada

© Ronny Priefer, 2002



National Library of Canada

Acquisitions and Bibliographic Services

395 Wellington Street Ottawa ON K1A 0N4 Canada Bibliothèque nationale du Canada

Acquisisitons et services bibliographiques

395, rue Wellington Ottawa ON K1A 0N4 Canada

> Your file Votre référence ISBN: 0-612-88561-5 Our file Notre référence ISBN: 0-612-88561-5

The author has granted a nonexclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou aturement reproduits sans son autorisation.

# Canadä

## This thesis is dedicated to my parents

.

Hella and Rudy Priefer

#### ABSTRACT

Chapter one of this thesis reviews some work on cubane, from its initial synthesis by Eaton in 1964, to the recent studies of explosive and medicinal applications. Considering the wide variety of compounds that have been synthesized, it is curious that sulfur functionalized cubane has received virtually no attention.

Chapter two discusses the synthesis of cubanethiol, dicubyl disulfide, and a range of derivatives. Dicubyl disulfide possesses the shortest C-S bond length of any reported molecule where the carbon is sp<sup>3</sup> hybridized. Calculations have confirmed that this apparently results from the high s-character that the external bonds of cubane possess. All four of the stable, oxidized versions of dicubyl disulfide have been prepared, as well as two trityl cubyl polysulfides.

In Chapter three, new synthetic pathways for the synthesis of cubylcarbinol have been established. One key step is the "two-in-one reaction" that performs the reduction of the carboxylic acid, as well as dehalogenation of 4-iodocubanecarboxylic acid using a single reagent to afford cubylcarbinol. This pathway increases the overall yield for obtaining cubylcarbinol, as well as being more economical.

Chapter four describes the work carried out on cubane-containing dialkoxy disulfides. The synthesis of two dialkoxy disulfides from cubylcarbinols was accomplished. The  $S_2$  liberation ability of these species was also investigated, and these represent the first non-benzylic dialkoxy disulfides that deliver trappable  $S_2$ . In addition, a study of the previously unknown rearrangement/oxidation of these molecules to sulfites has been carried out.

ii

In Chapter five, a thorough study of the reactivity of a vinyl cubane compound towards polymerization was performed. The subsequent cage opening and rearrangement to a styrene derivative, to our knowledge, is the first example of this kind known to occur without the assistance of a rhodium catalyst. In addition, cubane-containing norbornene polymers have been successfully synthesized. These represent the first examples of polymers that have a cubane tethered to the polymer backbone. It appears that this type of functionality does not impair solubility, which is the major problem associated with all other attempts to obtain cubane-based polymers.

## RÉSUMÉ

Le premier chapitre de cette thèse retrace l'historique des recherches accomplies jusqu'a ce jour sur le cubane, en débutant par sa synthèse par Eaton (1964) jusqu'aux récentes applications medicales ou comme agent explosif. Une grande varièté de ces molécules a donc été produite cependant, les cubanes soufres n'ont pas recu beaucoup d'attention, ce qui peut paraître surprenant.

Le deuxième chapitre se concentre sur la synthèse de "cubanethiol," de "dicubyl disulfide" et de leurs derivés. On y apprend que la liaison Carbone-Soufre des "dicubyl disulfide" s'est revelée être la liaison la plus courte parmi toutes les molécules étudiées possedant une hybridization sp<sup>3</sup> pour le carbone. Des calculs ont confirmé que cette observation est en fait liée au charactère "s" des liaisons externes du cubane. Les quatre formes stables et oxyde du "dicubyl disulfide" ont donc été préparées, ainsi que deux "trityl cubyl polysulfides."

Le troisième chapitre présente les nouvelles voies de synthèse de "carbinolcubyl". Une des étapes clefs est la réduction de la fonction acide du "4-iodocubane carboxylic acid" associé a une deshalogenation de la molécule, et ceci en une étape unique pour produire un "carbinolcubyl." Cette méthode beaucoup plus économique a ainsi permit d'améliorer le rendement.

Le quatrième chapitre décrit la synthèse de cubanes contenant des fonctions dialkoxy disulfide, et en particulier, la synthèse de deux dialkoxy disulfides derivés de "cubylcarbinols." La capacité de ces molécules a libérer  $S_2$  a également été étudiée et elles representent les premieres molecules dialkoxy disulfides non benziliques, connues pour libérer  $S_2$ . Des recherches ont enfin été effectuées sur le réarrangement peu connu de ces molécules en sulfites.

Le cinquième chapitre traite enfin d'une étude approfondie sur la réactivite des cubane vinyl par rapport a leur polymèrisation. La conséquence de cette polymèrisation a été l'ouverture de la cage du cubane suivit par un réarrangement en un derivé styrènique. Ceci représente à notre avis le première exemple de ce type de réarrangement, en absence de catalyseur rhodium. Un polymère de norbornène comprenant des cubanes a également été preparé, ce qui représente un première exemple d'un polymère portant des cubane liée a la stucture principale. Comme attendu, le polymère formé est apparu plus soluble que ne le sont les autres polymères de cubanes.

۷

### FORWARD

Some of the work that was carried out in Chapter 2 was performed at Emory University, Atlanta, Georgia, by Drs. Aiming Sun, Shaoxiong Wu, and James P. Snyder. All the computational and low temperature NMR studies were performed by the aforementioned people.

#### ACKNOWLEDGEMENTS

The composition of this section of the thesis was by far the most difficult. This was not because it was difficult to find people to thank, but because, unlike the rest of the thesis, where it consists mostly of stated facts and reasoning results, this section deals with some of the emotional impact certain individuals contributed during my tenure at McGill University.

First and foremost I must acknowledge my parents. Without them I would not be the person I am today. They instilled values in me as well as a drive to succeed. They also showed me that no matter how difficult life may be, it is important to go on, and most importantly, to do it smiling. What good is life if you are constantly upset about it? For these reasons, and for more than words can say, I thank them.

To my brother, Ricky, and my sister, Conny, I thank them for being wonderful siblings. Although it is inevitable not to have fights, ours were tame and their love has been a part of me, even at these great distances.

I would like to give an especially large thank-you to my fiancé. Susan has been a light in my life. When things did affect me enough for me to stop smiling, she was there for me. Her selfless caring and undying love are a great inspiration to me. She helped motivate me, and without her I am confident that I would not have submitted when I did.

To describe the supervision of Dr. Harpp in anything less than one hundred pages is a crime, which unfortunately I am now pleading guilty to. During my career at McGill, Dr. Harpp has been the most inspirational person in my life. When I first arrived in Montreal, a young man from a small town, Dr. Harpp showed me a courteousness that I was not expecting to receive from anyone in the big city. I clearly remember our first conversation. Before talking about the research, he asked about me; my past, my plans, my hobbies. We talked and joked. He showed in the first five minutes of talking with him, that my career at McGill should be much more than just chemistry. Don't get me wrong, it was not all jokes, there was also the chemistry. This man has a love for chemistry that is excreted through his skin. Talking with him, and sensing his excitement about his chemistry, is quite contagious. In our many discussions over the years, he has supplied me with excellent advice and most importantly, has treated me with respect. I will be forever grateful for your guidance and inspiration.

In addition to the excellent supervision of Dr. Harpp, I was also honoured to have an association with Dr. Farrell. Similar to Dr. Harpp, Dr. Farrell clearly enjoys chemistry and was more than willing to discuss any enquires that I had. His arrivals in the lab were looked upon as moments when questions could be answered, as well as some good oldfashion ribbing. Over the years we have become more comfortable with each other, and thus I have been able to discuss personal matters with him. I would like to acknowledge Dr. Farrell, my friend.

Dr. David Llewellyn is an inspiration to me in more ways than he will ever know. I can fairly confidently state that if Dave had not helped me get that first lab job back at UNBC, I would not be writing an acknowledgement section of a Ph. D. thesis. I thank him for this and being the best friend a person could ever hope to have. I also wish to thank his wonderful wife, Elysia. Her caring nature and bubbly presence helped make the initial transition to life in Montreal easier. Her concern about my well-being showed me what true friends are for.

viii

I wish to thank Ben Malcolm, whose excellent teaching ability caused me to go from hating chemistry, to truly enjoying it, and Dr. Guy Plourde, who not only inspired me to focus on organic chemistry, but to also pursue graduate work.

Cathy Robson, her friendship has been an important part of my life even though we are separated by thousands of kilometers. Her willingness to listen to me talk about my chemistry, even when she had no idea what I was talking about. Her happiness in her life has inspired me to attempt to try to obtain the specialness that she and her family possess.

Brad and Marta, back in Prince George, have special meaning to me.

I wish to thank the members of Lab 240, in particular, I would like to thank Pierre. His friendship during the time that we shared the lab will be something that I will cherish forever. Anj's subtle humor, and fountain of knowledge added to the pleasure I received from this lab. Imad's summer visits were moments of great enjoyment and laughter.

To Sophie, Fabiola, Marie-Therese, Julie, Janet, Emily, and Wan, whom I had the great honour of sharing a lab with, and in many cases teach.

Dr. James Gleason supplied me with some excellent chemistry advice and I thank him for that. I would also like to thank him for showing me that to become a caring, well-rounded person, it is very important to maintain a life outside of chemistry.

To the members of Dr. Gleason's lab, in particular, Diane, Andrew, Alain, Jeff, and James who supplied me with entertainment as well as stimulating chemistry conversations as well as allowing me to "borrow" some chemicals. I wish to especially thank Andrew, Alain, and Nicholas for the translation of the abstract. To Drs. Anne-Marie Lebuis, and Francine Bélanger-Gariépy, for running the Xray structures of many of my compounds. Quantitative Technologies Inc. for elemental analysis. To Drs. Fred Morin and Paul Xia, for assistance with the NMR instruments. Drs. Nadim Saade, Orvil Mamer, and Gaston Boulay for obtaining the mass spec. data that I needed. In particular, Nadim for running the high-res. M.S. of my smelly cubanethiol with no advance notice. I will be forever in his debt.

I sincerely thank Renée Charron, Chantal Marotte, Carol Brown, Sandra Aerssen, Fay Nurse, and Paulette Henault for the formidable jobs they perform, which made my stay easier. Even though Renée may feel the wrath of the students when they do not get paid on time, she maintains a smile. To Carol ("whazz upp") Brown; I have said too much already!

Drs. Aiming Sun, Shaoxiong Wu, and James P. Snyder of Emory University, I thank for performing the lower temperature NMR, and computation experiments.

I would like to thank Dr. Hay and Zaza for lengthy discussions concerning polymerizations, and Dr. Sleiman's group for supplying the Grubb's catalyst. In addition, I wish to acknowledge Owen for running the GPC's of my polymers and Dr. Antisar Hlil for carrying out the TGA and DSC.

Last, but certainly not least, I wish to thank all my friends that I have acquired during my time at McGill. Sophie, Julie, Janet, Marie-Therese, Pierre, Wan, Diane, Alain, Andrew, Jeff, Claudia, Shane, Lee, Stephanie, Jason, Ragiv, Francois, and especially Dr. Catherine Edgar. I would like to thank my friend, Eddie Myers, who dealt with my idiosyncrasies and hospital visits with great determination and grit, and truly was an excellent roommate.

Х

## TABLE OF CONTENTS

CHAPT	ER ONE: INTRODUCTION	1
1 - 1	CUBANE	2
1-2	NITROCUBANES	4
1-3	CUBYLAMINES	5
1-4	ORTHO LITHIATION	7
1-5	CUBYL GRIGNARD REAGENTS	9
1-6	CUBYL CATION	11
1-7	CUBYL RADICAL	13
1-8	CUBYL ANION	16
1-9	CUBENE	19
1-10	CAGE OPENING AND REARRANGEMENT WITH METALS	21
1-11	CUBANOL	23
1-12	REFERENCES	25
CHAP	TER TWO: DICUBYL DISULFIDE AND RELATED	29
2-1	INTRODUCTION	30
2-2	SYNTHESIS OF CUBANETHIOL AND DICUBYL DISULFIDE	31
2-3	X-RAY ANALYSIS OF <i>S</i> -CUBYL- <i>N</i> , <i>N</i> - DIMETHYLDITHIOCARBAMATE ( <b>2-7</b> )	33
2-4	X-RAY ANALYSIS OF DICUBYL DISULFIDE (2-2)	34

2-5	CALCULATIONS OF THE C-S BOND LENGTH OF DICUBYL DISULFIDE	36
2-6	CALCULATION OF THE ROTATIONAL BARRIER OF DICUBYL DISULFIDE	37
2-7	OXIDATION OF DICUBYL DISULFIDE	40
2-8	ATTEMPTED SULFUR INSERTION INTO DICUBYL DISULFIDE	42
2-9	EXPERIMENTAL	47
2-10	REFERENCES	59
CHAPT	ER THREE: EFFECTIVE SYNTHETIC ROUTES TO	62
	CUBYLCARBINOL DERIVATIVES	
3-1	INTRODUCTION	63
3-2	SYNTHESIS OF CUBYLCARBINOL AND COMPARISON OF ROUTES	64
3-3	EXPERIMENTAL	67
3-4	REFERENCES	74
CHAPT	ER FOUR: DIALKOXY DISULFIDES FROM	76
	CUBYLCARBINOLS	
4-1	INTRODUCTION	77
4-2	SYNTHESIS AND STUDIES ON DIALKOXY DISULFIDES DERIVED FROM CUBYL CARBINOLS	78
4-3	EXPERIMENTAL	85
4-4	REFERENCES	91

CI	IAPTI	ER FIVE: SYNTHESIS OF CUBANE-CONTAINING	93
		POLYMERS	
	5-1	INTRODUCTION	94
	5-2	SYNTHESIS OF VINYL CUBANE	98
	5-3	ATTEMPTED CATIONIC POLYMERIZATION	99
	5-4	VINYL CUBANE REARRANGEMENT	101
	5-5	ATTEMPTED ANIONIC POLYMERIZATION	104
	5-6	ATTEMPTED FREE RADICAL POLYMERIZATION	105
	5-7	ATTEMPTED PALLADIUM-CATALYZED CO-POLYMERIZATION	107
	6-1	ATTEMPTED CYCLOADDITION OF VINYL	109
		CUBANE WITH CYCLOPENTADIENE	
	6-2	SYNTHESIS OF CUBANE CONTAINING NORBORNENE MONOMERS	110
	6-3	SYNTHESIS OF CUBANE CONTAINING NORBORNENE POLYMERS	111
	5-11	EXPERIMENTAL	115
	5-12	REFERENCES	124
CI	HAPT	ER SIX: CONCLUSIONS, CONTRIBUTIONS TO ORIGINAL KNOWLEDGE, AND SUGGESTIONS FOR FUTURE WORK	128
	6-1	CONCLUSIONS, CONTRIBUTIONS TO ORIGINAL KNOWLEDGE	129
	6-2	FUTURE WORK	131

APPENDIXES

Appendix A: X-RAY STRUCTURE OF S-CUBYL-N,N- DIMETHYLDITHIOCARBAMATE (2-7)	132
Appendix B: X-RAY STRUCTURE OF DICUBYL DISULFIDE (2-2)	145
Appendix C: X-RAY STRUCTURE OF <i>BIS</i> -(4- IODOCUBYLMETHYL)-DIALKOXY DISULFIDE (4-5)	158
Appendix D: X-RAY STRUCTURE OF <i>BIS</i> - CUBYLMETHYLSULFITE (4-12)	173

Scheme 1-1: Modern day synthetic pathway for the formation of cubane 1-1	2
Scheme 1-2: Explosive nitrated molecules	5
Scheme 1-3: Adamantane and cubane-based anti-viral agents	6
Scheme 1-4: Enzyme mediated cage opening and deactivation	7
Scheme 1-5: Comparison of benzamide and cubylamide for <i>ortho</i> lithiation	8
Scheme 1-6: Transmetallation of <i>ortho</i> lithiated cubane for halogenation	9
Scheme 1-7: Transmetallation with magnesium for carboxylation of cubane	10
Scheme 1-8: Ortho magnesiation for synthesis of cubane derivatives and pyromellitic	11
Scheme 1-9: Reactions that are proposed to go through a cubyl cation intermediate	12
Scheme 1-10: Formation of dihalogenated cubane derivatives via Barton's decarboxylation	14
Scheme 1-11: Dehalogenated cubane via free radical mechanism	14
Scheme 1-12: Halogenation of cubane via a phase transfer system	15
Scheme 1-13: Mechanism of the Moriarty reaction from cubane carboxylic acid (1-14) to iodocubane (1-15)	16
Scheme 1-14: Synthetic utility of cubylanion from iodocubane (1-15)	18

Scheme 1-16: Synthetic pathways that require cubene, 1-17, as 20 a reactive intermediate

Scheme 1-15: Formation of cubyl anion in the gas phase using SORI

Scheme 1-17: Cubene, 1-17, trapping via a Diels-Alder reaction

19

21

Scheme 1-18: Mechanism for cubane, 1-1, rearrangement to cuneane, 1-19, with Ag <sup>+</sup>	22
Scheme 1-19: Mechanism for cubane, 1-1, opening to syn-tricyclooctadiene, 1-20, with Rh(I)	23
Scheme 1-20: Proposed mechanism for cage opening of 4-methylcubanol, 1-22 to 1-25	23
Scheme 2-1: Synthetic path towards cubanethiol (2-1) and dicubyl disulfide (2-2)	32
Scheme 2-2: Synthetic scheme for the oxidation of dicubyl disulfide (2-2)	40
Scheme 2-3: Intramolecular rearrangement of disulfinate (2-8) to thiosulfonate (2-9)	41
Scheme 2-4: Possible intramolecular H-bonding of dicubyl vic-disulfone (2-11)	42
Scheme 2-5: Known method for formation of polysulfides from disulfides	43
Scheme 2-6: Proposed mechanism for the formation of dicubyl tetrasulfide (2-18)	44
Scheme 2-7: Series of target trityl-cubyl polysulfides	45
Scheme 2-8: Mechanism for the attack of dicubyl disulfide (2-2) onto trityl sulfenyl chloride (2-13)	46
Scheme 3-1: Synthetic pathways towards cubylcarbinol, 3-1	65
Scheme 4-1: Intramolecular fragmentation of benzylic dialkoxy disulfides	77
Scheme 4-2: Synthetic pathway of dialkoxy disulfides from cubylcarbinols	78
Scheme 4-3: Proposed photolytic fragmentation of dialkoxy disulfides in an oxygen environment	83
Scheme 4-4: Proposed photolytic fragmentation of dialkoxy disulfides under nitrogen atmosphere	84

Scheme 5-1:	Metathesis polymerization of 1,4-bis(homoallyl)cubane (5-1)	94
Scheme 5-2:	Polycondensation of cubane-1,4-dicarboxylic acid (5-2) and a variety of aromatic diamines (5-4 to 5-7)	95
Scheme 5-3:	Polycondensation of cubane-1,4-dicarboxylic acid (5-2) and 1,4-diaminocubane (5-8) with a variety of diacids and diamines	97
Scheme 5-4:	Synthetic scheme for the synthesis of 4-iodo-1-vinylcubane (5-15)	99
Scheme 5-5:	Proposed pathway for cationic polymerization	100
Scheme 5-6:	r Possible mechanism for the rearrangement of 4-iodo-1-vinylcubane ( <b>5-15</b> ) to 4-vinyl- <i>trans</i> -β-iodostyrene ( <b>5-18</b> ) with light	102
Scheme 5-7	<ul> <li>Possible mechanism for the rearrangement of</li> <li>4-iodo-1-vinylcubane (5-15) to 4-vinyl-<i>trans</i>-β-iodostyrene</li> <li>(5-18) going through a zwitterion</li> </ul>	103
Scheme 5-8	Proposed pathway for anionic polymerization	104
Scheme 5-9	Proposed pathway for free radical polymerization	106
Scheme 5-1	0: Mechanism for co-polymerization of vinyl and carbon monoxide with Pd(Me)(bpy)(BARF) in acetonitrile	108
Scheme 5-1	1: Proposed synthetic pathway towards cubane containing-norbornene based polymer, <b>5-20</b>	109
Scheme 5-12	2: Synthesis of two cubane derivatives attached to norbornene <i>via</i> an ester linkage	111
Scheme 5-1	3: Commercially available ROMP catalysts	112
Scheme 5-1	4: Mechanism for ring opening metathesis polymerization (ROMP)	113
Scheme 5-1	5: Successful synthesis of cubane-containing norbornene-based polymers	114

xvii

## LIST OF FIGURES

Figure 2-1: X-ray structure of S-cubyl-N,N- dimethyldithiocarbamate (2-7)	34
Figure 2-2: X-ray structure of dicubyl disulfide (2-2)	35
Figure 2-3: Schematic representation of $LP_S \rightarrow \sigma^*(C-C)$ bonding- antibonding interaction of dicubyl disulfide (2-2)	39
Figure 4-1: X-ray structure of <i>bis</i> -(4-iodocubylmethyl)-dialkoxy disulfide (4-5)	79
Figure 4-2: X-ray structure of <i>bis</i> -cubylmethylsulfite (4-12)	81

xviii

## LIST OF TABLES

Table 1-1: List of physical parameters of cubane 1-1	3
Table 1-2: Experimental and calculated rates of solvolysis           for quaternary tosylates	13
Table 2-1: Experimental and calculated bond lengths for a series of methyl disulfides	36
Table 2-2: Calculated torsional barrier for series of symmetric disulfides	38
Table 4-1: S <sub>2</sub> trapping by dienes	80

## LIST OF ABBREVIATIONS

AIBN	2,2'-azobisisobutyronitrile
BARF	tetrakis(3,5-bis(trifluoromethyl)phenyl borane
BH <sub>3</sub> .SMe <sub>2</sub>	borane-methyl sulfide complex
bpy	2,2'-dipyridyl
$(C_4H_9)_3SnD$	tri( <i>n</i> -butyl)tin deuteride
$(C_4H_9)_3SnH$	tri( <i>n</i> -butyl)tin hydride
C <sub>8</sub> H <sub>7</sub>	cubyl
ca.	approximately
Ca(OCl) <sub>2</sub>	calcium hypochlorite
(COCl) <sub>2</sub>	oxalyl chloride
conc.	concentrated
cubane	pentacyclo[4.2.0.0 <sup>2,5</sup> .0 <sup>3,8</sup> .0 <sup>4,7</sup> ]octane
DFT	density functional theory
DMAP	4-dimethylaminopyridine
DPMP	diphenylmethylpotassium
EPR	electron paramagnetic resonance
eq.	equivalents
EtMgBr	ethylmagnesium bromide
Fl	flavin
GPC	gel permeation chromatography
IBDA	iodobenzene diacetate

IR	infrared
kcal	kilocalorie
kJ	kilojoule
LAH	lithium aluminum hydride
LDBB	lithium di-tert-butyl-di-benzylide
LiTMP	lithium tetramethylpiperidide
LPs	lone pair of electron on sulfur
MAO-B	monoamine oxidase-B
mCPBA	meta-chloroperoxybenzoic acid
Me-S-S-C <sub>8</sub> H <sub>7</sub>	cubyl methyl disulfide
Me-S-S-Me	dimethyl disulfide
Me-S-S-t-Bu	tert-butyl methyl disulfide
MHz	megahertz
mmol	millimole
M <sub>n</sub>	number average molecular weight
MS	mass spectrometry
NBO	natural bond orbital
NMR	nuclear magnetic resonance
NOR	norbornadiene
PDI	polydispersity index
Ph <sub>3</sub> CSSCPh <sub>3</sub>	ditrityl disulfide
ROMP	ring opening metathesis polymerization
S <sub>2</sub> Cl <sub>2</sub>	sulfur monochloride

xxi

satd.	saturated
SET	single electron transfer
SORI	sustained off-resonance irradiation
t-BuSH	tert-butylthiol
t-BuLi	tert-butyllithium
(TMP) <sub>2</sub> Mg	bis(tetramethylpiperidide) magnesium
ТМРН	2,2,6,6-tetramethylpiperdine
TMPMgBr	tetramethylpiperidide magnesium bromide
TMTD	tetramethylthiuram disulfide
TNT	trinitrotoluene
UV	ultraviolet

xxii

#### GENERAL EXPERIMENTAL

All commercial reagents were obtained from Aldrich Chemical Company and tested by <sup>1</sup>H NMR for purity. Solid reagents were recrystallized when needed and distillation was performed on liquid reagents when required. THF and benzene were distilled over sodium and benzophenone;  $CH_2Cl_2$  and  $Et_3N$  over calcium hydride.

Thin Layer Chromatography (TLC) was performed on 0.25mm Silicycle silica gel plates with aluminum backing and visualized using UV light, iodine absorbed onto silica gel, followed by a 10% aqueous sulfuric acid solution of ammonium molybdate-cerium sulfate developing dip. Column chromatography was carried out on Silicycle (230-400 mesh) using flash chromatography conditions.

Melting points were obtained using open end capillaries on Gallenkamp melting point apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded Varian Mercury 300 and 400 MHz. Chemical shifts are reported in parts per million (ppm) and referenced to the solvent peak noted.

Infrared spectra were recorded on a Nicolet Model 6000 FT-IR spectrometer.

## **CHAPTER 1**

## Introduction

#### **1-1 CUBANE**

The first successful synthesis of pentacyclo[ $4.2.0.0^{2.5}.0^{3.8}.0^{4.7}$ ]octane, more commonly referred to as cubane (1-1), was accomplished in 1964 by Eaton and Cole at the University of Chicago.<sup>1</sup> Although almost 40 years have passed since the initial synthesis, the operative synthetic scheme has remained much the same.<sup>2</sup> The procedure that is currently used is displayed below (**Scheme 1-1**).<sup>3</sup> The process can be described in four key steps. The initial Diels-Alder reaction of two identical cyclopentadiene derivatives, an intramolecular 2 + 2 cycloaddition, a Favorskii rearrangement, which completely closes the cage (1-2), and finally the decarboxylation.



Scheme 1-1: Modern day synthetic pathway for the formation of cubane 1-1

This process delivers cubane (1-1) as a white solid that has a melting point of 130-131°C and a boiling point of 133°C. This very narrow range between melting and boiling point, as well as its symmetry (D<sub>4</sub>) causes cubane to sublime quite easily, even at room temperature.<sup>1</sup> It has a density of 1.29 g/mL, which is the highest for any reported simple saturated hydrocarbon.<sup>4</sup>

To obtain access to a wider range of cubane derivatives, the last step of decarboxylation is not carried out, thus leaving the cubane 1,4-dicarboxylic acid (1-2) as a useful starting step for further chemistry. Currently, dimethyl-1,4-cubanedicarboxylate is commercially available from Sigma-Aldrich.

At first glance it may appear that cubane and its derivatives are extremely unstable due to the high degree of angle stain that each carbon-to-carbon bond endures; however, looks can sometimes be deceiving. Although there is considerable potential energy held within the cubane molecule (166 kcal/mol),<sup>5</sup> most derivatives are in fact rather stable with some interesting qualities that have sparked interest in both the medicinal<sup>6-10</sup> and explosive<sup>11-20</sup> areas. Listed below are some highlights of the physical properties of cubane, **1-1** (**Table 1-1**).<sup>2</sup>

C-C distance	1.5727 <u>+</u> 0.0019Å	Boiling point	~133 °C
C-H distance	1.118 <u>+</u> 0.008Å	Melting point	130-131 °C
Colour	transparent	Solubility	~18 wt%(hexane)
Toxicity	nontoxic	Heat of formation	+144 kcal/mol
Stability	inert to light, water, air	Strain energy	+166 kcal/mol
Decomposition	>220 °C	Density	1.29 g/mL
Vapour pressure	1.1 mm (25 °C)		

Table 1-1: List of physical parameters of cubane 1-1

3

#### **1-2 NITROCUBANES**

Although cubane derivatives are considered a relatively stable class of molecules, there are exceptions. One of these is the series of nitrocubanes. Perhaps not surprisingly, these are a very explosive class of molecules. Similar to trinitrotoluene (TNT, 1-3), the nitro substituents provide a source of energy that can be liberated to yield gases and a copious amount of energy. In the case of cubane, it is not difficult to imagine that with all eight corners of the cube nitrated [octanitrocubane (1-4)], a little "push," causes not only the release of a large amount of gas, as is the case with TNT, but there is also the high strain energy release associated with the opening of the cubane cage. The velocity of detonation for octanitrocubane has been calculated to be 10.1 mm/ms<sup>19</sup> compared to hexanitrobenzene (1-5) that has a velocity of 9.4 mm/ms.<sup>19</sup>

$$C_8(NO_2)_8 \longrightarrow 8CO_2 + 4N_2$$

Thus, over the past thirty years considerable research has been carried out in the field of nitrocubane chemistry. This culminated in the early part of 2000 with a publication by Eaton, Zhang, and Gilardi, entitled "Hepta- and Octanitrocubanes."<sup>17</sup> It is interesting that these molecules require more than a little "push" to set them off. Octanitrocubane (1-4) has been shown to be very shock *ins*ensitive and is set off only by the addition of a base. It is however considered the most powerful non-nuclear explosive known, with a heat of formation of 74 kJ per (CNO<sub>2</sub>)-mol, which can be compared to 33 kJ per (CNO<sub>2</sub>)-mol for hexanitrobenzene (1-5).<sup>20</sup>



Scheme 1-2: Explosive nitrated molecules

#### **1-3 CUBYLAMINES**

It is curious that one molecule can be derivatized to have explosive power, but when modified differently, can also be useful for medicinal applications. One cubane functionality that has attracted attention in the field of medicine is the amino group. Studies have shown that cubylamines (1-6) are virally active.<sup>7</sup> Notably, the reactivity of these molecules varies, depending upon what other substituents are present on the cube. The viral activity of this class of cubane derivatives comes as no surprise considering that the first anti-viral drug on the market was SYMMETREL<sup>®</sup>, which is the commercial name for adamantylamine (1-7). One aspect of 1-7 that allows it to be virally active is the high lipophilicity that the adamantane unit provides. Cubane derivatives of this type are analogous to their counterpart in adamantane, since they also possess a large hydrophobic cage and thus it is suspected that this may contribute to their ability to be virally active. Of the active derivatives, *N*,*N*-di-*t*-butylamido-4-cyano-2,6-dipivalylcubane, 1-8, has shown the most viral activity.<sup>7</sup>



Scheme 1-3: Adamantane and cubane-based anti-viral agents

If an amino group is separated from the cubane cage by a single carbon linker, the molecule becomes highly enzymatically active.<sup>6,9</sup> (Aminomethyl)cubane (1-9) similar to (aminomethyl)cyclopropane, reacts well with the MAO-B enzyme. This enzyme is disease.<sup>21</sup> known involved in Parkinson's to be However, unlike (aminomethyl)cyclopropane, cube, 1-9, can ring-open and irreversibly inactivates the MAO-B enzyme.<sup>6,9</sup> As illustrated below (Scheme 1-4), the cage of cube, 1-9, opens and thus forms a radical which can no longer be stabilized by the neighboring amino group. It is postulated that, unlike cyclopropane where there is only one possible orbital overlap for this ring opening (and within the enzyme's active site this may not be permitted), there are three such possibilities for cubane. Similar to the cyclopropane, analogue the aldehyde (1-10) was detected, which implies that not all of the (aminomethyl)cubane (1-9) undergoes ring opening. However, for those molecules that do undergo ring opening, there is complete inactivation of the enzyme.<sup>6,9</sup>



Scheme 1-4: Enzyme mediated cage opening and deactivation

#### **1-4 ORTHO LITHIATION**

As shown above with both octanitrocubane (1-4) and N,N-di-*t*-butylamido-4cyano-2,6-dipivalylcubane (1-8), cubane derivatives with substituents on positions other than *ipso* and *para*<sup>22</sup> are of interest. Eaton however devised a novel method that has been shown to be invaluable in the derivatization of cubane compounds.

Meyes, Beck, Snieckus, and others have done substantial work on *ortho* lithiation.<sup>23,24</sup> The principle of this technique is illustrated below (Scheme 1-5). The amide substituent on arenes coupled with the high s-character of the C-H bonds, allows a

lithiating agent (*e.g.* lithium tetramethylpiperidide (LiTMP)) to extract the *ortho* proton (Scheme 1-5). The cubane system has shown very similar results. When cubane carries an amide substituent, an *ortho* proton can be extracted with LiTMP.<sup>25</sup> This behaviour is believed to be due to the high s-character of the C-H bond. Cubane's external C-H bond has been shown to have ~31% s-character.<sup>26</sup> This can be compared to 25% for a simple alkane and 33% for an aromatic hydrogen.



Scheme 1-5: Comparison of benzamide and cubylamide for ortho lithiation

Unfortunately, *ortho* lithiation proceeds in only 3% yield. The equilibrium between the protonated and lithiated form strongly lies toward the former.<sup>25</sup> This problem was circumvented by transmetallation.<sup>18</sup> When a stoichiometric amount of mercuric chloride (HgCl<sub>2</sub>) was added to the mixture of the cubylamide with LiTMP, the lithium compound which was initially formed was mercuriated, which drove the reaction to completion.<sup>25</sup> The mercuriated cubane compound could then be halogenated with I<sub>2</sub>, (Scheme 1-6) and this derivative has many uses as will be discussed in Section 1-8.<sup>27-30</sup>



Scheme 1-6: Transmetallation of ortho lithiated cubane for halogenation

In addition to transmetallation with mercury, Eaton and others have shown that this can be performed with zinc, silicon, tin,<sup>31</sup> and most importantly, magnesium.<sup>32</sup>

#### **1-5 CUBYL GRIGNARD REAGENTS**

As illustrated above, *ortho* lithiation followed by transmetallation affords a key intermediate to perform additional reactions. Bashir-Hashemi was the first to introduce transmetallation with magnesium.<sup>32</sup> An example of the conversion of a disubstituted cubane system to a tetrasubstituted derivative by use of *ortho* lithiation followed by transmetallation with magnesium bromide (MgBr<sub>2</sub>) is shown in **Scheme 1-7**.<sup>32</sup>


Scheme 1-7: Transmetallation with magnesium for carboxylation of cubane

Expanding on this work, Eaton developed a new system that has shown useful synthetic utility both within and without the realm of cubane chemistry.<sup>33,34</sup> By reacting 2,2,6,6-tetramethylpiperidine (TMPH) with one equivalent of ethylmagnesium bromide (EtMgBr), the Hauser base, tetramethylpiperidide magnesium bromide (TMPMgBr), (in a mixture with bis(tetramethylpiperidide) magnesium ((TMP)<sub>2</sub>Mg)) is formed. These reagents can be used directly for *ortho* magnesiation.<sup>33,35</sup> If the electrophile of choice is carbon dioxide, the acid can be formed (**Scheme 1-8**). This has also been shown to be useful in the synthesis of pyromellitic acid (**1-11**).<sup>33</sup>



Scheme 1-8: Ortho magnesiation for synthesis of cubane derivatives and pyromellitic acid (1-11)

## **1-6 CUBYL CATION**

Of the many unusual cubane structures that have been discovered over the past forty years, one of the most unexpected is the cubyl cation. One would anticipate that this species would be too unstable to even be a reactive intermediate. The geometry is far from flat (sp<sup>2</sup>), as is expected for a cation; the exocyclic bonds of cubane are high in scharacter;<sup>26</sup> and finally, any stabilization due to hyperconjugation would need to pass through a cubene-type intermediate. All of these constraints would suggest that the cubyl cation is an "impossibility." However, as cubane chemistry has illustrated in the past, it is customary to expect the unexpected.

Ab initio calculations have suggested that the cubyl cation would be  $\sim$ 5 kcal/mol higher in energy than 1-norbornyl cation and  $\sim$ 20 kcal/mol higher in energy than the *tert*-

butyl cation.<sup>36</sup> However, many reactions have shown that the cubyl cation is in fact a very likely intermediate (Scheme 1-9).<sup>37-39</sup>



Scheme 1-9: Reactions that are proposed to go through a cubyl cation intermediate

The above reactions, although appearing to go through a cation intermediate, do not eliminate the possibility that there is an intramolecular rearrangement. The most compelling evidence that cubyl cations are acceptable intermediates was obtained from solvolysis experiments.<sup>38,39</sup> When cubyl triflate (1-12) was stirred in pure, dry methanol at 70°C, complete conversion to the cubyl methyl ether (1-13) was obtained in 30 minutes, with no rearrangement.<sup>38,39</sup> When the same reaction was carried out using 1-norbornyl triflate, after 10 days at 70°C, there is no noticeable solvolysis.<sup>37,40</sup>

Below is a list of the solvolysis rates of various tertiary tosylates. (Table 1-2)<sup>39</sup> It is clear that for all except the cubane tosylate, experimental and calculated values are

close. This difference was explained by the fact that the C-C bonds of cubane have high p-character compared to the other compounds listed in the **Table 1-2**, and thus could possibly donate electron density towards the cationic site. *Ab initio* calculations by Borden have suggested that the positive charge in the cubyl cation is delocalized onto *ortho* and *para* positions.<sup>36</sup> This conclusion was experimentally supported whereby the solvolysis reactions were performed on cubane tosylates with electron-withdrawing groups on the *para* position.<sup>38</sup> As expected, the rate of solvolysis decreased. However, the rates were greatly increased when the *para* position was substituted with a  $\sigma$  donor, such as trimethystannyl or trimethylsilyl groups.<sup>39</sup>

Tosylate	Calculated	Experimental
<i>tert</i> -butyl	1	1
1-adamantyl	10 <sup>-4</sup>	10 <sup>-3</sup>
1-bicyclo[2.2.2]octyl	10 <sup>-8</sup>	10-7
1-norbornyl	10 <sup>-14</sup>	10 <sup>-13</sup>
cubyl	<10 <sup>-25</sup>	10 <sup>-10</sup>

Table 1-2: Experimental and calculated rates of solvolysis for quaternary tosylates

### 1-7 CUBYL RADICAL

It is not difficult to predict that if the cubyl cation can exist, then the cubyl radical is also a reasonable intermediate. The formation of the cubyl radical, as well as its uses, have been reported upon since the initial papers by Eaton in 1964.<sup>1</sup> The final decarboxylation step in his initial synthesis requires the intermediacy of a cubyl radical intermediate, this decarboxylation having been carried out using a *tert*-butyl perester. Presently, the most efficient technique for decarboxylation is the Barton method.<sup>2</sup> This

process can be used in many more ways than conversion of an acid to a hydrocarbon. Della has employed this procedure for the conversion of a cubane carboxylic acid to dihalogenated cubanes (**Scheme 1-10**).<sup>28</sup> In addition, Della has shown that free-radical reduction of cubane bromides to hydrocarbons can be performed using tri(*n*-butyl)tin hydride  $[(C_4H_9)_3SnH]$  with 2,2'-azobisisobutyronitrile (AIBN) (**Scheme 1-11**).<sup>41</sup> This type of reaction has been shown to proceed *via* radical intermediates.



(a) SOCl<sub>2</sub> (b) C<sub>5</sub>H<sub>4</sub>NSONa, DMAP (c) CF<sub>3</sub>CH<sub>2</sub>I,  $h\nu$  (d) CF<sub>3</sub>CHClBr,  $h\nu$  (e) CF<sub>3</sub>CCl<sub>3</sub>,  $h\nu$ 

Scheme 1-10: Formation of dihalogenated cubane derivatives *via* Barton's decarboxylation



Scheme 1-11: Dehalogenated cubane via free radical mechanism

Cubane (1-1) will also undergo monohalogenation under phase-transfer conditions (Scheme 1-12).<sup>42</sup> Schreiner has performed *ab initio* calculations that show that, energetically, the formation of the cubyl radical is favoured over the cage opening.<sup>42</sup>



Scheme 1-12: Halogenation of cubane via a phase transfer system

Yet another reaction in which a cubyl radical intermediate is assumed is iodinative decarboxylation. This method, although yielding the same product as that with Barton's iododecarboxylation,<sup>28</sup> employs hypervalent iodine. This procedure, usually known as the Moriarty reaction, employs the reagents iodobenzene diacetate (IBDA) and I<sub>2</sub>; although this reaction was originally reported by Suarez,<sup>43</sup> extensive work by Moriarty has associated his name with the reaction. The proposed mechanism for the conversion of cubane carboxylic acid (1-14) to iodocubane (1-15) is illustrated in Scheme 1-13.<sup>43,44</sup> It is interesting to note that, although the reaction normally requires the use of UV-light,

in the case of cubane compounds it has been reported that only ambient light is required.<sup>45</sup>



Scheme 1-13: Mechanism of the Moriarty reaction from cubane carboxylic acid (1-14) to iodocubane (1-15)

### **1-8 CUBYL ANION**

It is clear that cubane derivatives cannot undergo  $S_N2$  reactions since the back side of all the cubane carbons are within the cage of cube. As seen in Section 1-6, it is possible to perform some  $S_N1$  reactions on the cube, but this is not always the best route to the functionalization of cubane.

A common alternative that has been employed is *via* the cubyl anion. Ortholithiation and ortho-magnesiation (Section 1-4 and 1-5) are commonly used methods for obtaining this intermediate. Another useful mode is direct metallation of cubyl halides.<sup>27-</sup>

<sup>30</sup> Section 1-7 highlighted some methods of forming cubyl halides, the most useful of which is the Moriarty reaction.<sup>43-45</sup> Once the cubyl halide has been formed, lithiation can be accomplished with an array of lithiating reagents, the most common of which are alkyl lithium compounds.<sup>27-30</sup>

Emrick has shown that the equilibrium between cubyllithium plus iodobenzene, and iodocubane, **1-15**, plus phenyllithium, lies strongly toward the latter.<sup>45</sup> Although the exact  $pK_a$  value for cubane is unknown, this would suggest that the  $pK_a$  of cubane is greater than 43;<sup>46</sup> it is usually assumed to be >50.<sup>47</sup> Thus, in performing reactions for lithiation, it is common to add at least 3 equivalents of the alkyl lithium reagent to drive the reaction to the right. This however, can cause problems since the electrophile that is subsequently added must also be in excess. In addition, the polarity of *t*-Bu-E (where E is the electrophile added) and C<sub>8</sub>H<sub>7</sub>-E can be quite similar and therefore can present difficulties during isolation by column chromatography.<sup>48</sup>

In spite of potential problems, generation of the cubyl anion is commonly employed in the field of cubane chemistry.<sup>27-30</sup> Scheme 1-14 illustrates a range of electrophiles that have been successfully added to the cube after the lithiation of iodocubane, 1-15.



Scheme 1-14: Synthetic utility of cubylanion from iodocubane (1-15)

Of further potential interest, is the report by Eaton indicating that he had successfully been able to generate the cubyl anion in the gas phase.<sup>49</sup> This was accomplished by sustained off-resonance irradiation (SORI), which increases the kinetic energy of fluoride ions (**Scheme 1-15**). The cubyl anion was than detected by mass spectrometry.<sup>49</sup>



Scheme 1-15: Formation of cubyl anion in the gas phase using SORI

## **1-9 CUBENE**

As mentioned in Section 1-8, iodocubane (1-15) can be readily lithiated using *t*-BuLi. If the cube is 1,2-diiodinated (1-16) then a very interesting set of reactions can occur whereby a proposed intermediate is cubene (1-17), which represents the most pyramidalized olefin known to date (Scheme 1-16).<sup>50</sup>



Scheme 1-16: Synthetic pathways that require cubene, 1-17, as a reactive intermediate

The rationale for the proposed cubene (1-17) intermediate is that the reaction of iodocubane (1-15) with *t*-BuLi affords almost exclusively cubyllithium, with insignificant amounts of *t*-butylcubane. Szeimies has shown that reactions on strained olefins (bridged bicyclobutenes) can be performed with appropriate nucleophiles,<sup>51</sup> thus in the above

scheme it is possible to envision that cubene, 1-17 could very well be a feasible intermediate to afford the products isolated.



Scheme 1-17: Cubene, 1-17, trapping via a Diels-Alder reaction

The most convincing evidence for the cubene intermediate is the trapping with 11,12-dimethylene-9,10,-dihydro-9,10-ethanoanthracene, in a Diels-Alder reaction to form adduct **1-18**.<sup>50</sup>

#### **1-10 CAGE OPENING AND REARRANGEMENT WITH METALS**

As has been stated in Section 1-1, cubane (1-1) is a shelf stable, inert compound. Its behaviour is similar to that of most simple hydrocarbons but, due to the high scharacter of its external bonds, it has been shown to also behave in a similar way to arenes, as in the case of reactivity towards metals.

One of the first reported cases of rearrangement of the cubane cage was reported in 1970.<sup>52</sup> Eaton showed that cubane (1-1) in the presence of  $Ag^+$ , rearranges to form cuneane, 1-19. Recently, Eaton also showed that  $Li^+CB_{11}Me_{12}^-$  can also initiate the same rearrangement.<sup>53</sup> The exact mechanism for this rearrangement has not been determined, however it is believed that with  $Ag^+$  the rearrangement follows the mechanism shown below (Scheme 1-18).<sup>54</sup>



Scheme 1-18: Mechanism for cubane, 1-1, rearrangement to cuneane, 1-19, with Ag<sup>+</sup>

Another metal that also triggers rearrangement of cubane (1-1), is rhodium(I).<sup>55</sup> [Rh(NOR)Cl(PPh<sub>3</sub>)] can cause the cage to open to form syn-tricyclooctadiene (1-20). Subsequent heating of this molecule causes further ring opening to ultimately form cyclooctatetraene (1-21).<sup>56</sup> This cage-opening reaction has been shown to work on both substituted and unsubstituted systems. It is believed that two  $\sigma$  bonds form between the carbon and the rhodium, to form Rh(III), thus causing the ring opening.<sup>54</sup> The proposed mechanism is illustrated in Scheme 1-19.



Scheme 1-19: Mechanism for cubane, 1-1, opening to syn-tricyclooctadiene, 1-20, with Rh(I)

## **1-11 CUBANOL**

It has also been shown that there is a propensity for the cage of cubane to open when an electron donating group, bearing an acidic proton, was attached directly to the cube.<sup>57,58</sup> In the case of 4-methylcubanol, 1-22, the cage opens to form the tricyclooctenone, 1-23, which further opens to form the vinylcyclobutenylketene, 1-24.<sup>57,58</sup> This species was ultimately trapped as the ester, 1-25, when MeOH was added (Scheme 1-20).





This instability was not only observed with alcohols, but with amines as well.<sup>2</sup> Cubylamines give rise to cage opening, however not surprisingly, the ammonium salts are very stable.<sup>2</sup> This tendency towards ring opening was even further enhanced when an electron withdrawing group was located on the C2 position.<sup>2</sup> Of all the work that has been performed on the cubane system, there have only been two reported examples where a sulfur atom was attached to the cage.<sup>45,59</sup> Emrick reported the syntheses of a series of 4-arylcubylthiols but his characterization data was incomplete<sup>45</sup> and his claim that these thiols spontaneously decompose by oxidation to the disulfide is highly suspect due to results obtained here (*vide infra*) The second report was by Munavalli, who synthesized trifluoromethylthiocubane derivatives. The characterizations were incomplete and no additional data was reported concerning the stability of these compounds.<sup>59</sup>

#### **1-12 REFERENCES**

- 1. Eaton, P. E., Cole, T. W. Jr. J. Am. Chem. Soc. 1964, 86, 962, 3157.
- 2. Eaton, P. E. Angew. Chem., Int. Ed. Engl. 1992, 31, 1421.
- 3. Chapman, N. B., Key, J. M., Toyne, K. J. J. Org. Chem. 1970, 35, 3860.
- 4. Fleischer, E. B. J. Am. Chem. Soc. 1964, 86, 3889.
- Kybett, K. D., Carroll, S., Natalis, P., Bonnell, D. W., Margrave, J. L., Franklin, J. L. J. Am. Chem. Soc. 1966, 88, 626.
- 6. Silverman, R. B., Zhou, J. P., Eaton, P. E. J. Am. Chem. Soc. 1993, 115, 8841.
- 7. Bashir-Hashemi, A. NASA Conference Publication, 1994, 127.
- Choi, S-Y., Eaton, P. E., Hollenberg, P. F., Liu, K. E., Lippard, S. J., Newcomb, M., Putt, D. A., Upadhyaya, S. P., Xiong, Y. J. Am. Chem. Soc. 1996, 118, 6547.
- Zhou, J. J. P., Li, J., Upadhyaya, S. P., Eaton, P. E., Silverman, R. B. J. Med. Chem. 1997, 40, 1165.
- 10. Jin, Y., Lipscomb, J. D. Biochemistry, 1999, 38, 6178.
- Eaton, P. E., Shankar, B. K. R., Price, G. D., Pluth, J. J., Gilbert, E., Alster, J., Sandus, O. J. Org. Chem. 1984, 49, 185.
- 12. Eaton, P. E., Wicks, E. J. Org. Chem. 1988, 53, 5353.
- 13. Eaton, P. E., Xiong, R., Gilardi, R. J. Am. Chem. Soc. 1993, 115, 10195.
- Lukin, K. A., Li, J., Eaton, P. E., Kanomata, N., Hain, J., Punzalan, E., Gilardi, R. J. Am. Chem. Soc. 1997, 119, 9591.
- Bashir-Hashemi, A. Angew. Chem. 1993, 105, 585; Angew. Chem. Int. Ed. Engl.
   1993, 32, 612.
- 16. Bashir-Hashemi, A., Li. J., Gelber, N., Ammon, H. J. Org. Chem. 1995, 60, 698.

- 17. Zhang, M-X., Eaton, P. E., Gilardi, R. Angew. Chem. Int. Ed. Engl. 2000, 39, 401.
- 18. Service, R. F. Science, 2000, 287, 564.
- 19. Eaton. P. E., Gilardi, R. L., Zhang, M-X. Adv. Mater. 2000, 12, 1143.
- Eaton, P. E., Zhang, M-X., Gilardi, R., Gelber, N., Iyer, S., Surapaneni, R.
   Propellants, Explosives, Pyrotechnics, 2002, 21, 1.
- 21. Kalgutkar, A. S., Castagnoli, N. Jr., Testa, B. Med. Res. Rev. 1995, 15, 325.
- 22. Nomenclature of cubane compounds is analogous to benzene. C1 = ipso; C2, 6, and 8 = ortho; C3, 5, and 7 = meta; C4 = para.
- 23. Geschwend, H. W., Rodriguez, H. R. Org. React. N. Y. 1979, 26, 1.
- 24. Beak, P. Snieckus, V. Acc. Chem. Res. 1982, 15, 306.
- 25. Eaton, P. E., Castaldi, G. J. Am. Chem. Soc. 1985, 107, 724.
- 26. Della, E. W., Hine, P. T., Patney, H. K. J. Org. Chem. 1977, 42, 2940.
- 27. Eaton, P. E., Galoppini, E., Gilardi, R. J. Am. Chem. Soc. 1994, 116, 7588.
- 28. Della, E. W., Head, N. J. J. Org. Chem. 1995, 60, 5303.
- 29. Eaton, P. E., Stossel, D. J. J. Org. Chem. 1991, 56, 5138.
- 30. Eaton, P. E., Yang, C.-X., Xiong, Y. J. Am. Chem. Soc. 1974, 96, 4555.
- 31. Eaton, P. E., Higuchi, H., Millikan, R. Tetrahedron Lett. 1987, 28, 1055.
- 32. Bashir-Hashemi, A. J. Am. Chem. Soc. 1988, 110, 7234.
- 33. Eaton, P. E., Lee, C.-H., Xiong, Y. J. Am. Chem. Soc. 1989, 111, 8016.
- Eaton, P. E., Daniels, R. G., Casucci, D., Cunkle, G. T. J. Org. Chem. 1987, 52, 2100.
- 35. Sanchez, C. R., Scott, W. Tetrahedron Lett. 1998, 29, 139.
- 36. Hrovat, D. A, Borden, W. T. J. Am. Chem. Soc. 1990, 112, 3227.

- 37. Eaton, P. E., Yang, C.-X., Xiong, Y. J. Am. Chem. Soc. 1990, 112, 3225.
- Moriarty, R. M., Tuladhar, S. M., Penmasta, R., Awasthi, A. K. J. Am. Chem. Soc.
   1990, 112, 3228.
- 39. Eaton, P. E., Zhou, J. P. J. Am. Chem. Soc. 1992, 114, 3118.
- Bingham, R. C., Sliwinski, W. F., Schleyer, P. R. J. Am. Chem. Soc. 1970, 92, 3471.
- 41. Della, E. W., Patney, H. K. Synthesis, 1976, 251.
- Fokin, A. A., Lauenstein, O., Gunchenko, P. A., Schreiner, P. R. J. Am. Chem. Soc,
   2001, 123, 1842.
- 43. Concepcion, J. I., Francisco, C. G., Freire, R., Hernandez, R., Salazar, J. A., Suarez,
  E. J. Org. Chem. 1986, 51, 402.
- 44. Moriarty, R. M., Khosrowshahi, J. S., Dalecki, T. M. J. Chem. Soc., Chem. Commun. 1987, 675.
- 45. Emrick, T. S. Ph. D. Dissertation, University of Chicago, 1997.
- 46. pK<sub>a</sub> value for benzene: Smith, M. B., March, J. March's Advanced Organic Chemistry: Reaction, Mechanisms, and Structure, 5<sup>th</sup> ed. John Wiley & Sons: New York, 2001, p 331.
- 47. pK<sub>a</sub> value of butanes: Smith, M. B., March, J. March's Advanced Organic
  Chemistry: Reaction, Mechanisms, and Structure, 5<sup>th</sup> ed. John Wiley & Sons: New
  York, 2001, p 331.
- 48. Wosnick, J. H. Personal communication.
- 49. Hare, M., Emrick, T., Eaton, P. E., Kass, S. R. J. Am. Chem. Soc. 1997, 119, 237.
- 50. Eaton, P. E., Maggini, M. J. Am. Chem. Soc. 1988, 110, 7230.

- 51. Szeimies, G. React. Intermed. (Plenum), 1983, 3, 299.
- 52. Cassar, L., Eaton, P. E., Halpern, J. J. Am. Chem. Soc. 1970, 92, 6366.
- 53. Moss, S., King, B. T., de Meijere, A., Kozhushkov, S. I., Eaton, P. E., Michl, J. J. Org. Lett. 2001, 3, 2375.
- Eaton, P. E., Cassar, L., Hudson, R. A., Hwang, D. R. J. Org. Chem. 1976, 41, 1445.
- 55. Cassar, L., Eaton, P. E., Halpern, J. J. Am. Chem. Soc. 1970, 92, 3515.
- Byrd, J. E., Cassar, L., Eaton, P. E., Halpern, J. J. Chem. Soc., Chem. Commun. 1971, 40.
- 57. Cole, T. W. Jr. Ph. D. Dissertation, University of Chicago, 1966.
- 58. Hormann, R. E. Ph. D. Dissertation, University of Chicago, 1987.
- Munavalli, S., Wagner, G. W., Bashir-Hashemi, A., Rohrbaugh, D. K., Durst, H. D. Synth. Commun. 1997, 27, 2847.

## **CHAPTER 2**

# Dicubyl Disulfide and Related Derivatives

Some of the work in this chapter has been published: Ronny Priefer, Yoon Joo Lee, Fabiola Barrios, Jordan H. Wosnick, Anne-Marie Lebuis, Patrick G. Farrell, David N. Harpp, Aiming Sun, Shaoxiong Wu, James P. Snyder *Journal of the American Chemical Society* **124**, 5626-5627, (2002)

## **2-1 INTRODUCTION**

A class of compounds for which little work has been reported, are cubanes covalently functionalized with sulfur.<sup>1,2</sup> In this respect, we were drawn to the unknown cubanethiol (2-1) and dicubyl disulfide (2-2). As stated in Chapter 1-11, cubyl alcohols and amines are unstable,<sup>3</sup> the former and its analogues apparently fragmenting to a ketene and ultimately in the presence of methanol, form an ester.<sup>4,5</sup> In general, although thiols are more acidic than their alcohol counterparts, thioketenes are thermodynamically less stable than ketenes. Accordingly, we reasoned that cubanethiol might be less prone to decomposition by this pathway than cubanol, thus allowing studies of its structure and chemistry. At the very least, it was expected that the enhanced stability of the thiol may permit its capture by oxidation to form the unknown dicubyl disulfide (2-2).

As stated in Chapter 1-11 attempts to prepare cubane thiols and disulfides have been recorded by Emrick and Eaton;<sup>2</sup> however, the products apparently were too labile to be characterized fully.





2-2

### 2-2 SYNTHESIS OF CUBANETHIOL AND DICUBYL DISULFIDE

The synthesis of cubanethiol (2-1) and dicubyl disulfide (2-2) are shown in Scheme 2-1. Commercially available dimethyl-1,4-cubanedicarboxylate (2-3) was base hydrolyzed to cubane-1,4-dicarboxylic acid (2-4) with four equivalents of sodium hydroxide. Under Moriarty conditions, (iodobenzene diacetate, iodine, refluxing benzene for 6 hours) 2-4 was converted to 1,4-diiodocubane (2-5). Ultimately, 2-5 was converted to iodocubane (2-6), by reacting first with EtMgBr, transmetallation with *n*-BuLi, and protonation with MeOH. Before purification *via* column chromatography, the mixture was refluxed with NaOMe for 1 hour to ensure that any butyl halides that had formed could be converted to the corresponding methyl ether for easier separation. This reaction however is not the most reproducible. Yields could range from 25-86%, even when two reactions are performed in parallel, using similar concentrations, and reagents from identical bottles. This however, was the mode employed for obtaining iodocubane (2-6) which could easily be converted to cubyl anion with lithiating agents (Chapter 1-8).

Iodocubane (2-6) was lithiated using *n*-BuLi, followed by addition of tetramethylthiuram disulfide (TMTD) at -78°C, to ensure carbanionic attack at the sulfur rather than at the carbon.<sup>6-8</sup> This afforded *S*-cubyl-*N*,*N*-dimethyldithiocarbamate (2-7) in 82% yield; various electrophiles were used with varied success.<sup>9</sup> What was however difficult in the above mentioned reaction was purification. As stated in Chapter 1-8, it is necessary to add an excess amount of *n*-BuLi to drive the reaction to completion. It was therefore required that excess electrophile was also employed; which did cause problems for purification. In this particular reaction a trituration was initially performed with cold hexanes to remove much of the excess TMTD. This was followed by column

chromatography. This led ultimately to a mixture of 2-7 as well as the *n*-butyl analogue. The similarity of polarity of 2-7 and butyl analogues was also observed when *t*-BuLi was used at the lithiating agent. To purify this mixture, recrystallization was performed using pentane (yield 82%). More recently, the conversion of 2-6 to 2-7 has been accomplished with the use of lithium di-*t*-butyl-di-benzylide (LDBB) as the lithiating agent. This has reduced the purification steps to simply a column, which affords 2-7 in 88% yield.



Scheme 2-1: Synthetic path towards cubanethiol (2-1) and dicubyl disulfide (2-2)

The reduction of 2-7 to cubanethiol (2-1) was accomplished with LAH under reflux in ether; the solvent employed was of importance. Experience showed that the use of a higher boiling solvent, such as THF, causes decomposition to occur. The reaction mixture was quenched with water, than acidified and extracted with pentane. When cubanethiol (2-1) in the pentane mixture was evaporated under reduced pressure, only a mixture of decomposed products was obtained. Therefore, the system was oxidized immediately with iodine and pyridine to afford dicubyl disulfide (2-2). When the cubanethiol/pentane mixture was slowly evaporated under a stream of nitrogen, pure 2-1 was obtained as a yellow oil with a powerful stench.

Although it was believed that cubanethiol may be unstable and prone to cage opening, 2-1 has been shown to be sufficiently stable to remain in solution (methanol or chloroform) for up to two weeks. Some decomposition was detected, (olefinic peaks in <sup>1</sup>H-NMR) however, 2-1 remains as the predominant compound (~90%).

# 2-3 X-RAY ANALYSIS OF S-CUBYL-N,N-DIMETHYLDITHIOCARBAMATE (2-7)

During the synthesis and ultimate purification of many of the intermediates towards dicubyl disulfide (2-2), recrystallization was employed. This allowed for the opportunity to perform X-ray analysis of some of these new compounds. A crystal of *S*cubyl-*N*,*N*-dimethyldithiocarbamate (2-7) was obtained and revealed some interesting information (**Figure 2-1**). In solution, the thioamide exists in the predominant zwitterion form. <sup>1</sup>H-NMR of 2-7 showed the protons on the methine carbons attached to the nitrogen exist as a set of rotamers that coalesce at ~90°C. This is also the case in the solid state, as the  $\phi$ (C(10)-N(1)-C(9)-S(2)) = 180° (**Appendix A**). What was most remarkable was the carbon-sulfur bond length. It is especially short, with a length of 1.760 Å. It was assumed that this shortened bond length is a result of the high s-character that exists in the exocyclic bonds of cubane.<sup>10</sup> Although the results obtained suggest that dicubyl disulfide (**2-2**) would also have shortened bond lengths, the results obtained were more unusual than expected.



**Figure 2-1**: X-ray structure of *S*-cubyl-*N*,*N*-dimethyldithiocarbamate (2-7)

## 2-4 X-RAY ANALYSIS OF DICUBYL DISULFIDE (2-2)

As stated above (Section 2-3) it was suspected that the carbon-sulfur bond length for dicubyl disulfide (2-2) may be shortened compared to that of other aliphatic disulfides. It was however surprising to note that dicubyl disulfide contains by far the shortest known carbon-sulfur bond length where the carbon is sp<sup>3</sup> hybridized. Figure 2-2 illustrates the X-ray structure obtained. The C-S-S-C dihedral angle of 86.5° (Appendix B) is unexceptional when compared with disulfides bearing primary and secondary S-C carbons. However, it falls 20-30° lower than disulfides with tertiary carbons at sulfur.

Diadamantyl disulfide, for example, exhibits  $\phi(CSSC)=110.4^{\circ}.^{11}$  Obviously, the cubyl geometry pins back the  $\beta$ -carbons of **2-2** so as to avoid the steric effect engendered by the "bulkier" disulfides.



Figure 2-2: X-ray structure of dicubyl disulfide (2-2)

What was of the greatest interest however, was the exceptionally short C-S bond of 1.771 Å. This value is 0.09 Å shorter that the average C-S bond length (1.863 Å) for aliphatic disulfides where the carbon is tertiary<sup>12</sup> and can be compared with the shortest and longest aliphatic C-S bonds on record: 1.810 Å (MeSSMe)<sup>13</sup> and 1.952 Å (Ph<sub>3</sub>CSSCPh<sub>3</sub>).<sup>14,15</sup> To substantiate these observations within a coherent series, computational experiments were carried out in collaboration with Dr. James P. Snyder and colleagues at Emory University, Atlanta, Georgia.

**2-5 CALCULATIONS OF THE C-S BOND LENGTH OF DICUBYL DISULFIDE** Sections 2-5 and 2-6 represent work that Aiming Sun, Shaoxiong Wu, and James P. Snyder performed at Emory University

Short exocyclic C<sub>cube</sub>-C bonds have been observed previously and rationalized in terms of high s-character at the cubyl carbons.<sup>10,16,17</sup> Optimizing geometries of MeSSR (R = *t*-Bu, Me, C<sub>8</sub>H<sub>7</sub>) with density functional theory (DFT) at the Becke3LYP/6-31G(3df) level predicted (R)C-S bond lengths for the series (**Table 2-1**). It can be seen that in all cases the experimental and calculated bond length are fairly similar. In addition, the percent s-character of the C-S bond was determined by natural bond orbital (NBO) transformation<sup>18,19</sup> from the DFT calculations. For the above series, the calculations gave values of 18, 22, and 27%, respectively, implying a linear correlation between this quantity and C-S bond length. Interestingly, the latter suggests that the C-S bond length should be similar to that found for C(sp<sup>2</sup>)-S bonds, as is observed for aryl disulfides (1.772 Å (av.)).<sup>20</sup>

	Experimental Bond Length	Calculated Bond Length
Me-S-S-Me	0 ref. 13	٥ 1.826 Å
Me-S-S- <i>t</i> -Bu	0 ref. 21	٥ 1.874 A
Me-S-S-C <sub>8</sub> H <sub>7</sub>	0 1.771 Å	0 1.785 Å

Table 2-1: Experimental and calculated bond lengths for a series of methyl disulfides

# 2-6 CALCULATION OF THE ROTATIONAL BARRIER OF DICUBYL DISULFIDE

In addition to influencing geometry, it was believed that the high s-character of the cubyl C-S bonds may increase the S-S barrier of rotation. Recently, it has been reported that the disulfide rotation barrier is doubled by replacing carbon in CSSC with electronegative oxygen to give the dialkoxy disulfide moiety OSSO ( $\Delta G^{\neq}_{rot} = 18-19$  kcal/mol) (Chapter 4).<sup>22-24</sup> Given the hybridization-enhanced electronegativity of the carbon in the compressed C-S bond of dicubyl disulfide (2-2), it was conceivable that the S-S torsional barrier might be magnified relative to the 8-10 kcal/mol observed for simple disulfides.<sup>25,26</sup>

Optimization of the trans S-S rotational transition states for MeSSR (R =Me, *t*-Bu, C<sub>8</sub>H<sub>7</sub>) with the same DFT basis set predicts torsional barriers of 6.1, 6.9 and 5.9 kcal/mol, respectively. While these gas-phase values for the methyl and *tert*-butyl analogues are about 1 kcal/mol less that those measured in solution,<sup>26</sup> the direction and magnitude of  $\Delta\Delta G^{\neq}_{rot}$  for the corresponding benzyl and *tert*-butyl congeners (+0.6-0.9 kcal/mol) are accurately reproduced (+0.8 kcal/mol). Surprisingly, in contrast to the OSSO system, the cubyl-SS-Me is predicted to show a slightly lower S-S rotation barrier. Barrier calculations for the fully symmetrical disulfides (R-S-S-R, R= Me, *t*-Bu, C<sub>8</sub>H<sub>7</sub>) at the lower Becke3LYP/6-31G<sup>\*</sup>/Becke3LYP/6-31G<sup>\*</sup> level are shown below (**Table 2-2**). It can be seen that **Table 2-2** reveals a correlation between the mixed disulfides (stated above) and the symmetrical ones. However, it does still place the torsional barrier for dicubyl disulfide (**2-2**) lower than the others.

	Calculated Torsional Barrier $\Delta E_{rot}^{\neq}$
Me-S-S-Me	5.7 kcal/mol
<i>t</i> -Bu-S-S- <i>t</i> -Bu	6.0 kcal/mol
C <sub>8</sub> H <sub>7</sub> -S-S-C <sub>8</sub> H <sub>7</sub>	5.2 kcal/mol

Table 2-2: Calculated torsional barrier for series of symmetric disulfides

To verify this counterintuitive barrier prediction for dicubyl disulfide (2-2), the compound's low temperature proton-decoupled <sup>13</sup>C NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> in a mixture with *t*-Bu-S-S-*t*-Bu and chiral Pirkle alcohol (*ca.* 1:1:100, respectively)<sup>23,27,28</sup> was examined. From -85 to -110°C (the lowest achievable temperature with this mixture), the C $\beta$  of both disulfides broadened about equally in agreement with similar S-S rotation barriers below 8.0 kcal/mol.<sup>25,26</sup> As predicted, dicubyl disulfide (2-2) exhibited exchange between its S-S conformational enantiomers with an energy requirement apparently equal to or below that of all other alkyl analogues. The result is at odds with previous observations that the S-S barrier height increases with the introduction of both electronegativity and increasing size in the disulfide substituent.<sup>22-24,26</sup>

To understand this phenomenon, NBO analysis<sup>18,19</sup> for the MeSSR trans transition states (R= t-Bu, C<sub>8</sub>H<sub>7</sub>) was performed. The results illustrated that the p- $\pi$  sulfur lone electron pair adjacent to the C<sub>8</sub>H<sub>7</sub> moiety engages in a LP<sub>S</sub> $\rightarrow \sigma^*$ (C-C) interaction (**Figure** 2-3) that is twice as strong as that for the t-Bu structure. This factor elicits a small reduction in the rotational barrier for R = C<sub>8</sub>H<sub>7</sub> relative to R= t-Bu (0.5 kcal/mol) in close agreement with the equally small total relative barrier reduction calculated (0.8 kcal/mol). Two factors contribute to these differences. First, the cubyl C-S bond is shorter by nearly 0.1 Å (Section 2-3 and 2-4). Second, the highly condensed C<sub>8</sub>H<sub>7</sub> cage enjoys lower energy  $\sigma^*$ (C-C) orbitals than the t-Bu system. It is therefore proposed that both effects promote a slightly greater LP<sub>S</sub> $\rightarrow \sigma^*$ (C-C) bonding-antibonding interaction, reducing S-S lone pair repulsion, and thereby stabilizing the torsional transition state structure of 2-2.



Figure 2-3: Schematic representation of  $LP_S \rightarrow \sigma^*(C-C)$  bonding-antibonding interaction of dicubyl disulfide (2-2)

## 2-7 OXIDATION OF DICUBYL DISULFIDE

Dicubyl disulfide (2-2) had shown some interesting properties as stated in Section 2-4 to 2-6, therefore it was hoped that derivatizing the disulfide would also afford some unusual features. Although the lone pair electrons on sulfur do interact with the  $\sigma^*(C-C)$  bond, it was believed that there may still be enough electron density to react with *m*CPBA to oxidize the system.<sup>29-32</sup> If there was not a significant amount of electron density on the sulfur atoms, it should still be possible to oxidize with hydrogen peroxide  $(H_2O_2)$ .<sup>32-36</sup> As it turned out, the oxidations were successful, and a series of oxidized dicubyl disulfides were synthesized.

Scheme 2-2 illustrates the successful synthesis of all four oxidized products from dicubyl disulfide (2-2). When one equivalent of mCPBA in CH<sub>2</sub>Cl<sub>2</sub> was added to the disulfide, dicubyl thiosulfinate (2-8: 91%) was the major product with minor amounts of the other oxidized cubane products.



Scheme 2-2: Synthetic scheme for the oxidation of dicubyl disulfide (2-2)

Upon an additional oxidation of 2-8, it was hoped that the dicubyl *vic*-disulfoxide (2-12) may be isolated, however, as is common with most disulfoxides,<sup>30,32-34,37</sup> an intramolecular rearrangement apparently occurred (Scheme 2-3) to afford the thiosulfonate 2-9 (85%). The dicubyl thiosulfonate (2-9) was further oxidized to the trioxide, 2-10 (78%), and with an additional equivalent of *m*CPBA, the tetraoxide, 2-11 (93%), was obtained. The tetraoxide (2-11) could also be obtained directly with the addition of excess *m*CPBA to the dicubyl disulfide (2-2) (94%). All four oxidized versions of dicubyl disulfide (2-2) were fully characterized.



Scheme 2-3: Intramolecular rearrangement of disulfinate (2-8) to thiosulfonate (2-9)

One point of interest is the <sup>1</sup>H NMR of tetraoxide, **2-11**. The <sup>1</sup>H NMR of cubane displays a signal at 4.00 ppm. All other derivatives of cubane typically display proton signals ranging from 3.5 to 4.5 ppm depending on the functionalization.<sup>38</sup> What was interesting, although not surprising, was the large downfield shift of the protons on the *ortho* position of **2-11**. These protons absorb at 4.7 ppm which are the furthest downfield reported for any mono-substituted uncharged cubane derivative. The interaction of between carbonyl oxygens attached to the cube and protons on the *ortho* position have been observed before, as in *ortho* lithiation (Section 1-4). It is therefore reasonable to

postulate that there is intramolecular hydrogen bonding occurring between the protons on the *ortho* position and the oxygens attached to sulfur (**Scheme 2-4**).



Scheme 2-4: Possible intramolecular H-bonding of dicubyl vic-disulfone (2-11)

## 2-8 ATTEMPTED SULFUR INSERTION INTO DICUBYL DISULFIDE

Yet another derivatization of dicubyl disulfide that was attempted was the formation of dicubyl polysulfides. Earlier work in this laboratory has shown sulfur units (1-3) can be inserted into various disulfides using certain trityl compounds (Scheme 2-5).<sup>39-42</sup> When trityl sulfenyl chloride (2-13) was reacted with a disulfide, the trisulfide was formed.<sup>41</sup> If instead, trityl thiosulfenyl chloride (2-14) was used, the tetrasulfide was obtained.<sup>39</sup> As well, trityl dithiosulfenyl chloride (2-15) with a disulfide ultimately affords the pentasulfide.<sup>40</sup> Using this methodology, it was hoped that the dicubyl tri- to pentasulfides could be obtained.



43

Scheme 2-5: Known method for formation of polysulfides from disulfides

This expected chemistry did not take place to the desired extent. What was ultimately obtained were two mixed tri- and tetrasulfides, **2-16** and **2-17**. This result was rationalized by steric considerations. Scheme 2-6 illustrates the proposed mechanism for the attempted formation of the dicubyl tetrasulfide (**2-18**).<sup>39,42</sup> However, what was actually obtained was the tritylmethyl cubyl trisulfide (**2-16**). The formation of this compound is rationalized by examining the mechanistic step required for the last step. The sulfur attached to the trityl performs a S<sub>N</sub>2 reaction on the sulfur attached directly to the cube. Sterically, this is improbable, since the trityl group and the cube are fairly bulky. This steric effect is further complicated by the fact that the carbon-sulfur bond is extremely short (Sections 2-4 and 2-5).



Scheme 2-6: Proposed mechanism for the formation of dicubyl tetrasulfide (2-18)

Although, this steric hindrance did create a problem for the formation of a series of dicubyl polysulfides, it was believed that it was possible to form a series of mixed trityl-cubyl polysulfides (Scheme 2-7). Ultimately, tritylmethyl cubyl tetrasulfide (2-17) was also formed. However, the synthesis of tritylmethyl cubyl disulfide (2-19) was unsuccessful.



Scheme 2-7: Series of target trityl-cubyl polysulfides

This was again rationalized by steric effects (Scheme 2-8). In this case, the sulfur, which is very close to the cube (Sections 2-4 and 2-5), must perform an  $S_N 2$
reaction on the sulfur connected to the trityl group of 2-13.<sup>41</sup> Sterically, this is improbable. In hopes that any of the above mentioned reactions could be driven to react in an  $S_N1$  fashion, increasing the polarity of the solvent was attempted. However, in all cases, the trityl compounds decomposed in the polar solvents.



Scheme 2-8: Mechanism for the attack of dicubyl disulfide (2-2) on trityl sulfenyl chloride (2-13)

46

#### **2-9 EXPERIMENTAL**

Cubane-1,4-dicarboxylic acid (2-3)<sup>43</sup>



Commercially available dimethyl-1,4-cubane dicarboxylate (2-3, 5.04g, 22.9mmol) was added to a dissolved solution of NaOH (3.72g, 93.0mmol) in MeOH (150mL) and H<sub>2</sub>O (10mL). After 10 minutes, 2-3 was completely dissolved. The mixture was refluxed for 4.5 hours, at which time the solution was cloudy white. The solvent was removed *via* evaporation. The white residue was dissolved in H<sub>2</sub>O (100mL), and acidified to pH~1 with conc. HCl. The white precipitate was vacuum filtered, washed with water and dried under vacuum to constant weight affording cubane-1,4-dicarboxylic acid (2-4: 4.35g, 99%); mp. dec. 220-222°C (lit<sup>4,44</sup> 220°C).

<sup>1</sup>H-NMR (400 MHz, MeOD):  $\delta = 4.18$  (s, 6H, cubyl H).

<sup>13</sup>C-NMR (100.6 MHz, MeOD): δ = 48.1, 57.7, 175.4.

1,4-Diiodocubane (2-5)<sup>2,45</sup>



Dry benzene (350mL) was added to cubane–1,4-dicarboxylic acid (2-4: 3.50g, 18.3mmol) under N<sub>2</sub>, forming a suspension. To this IBDA (17.62g, 54.7mmol) and I<sub>2</sub> (14.40g, 56.7mmol) were added. The dark purple solution was refluxed for 6 hours. After cooling to room temperature, satd. Na<sub>2</sub>SO<sub>3</sub> (100mL) was added, and the mixture was stirred until the top organic layer was light yellow (15-20 minutes). The layers were separated, the organic layer was washed with satd. Na<sub>2</sub>SO<sub>3</sub> (2 X 100mL), H<sub>2</sub>O (2 X 100mL), and brine (100mL). The solution was dried with MgSO<sub>4</sub>, filtered, and evaporated. The suspension that remained was triturated with cold hexanes to remove iodobenzene, affording the desired 1,4-diiodocubane (2-5: 5.45g, 84%) as a white solid; mp. 225-227°C (lit<sup>2,45</sup> 226-227°C).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.39 (s, 6H, cubyl H).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 35.7, 57.4.

Iodocubane (2-6)<sup>2,46</sup>



1,4-Diiodocubane (2-5, 4.28g, 12.0mmol) was dissolved in dry THF (130mL) under N<sub>2</sub>. A 1.0M EtMgBr in THF (48mL) solution was added and cooled to  $-78^{\circ}$ C whereby the solution became off-white cloudy. A 1.6M *n*-BuLi in hexanes (31mL) solution was added till the mixture turned bright yellow. The mixture was stirred for an additional 5 minutes at  $-78^{\circ}$ C, whereupon cold MeOH (30mL) was added. The cloudy white mixture was slowly warmed to room temperature and sodium methoxide in methanol (25 wt%, 35mL) was added. The system was refluxed for 1 hour to destroy the iodobutane by-product. After cooling to room temperature, pentane (200mL) and H<sub>2</sub>O (100mL) were added. The mixture was acidified to pH 1 with concentrated HCl, extracted, washed with H<sub>2</sub>O (2 X 100mL) and brine (100mL). The solution was dried with MgSO<sub>4</sub>, filtered and evaporated. Column chromatography in pentane afforded cubyl iodide (**2-6**: 2.38g, 86%) as a white low-melting solid; mp. 31-33°C (lit<sup>2,46</sup> 32-34°C).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.17 (m, 4H, H-3,4,5,7), 4.31 (m, 3H, H-2,6,8).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 38.7, 47.9, 48.5, 58.1.

S-Cubyl-N,N-dimethyldithiocarbamate (2-7)



To a dissolved solution of iodocubane (2-6: 0.831g, 3.61mmol) in dry THF (50mL) under  $N_2$  cooled to -78°C, 1.6M *n*-BuLi in hexanes (4.55mL, 7.28mmol) was added dropwise *via* syringe. TMTD (3.21g, 13.4mmol) was added in one portion, and the mixture was allowed to slowly reach room temperature (~1 hour). The reaction was quenched with H<sub>2</sub>O (40mL), extracted with hexanes (2 X 50mL), and washed twice with H<sub>2</sub>O (2 X 50mL). The aqueous layer was back extracted with hexanes (50mL), and the combined organic layer was dried with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure. Trituration with cold hexanes to remove excess TMTD, followed by column

chromatography [hexanes/CHCl<sub>3</sub> (2:1)] on the light yellow-orange solid followed by recrystallization [hexanes/CHCl<sub>3</sub> (1:1)], afforded *S*-cubyl-*N*,*N*-dimethyldithiocarbamate (2-7: 0.66g, 82%) as a white solid; mp 62-64°C.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.30 (s, 3H), 3.45 (s, 3H), 3.93 (m, 1H, H-4), 4.06 (m, 3H, H-3,5,7), 4.25 (m, 3H, H-2,6,8).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): δ = 42.1, 43.6, 46.0, 46.5, 51.8, 59.2, 195.8.

MS: calcd. 224.05677; found: 224.05668.

S-Cubyl-N,N-dimethyldithiocarbamate (2-7)



To a dissolved solution of iodocubane (2-6: 1.63g, 7.07mmol) in dry THF (80mL) under  $N_2$  cooled to -78°C, a green solution of LDBB in THF was added dropwise *via* syringe, till solution remained green. TMTD (4.01g, 16.7mmol) was added in one portion, and allowed to slowly reach room temperature (~45 minutes). The system was quenched with H<sub>2</sub>O (40mL), extracted with hexanes (2 X 50mL), washed twice with H<sub>2</sub>O (2 X 50mL). The aqueous layer was back extracted with hexanes (50mL), and the combined organic layer was dried with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure. Column chromatography [hexanes/CHCl<sub>3</sub> (2:1)] on the light yellow-orange solid afforded *S*-cubyl-*N*,*N*-dimethyldithiocarbamate (2-7: 1.39g, 88%) as a white solid; mp 63-64°C.

Cubanethiol (2-1)



To a dissolved solution of *S*-cubyl-*N*,*N*-dimethyldithiocarbamate (2-7: 0.381g, 1.69mmol) in Et<sub>2</sub>O (50mL), under N<sub>2</sub>, LAH (0.739g, 18.6mmol) was added in one portion and the mixture was refluxed for 5 hours. The mixture was cooled to 0°C, and quenched slowly with H<sub>2</sub>O (25mL), and pentane (50mL) was added. The system was acidified to pH~1 with conc. HCl, extracted, and washed with H<sub>2</sub>O (3 X 50mL). The organic layer was dried with MgSO<sub>4</sub>, filtered, and evaporated to complete dryness with a stream of N<sub>2</sub>, to afford cubanethiol (2-1: 0.20g, 86%) as a smelly, yellow oil.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.09 (s, 1H), 3.89 (m, 3H), 3.97 (m, 3H), 4.05 (m, 1H). <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 44.6, 48.4, 54.5, 55.5.

MS: calcd. 136.03467; found: 136.03396.





A typical reaction involved the initial synthesis of the cubanethiol (2-1), where the solvent was not evaporated.

S-cubyl-*N*,*N*-dimethyldithiocarbamate (**2-7**: 0.380g, 1.69mmol), Et<sub>2</sub>O (50mL), LAH (0.740g, 18.6mmol).

To solution of cubanethiol (2-1) dissolved in pentane and Et<sub>2</sub>O (100mL), iodine crystals (0.21g, 0.85mmol) followed by pyridine (5 drops) were added. The solution instantly turned red-brown, and within 5 minutes was cloudy. The solution was stirred overnight at room temperature, and satd. Na<sub>2</sub>SO<sub>3</sub> (25mL) was added and allowed to mix until organic layer was clear colourless. The layers were separated, washed with satd. Na<sub>2</sub>SO<sub>3</sub> (2 X 25mL), H<sub>2</sub>O (2 X 25mL), and brine (25mL), dried with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure. Column chromatography [hexanes] of the off-white solid followed by recrystallization [pentane] afforded dicubyl disulfide (2-2: 0.19g, 81%) as a white solid; mp 123-123°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.95 (m, 12H, H-2,2',3,3',5,5',6,6',7,7',8,8'), 4.04 (m, 2H, H-4,4').

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 44.1, 48.5, 52.2, 61.3.

Elemental anal.: calcd. C<sub>16</sub>H<sub>14</sub>S<sub>2</sub>: C 71.01, H 5.22; found C 70.72, H 5.27.

**Dicubyl thiosulfinate (2-8)** 



To a solution of dicubyl disulfide (2-2: 0.12g, 0.45mmol) dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (50mL) under N<sub>2</sub>, at 0°C, *m*CPBA (0.090g, 0.45mmol) was added in one portion. After 10 minutes the solution was warmed to room temperature and allowed to stir for 4 hours. The reaction was quenched with the addition of H<sub>2</sub>O (25mL) and the layers were separated. The organic layer was washed with H<sub>2</sub>O (2 X 25mL) and brine (25mL), dried with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure to dryness. Column chromatography [CHCl<sub>3</sub>] afforded dicubyl thiosulfinate (2-8: 0.12g, 91%) as a white solid; mp 128-130°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.04 (m, 1H), 4.08 (m, 7H), 4.24 (m, 3H), 4.44 (m, 3H).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 45.0, 45.4, 48.3, 48.5, 49.9, 54.1, 58.7, 70.0.

Elemental anal.: calcd. C<sub>16</sub>H<sub>14</sub>S<sub>2</sub>O: C 67.10, H 4.93; found C 67.06, H 4.88.

**Dicubyl thiosulfonate (2-9)** 



To a solution of dicubyl thiosulfinate (2-8: 0.10g, 0.35mmol) dissolved in dry  $CH_2Cl_2$  (50mL) under N<sub>2</sub>, at 0°C, *m*CPBA (0.071g, 0.36mmol) was added in one portion. After 10 minutes the solution was warmed to room temperature and allowed to stir for 3 hours. The reaction was quenched with the addition of H<sub>2</sub>O (25mL) and the layers were separated. The organic layer was washed with H<sub>2</sub>O (2 X 25mL) and brine (25mL), dried

with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure to dryness. Column chromatography [CHCl<sub>3</sub>] afforded dicubyl thiosulfonate (**2-9**: 0.091g, 85%) as a white solid; mp 68-70°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.07 (m, 8H), 4.16 (m, 3H), 4.49 (m, 3H).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 44.3, 45.6, 48.0, 48.3, 50.4, 54.8, 60.2, 71.7.

Elemental anal.: calcd. C<sub>16</sub>H<sub>14</sub>S<sub>2</sub>O<sub>2</sub>: C 63.55, H 4.67; found C 63.67, H 4.51.

**Cubylsulfinyl cubylsulfone (2-10)** 



To a solution of dicubyl thiosulfonate (2-9: 0.070g, 0.24mmol) dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (30mL) under N<sub>2</sub>, at 0°C, *m*CPBA (0.050g, 0.26mmol) was added in one portion. After 10 minutes the solution was warmed to room temperature and allowed to stir for 7 hours. The reaction was quenched with the addition of H<sub>2</sub>O (25mL) and the layers were separated. The organic layer was washed with H<sub>2</sub>O (2 X 25mL) and brine (25mL), dried with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure to dryness. Column chromatography [CHCl<sub>3</sub>] afforded cubylsulfinyl cubylsulfone (2-10: 0.061g, 78%) as a white solid; mp 79-80°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.07 (m, 5H), 4.18 (m, 3H), 4.58 (m, 3H), 4.63 (m, 3H).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 45.3, 46.2, 47.9, 48.1, 51.6, 53.8, 69.2, 70.3.

Elemental anal.: calcd.  $C_{16}H_{14}S_2O_3$ : C 60.35, H 4.43; found C 60.07, H 4.41.

### Dicubyl vic-disulfone (2-11)



To a solution of cubylsulfinyl cubylsulfone (2-9: 0.051g, 0.16mmol) dissolved in dry  $CH_2Cl_2$  (30mL) under N<sub>2</sub>, at 0°C, *m*CPBA (0.030g, 0.17mmol) was added in one portion. After 10 minutes the solution was warmed to room temperature and allowed to stir for 6 hours. The reaction was quenched with the addition of H<sub>2</sub>O (25mL) and the layers were separated. The organic layer was washed with H<sub>2</sub>O (2 X 25mL) and brine (25mL), dried with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure to dryness. Column chromatography [CHCl<sub>3</sub>] afforded dicubyl *vic*-disulfone (2-11: 0.050g, 93%) as a white solid; mp 150-153°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.00 (m, 2H, H-4,4'), 4.17 (m, 6H, H-3,3',5,5',7,7'), 4.68 (m, 6H, H-2,2',6,6',8,8').

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 46.4, 47.8, 51.4, 68.9.

Elemental anal.: calcd. C<sub>16</sub>H<sub>14</sub>S<sub>2</sub>O<sub>4</sub>: C 57.47, H 4.22; found C 57.46, H 4.16.

Dicubyl vic-disulfone (2-11)



To a solution of dicubyl disulfide (2-2: 0.110g, 0.390mmol) dissolved in dry  $CH_2Cl_2$  (50mL) under N<sub>2</sub>, at 0°C, *m*CPBA (0.380g, 1.96mmol) was added in one portion. After 10 minutes the solution was warmed to room temperature and allowed to stir overnight. The reaction was quenched with the addition of H<sub>2</sub>O (25mL) and the layers were separated. The organic layer was washed with H<sub>2</sub>O (2 X 25mL) and brine (25mL), dried with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure to dryness. Column chromatography [CHCl<sub>3</sub>] afforded dicubyl *vic*-disulfone (2-11: 0.12g, 94%) as a white solid; mp 151-153°C.

Tritylmethyl cubyl trisulfide (2-16)



To a solution of dicubyl disulfide (2-2: 0.050g, 0.19mmol) dissolved in dry  $CH_2Cl_2$  (3mL) under N<sub>2</sub>, tritylmethyl thiosulfenyl chloride (2-14: 0.070g, 0.20mmol) dissolved in dry  $CH_2Cl_2$  (3mL) under N<sub>2</sub> was cannulated in. The solution was stirred for 2 hours at room temperature, evaporated to dryness, followed by column chromatography [hexanes] affording tritylmethyl cubyl trisulfide (2-16: 0.030g, 45%) as a off-white solid; mp 84-86°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.96 (m, 3H), 4.02 (m, 1H), 4.07 (m, 3H), 7.25-7.36 (m, 15H).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 44.7, 48.8, 52.6, 62.7, 73.3, 127.0, 127.8, 130.2, 143.3.

Elemental anal.: calcd. C<sub>27</sub>H<sub>22</sub>S<sub>3</sub>: C 73.26, H 5.01; found C 72.98, H 5.14.

Tritylmethyl cubyl tetrasulfide (2-17)



To a solution of dicubyl disulfide (2-2: 0.050g, 0.19mmol) dissolved in dry  $CH_2Cl_2$  (3mL) under N<sub>2</sub>, tritylmethyl dithiosulfenyl chloride (2-15: 0.070g, 0.19mmol) dissolved in dry  $CH_2Cl_2$  (3mL) under N<sub>2</sub> was cannulated in. The solution was stirred for 2 hours at room temperature, evaporated to dryness, followed by column chromatography [hexanes]

affording tritylmethyl cubyl tetrasulfide (**2-17**: 0.041g, 43%) as a off-white solid; mp 89-91°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.95 (m, 3H), 4.02 (m, 1H), 4.06 (m, 3H), 7.26-7.38 (m, 15H).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 44.6, 48.6, 52.8, 62.0, 73.5, 127.1, 127.8, 130.1, 142.9.

Elemental anal.: calcd.  $C_{27}H_{22}S_4$ : C 68.31, H 4.67; found C 68.55, H 4.61.

#### **2-10 REFERENCES**

- Munavalli, S., Wagner, G. W., Bashir-Hashemi, A., Rohrbaugh, D. K., Durst, H. D. Synth. Commun. 1997, 27, 2847.
- 2. Emrick, T. S. Ph. D. Dissertation, University of Chicago, 1997.
- 3. Eaton, P. E. Angew. Chem., Int. Ed. Engl. 1992, 31, 1421.
- 4. Cole, T. W. Jr. Ph. D. Dissertation, University of Chicago, 1966.
- 5. Hormann, R. E. Ph. D. Dissertation, University of Chicago, 1987.
- 6. Grunwell, J. R. J. Org. Chem. 1970, 35, 1500.
- 7. Jen, K.-Y., Cava, M. P. Tetrahedron Lett. 1982, 23, 2001.
- 8. Gronowitz, S., Hornfeldt, A. B., Temciuc, M. Synthesis, 1993, 3, 483.
- Unsuccessful reagents for sulfurization include S<sub>8</sub>, SO<sub>2</sub>Cl<sub>2</sub>, RSCl, thiourea,
   Ph<sub>3</sub>CSSCl, S-alkyl-O-ethylxanthate, and N-hydroxy-2-thiopyridone.
- 10. Della, E. W., Hine, P. T., Patney, H. K. J. Org. Chem. 1977, 42, 2940.
- 11. Rindorf, G., Jorgensen, F. S., Snyder, J. P. J. Org. Chem. 1980, 45, 5343.
- 12. The Cambridge structural database; http://www.ccdc.cam.ac.uk/.
- Microwave structure: Sutter, D., Dreizler, H., Rudolph, H. D. Z. Naturforsch. 1965, 20a, 1676.
- 14. Ostrowski, M., Jeske, J., Jones, P. G., du Mont, W.-W. Chem. Ber. 1993, 126, 1355.
- 15. Harpp, D. N., Williams, C. R. Unpublished X-ray structure of Ph<sub>3</sub>CSSCPh<sub>3</sub> yields r(C-S) = 1.939, 1.904 Å and r(S-S) = 2.006 Å.
- 16. Gilardi, R., Maggini, M., Eaton, P. E. J. Am. Chem. Soc. 1988, 110, 7232.
- 17. Della, E. W., Head, N. J. J. Org. Chem. 1992, 57, 2850.
- 18. Foster, J. P., Weinhold, F. J. Am. Chem. Soc. 1980, 102, 7211.

- 19. Reed, A. E., Curtis, L. A., Weinhold, F. Chem. Rev. 1988, 88, 899.
- 20. A CSD substructure search (ref 12) identified over 200 aryl disulfide X-ray structures with an average C-S bond length of 1.772 Å.
- 21. The average of eight tertiary C-S bond lengths for RC(Me2)-SS-R' as obtained from the CSD; ref 12.
- Snyder, J. P., Nevins, N., Tardif, S. L., Harpp, D. N. J. Am. Chem. Soc. 1997, 119, 12685.
- Borghi, R., Lunazzi, L., Placucci, G., Cerioni, G., Foresti, E., Plumitallo, A. J. Org. Chem. 1997, 62, 4924.
- Cerioni, G., Cremonini, M. A., Lunazzi, L., Placucci, G., Plumitallo, A. J. Org. Chem. 1998, 63, 3933.
- Thompson, Q. E., Crutchfield, M. M., Dietrich, M. W., Pierron, E. J. Org. Chem.
   1965, 30, 2692.
- Fraser, R. R., Boussard, G., Saunders, J. K., Lambert, J. B. J. Am. Chem. Soc. 1971, 93, 3822.
- 27. (R)-l-1-(9-Anthryl)-2,2,2-trifluoroethanol, as in: Pirkle, W. H. J. Am. Chem. Soc.
  1966, 88, 1837.
- 28. Grilli, S., Lunazzi, L., Mazzanti, A., Mazzanti, G. J. Org. Chem. 2001, 66, 748.
- 29. Abu-Yousef, I. A., Harpp, D. N. J. Org. Chem. 1997, 62, 8366.
- 30. Derbesy, G., Harpp, D. N., J. Org. Chem. 1996, 61, 991.
- 31. Derbesy, G., Harpp, D. N., J. Org. Chem. 1995, 60, 1044.
- 32. Derbesy, G. Ph. D. Dissertation, McGill University, 1994.
- 33. Freeman, F., Ma, X.-B., Lin, R. I.-S. Sulfur Lett. 1993, 15, 253.

- 34. Freeman, F., Lee, C. Mag. Res. Chem. 1988, 26, 813.
- 35. Steudel, R. Phosphorus Sulfur, 1985, 23, 33.
- 36. Steudel, R., Latte, J. Chem. Ber. 1977, 110, 423.
- 37. Derbesy, G., Harpp, D. N., J. Org. Chem. 1996, 61, 9471.
- 38. Chapter 1 gives many references of cubane derivatives.
- 39. Rys, A. Z., Harpp, D. N., Tetrahedron Lett. 2000, 41, 7169.
- 40. Hou, Y., Abu-Yousef, I. A., Harpp, D. N. Tetrahedron Lett. 2000, 41, 7809.
- 41. Hou, Y., Abu-Yousef, I. A., Boung, Y., Harpp, D. N. Tetrahedron Lett. 2001, 42, 8607.
- 42. Rys, A. Z. Ph. D. Dissertation, McGill University, 2002.
- 43. Eaton, P. E., Nordari, N., Tsanaktsidis, J., Upadhyaya, S. P. Synthesis, 1995, 5, 501.
- 44. Abeywickrema, E. W., Della, E. W. J. Org. Chem. 1980, 45, 4226.
- 45. Tsanaktsidis, J., Eaton, P. E. Tetrahedron Lett. 1989, 30, 6967.
- 46. Eaton, P. E., Galoppini, E. Gilardi, R. J. Am. Chem. Soc. 1994, 116, 7588.

## **CHAPTER 3**

# **Effective Synthetic Routes to Cubylcarbinol Derivatives**

Some of the work in this chapter has been published: Ronny Priefer, Patrick G. Farrell, David N. Harpp *Synthesis*, 2671, (2002)

#### **3-1 INTRODUCTION**

Mono-substituted cubane compounds have shown some very interesting properties, *e.g.* cubanol has been reported to go through an intramolecular rearrangement to open the cubane cage (Section 1-11);<sup>1,2</sup> (aminomethyl)cubane shows enzyme activity (Section 1-3).<sup>3-5</sup> The exocyclic bonds of cubanes have enhanced s-character<sup>6</sup> and this allows for some chemistry to be performed which is similar to arene chemistry. As part of our studies of convenient precursors for other cubane chemistry (Chapter 4), we needed synthetic procedures to prepare cubylcarbinol (3-1) in superior yields.



#### 3-2 SYNTHESIS OF CUBYLCARBINOL AND COMPARISON OF ROUTES

Cubylcarbinol (3-1) has previously been prepared in three steps from commercially available dimethyl-1,4-cubane dicarboxylate (3-2).<sup>7,8</sup> Partial hydrolysis of 3-2 yields 4-methoxycarbonyl cubane carboxylic acid (3-3) which was converted to cubanecarboxylic acid (3-4) *via* a Barton decarboxylation followed by additional hydrolysis (Lit. 82% yield).<sup>7</sup> Reduction of 3-4 affords cubylcarbinol (3-1).<sup>8</sup> The best literature preparation delivers 3-1 in 70% overall yield from 3-2.

From the 4-methoxycarbonyl cubane carboxylic acid (**3-3**), a Moriarty reaction<sup>9</sup> followed by hydrolysis of the unpurified intermediate yielded 4-iodocubanecarboxylic acid (**3-5**).

Three new avenues can be utilized for the synthesis of 3-1 from 3-5. The removal of iodine from 3-5 with *n*-BuLi, followed by protonation with methanol delivers 3-4 in high yield (88%). Reduction of 3-4 with borane is analogous to that reported with LAH,<sup>8</sup> producing 3-1 in identical yield (93-94%). Reduction of 3-5 with borane affords 1-iodo-4-(hydroxymethyl)cubane (3-6).<sup>10</sup> The removal of iodine from 3-6 with *n*-BuLi, followed by protonation with methanol gave 3-1 in 84% yield. However, what was initially surprising was the one step reduction and iodine removal from 3-5 to give 3-1 in 91% yield using excess amounts of LAH under reflux for an extended period of time.

Removal of halogens from tertiary carbons by LAH has been reported in the past.<sup>11</sup> Ashby has carried out considerable research in this area and has shown that in some cases the reaction occurs *via* a single electron transfer (SET) mechanism<sup>12</sup> and in reactions of trityl halides, the trityl radical was detected using electron paramagnetic resonance (EPR) spectroscopy.<sup>13</sup> It was believed that in the conversion of **3-5** to **3-1** this

is also the likely mode of reaction since a  $S_N 2$  mechanism is impossible and studies of the cubyl radical are well-documented (Section 1-7).<sup>14</sup>



Scheme 3-1: Synthetic pathways towards cubylcarbinol, 3-1

In contrast to the trityl halides where the reaction was completed in 5 hours with one equivalent of LAH, our system required 5 days, using 50 equivalents of LAH under

65

reflux conditions. A possible explanation for the extended time requirement is the fact that the carboxylic acid would first be reduced to the alkoxy anion providing a charged species that would not be very soluble in THF. This is supported by the fact that after 24 hours the starting acid 3-5 was converted to a mixture of alcohols 3-6 and 3-1.

The one-step reaction with excess LAH thus provides a simple procedure to convert 4-iodocubanecarboxylic acid (3-5) into cubylcarbinol (3-1) in excellent yield. An examination of the cost of these various synthetic routes reveals that these new routes are cheaper. If one were to prepare one gram of cubylcarbinol (3-1) *via* the previously reported pathway (3-2/3-3/3-4/3-1), the cost (ignoring solvents) would be ~\$510. Comparing this to pathway 3-2/3-3/3-5/3-6/3-1, there is a moderate increased overall yield of 66 to 68% with a total cost of ~\$490. Pathway 3-2/3-3/3-5/3-4/3-1 gives an overall yield of 70% at a cost of ~\$475. Ultimately, the highest yielding synthetic pathway is also the least expensive. Pathway 3-2/3-3/3-5/3-1 affords the cubylcarbinol, 3-1, in 77% overall yield with a cost of ~\$435. It is therefore justifiable to state that these new synthetic routes provide a less expensive synthesis of 3-1. In addition, depending upon the reducing agent employed, two different cubylcarbinols (3-1 and 3-6) can be obtained through the single precursor, 3-5, which has been shown to be a versatile intermediate, where it is possible to manipulate either the acid group<sup>8,10,15-17</sup> and/or the iodo functionality.<sup>10,18-20</sup>

66

#### **3-3 EXPERIMENTAL**



4-Methoxycarbonyl cubane carboxylic acid (3-3) from dimethyl-1,4-cubane dicarboxylate  $(3-2)^7$ 

To a solution of commercially available dimethyl-1,4-cubane dicarboxylate (3-2: 5.06g, 23.0mmol) dissolved in THF (175mL) at room temperature, NaOH (0.900g, 22.4mmol) dissolved in MeOH (15mL) was added dropwise. The mixture was then stirred overnight and evaporated to dryness. The white solid was dissolved in H<sub>2</sub>O (100mL), and extracted with CHCl<sub>3</sub> (2 X 25mL), dried with MgSO<sub>4</sub>, filtered and evaporated, affording 0.330g of excess starting ester 3-2 (7%). The remaining aqueous layer was acidified with conc. HCl to pH~2, extracted with CHCl<sub>3</sub> (3 X 50mL), dried with MgSO<sub>4</sub>, filtered and evaporated, siltered and evaporated, yielding of 4-methoxycarbonyl cubane carboxylic acid (3-3: 4.33g, 92%); mp 182-183°C (Lit<sup>1.7,21</sup> mp 182-183°C, 176-179°C<sup>22</sup>).

<sup>1</sup>H-NMR (400 MHz, MeOD):  $\delta$  = 3.69 (s, 3H, CH<sub>3</sub>), 4.19 (s, 6H, cubyl H).

<sup>13</sup>C-NMR (100.6 MHz, MeOD): δ = 48.1, 48.2 (cubyl CH), 52.1 (CH<sub>3</sub>), 57.4, 57.6 (cubyl C), 173.4 (CO), 175.0 (CO).

Cubanecarboxylic acid (3-4) from 4-methoxycarbonyl cubane carboxylic acid  $(3-3)^7$ 



To a suspension of 4-methoxycarbonyl cubane carboxylic acid (3-3: 0.50g, 2.4mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (15ml) under N<sub>2</sub>, oxalyl chloride (0.70mL, 8.0mmol) was added via syringe, and the mixture was stirred at room temperature for 15 minutes. The magnetic stir-bar was removed and the solution was evaporated to dryness (without heat), then opened to a dry atmosphere. The off-white solid was dissolved in dry benzene (20mL) and cannulated over 10 minutes into a suspension of 2-mercaptopyridine-N-oxide sodium salt hydrate (0.40g, 2.7mmol),<sup>24</sup> DMAP (0.010g, 0.070mmol), and freshly distilled *t*-butyl thiol (0.55mL, 4.9mmol) being irradiated with a sunlamp (GE-Ultraviolet). After 1 hour, the mixture was allowed to cool to  $0^{\circ}$ C. Et<sub>2</sub>O (20mL) was added and the solution was washed with satd. Ca(OCl)<sub>2</sub> (10mL), and H<sub>2</sub>O (25mL), back extracted with Et<sub>2</sub>O (2 X 20mL), and the combined organic layer was dried with MgSO<sub>4</sub>, filtered, and evaporated until ~20mL of solvent remained. NaOH (0.28g, 6.9mmol) dissolved in MeOH (10mL) was added and the mixture was refluxed for 1 hour. The solution was cooled, evaporated to near dryness, 3mL of benzene were added (to ensure all MeOH evaporated) and then evaporated to dryness, dissolved in H<sub>2</sub>O (20mL), and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 X 20mL). The aqueous layer was acidified with conc. HCl to pH<1, extracted with  $CH_2Cl_2$  (3 X dried with MgSO<sub>4</sub>, filtered, and evaporated to dryness affording 20mL). cubanecarboxylic acid (**3-4**: 0.27g, 76%); mp 123-125°C (Lit<sup>24,25</sup> mp 124-125°C).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.01 (m, 4H, H-3,4,5,7), 4.28 (m, 3H, H-2,6,8), 11.12 (s, 1H, COOH).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): δ = 45.2 (C-3,5,7), 47.9 (C-4), 49.5 (C-2,6,8), 55.3 (C-1), 117.8 (CO).

4-Iodocubanecarboxylic acid (3-5) from 4-methoxycarbonyl cubane carboxylic acid (3-3)



IBDA (18.32g, 56.9mmol) and I<sub>2</sub> (14.45g, 56.9mmol) were added to a suspension of 4methoxycarbonyl cubane carboxylic acid (**3-3**: 3.91g, 19.0mmol) in dry benzene (300mL) under N<sub>2</sub>. After refluxing for 7 hours, the mixture was cooled to room temperature, whereupon pentane (150mL) was added. The solution was washed with satd. Na<sub>2</sub>SO<sub>3</sub> (2 X 50mL), H<sub>2</sub>O (50mL) and brine (50mL), dried with MgSO<sub>4</sub>, filtered, and evaporated to near dryness. The red-brown liquid that remained was dissolved in THF (100mL), and to it, NaOH (7.67g, 19.2mmol) dissolved in MeOH (75mL) and H<sub>2</sub>O (25mL) was added and stirred overnight at room temperature. The solution was evaporated to near dryness, dissolved in H<sub>2</sub>O (50mL) and acidified with conc. HCl (pH<1). The white precipitate was collected and kept under vacuum to constant weight affording 4-iodocubanecarboxylic acid (**3-5**: 4.76g, 92%); mp 213-215°C (Lit<sup>23</sup> mp 174-178°C).

<sup>1</sup>H-NMR (400 MHz, MeOD):  $\delta = 4.23$  (m, 3H, H-2,6,8), 4.35 (m, 3H, H-3,5,7).

<sup>13</sup>C-NMR (100.6 MHz, MeOD): δ = 37.0 (C-4), 51.2, 56.0 (cubyl CH), 57.9 (C-1), 174.8 (CO).



Cubanecarboxylic acid (3-4) from 4-iodocubanecarboxylic acid (3-5)

To 4-iodocubanecarboxylic acid (**3-5**: 0.10g, 0.37mmol) dissolved in dry THF (50mL) under N<sub>2</sub> at  $-78^{\circ}$ C, 2.63M *n*-BuLi in hexanes (0.80mL, 2.1mmol) was added. Cold MeOH (5mL) was added after 5 minutes, and the solution was slowly allowed to reach room temperature. Hexanes (25mL) were added and the solution was extracted with H<sub>2</sub>O (3 X 50mL). The aqueous layer was acidified to pH<1 with conc. HCl, extracted with CHCl<sub>3</sub> (3 X 50mL), dried with MgSO<sub>4</sub>, filtered, and evaporated to dryness, affording pure cubanecarboxylic acid (**3-4**: 0.051g, 88%); mp 124-125°C (Lit<sup>7,25</sup> mp 124-125°C).

1-Iodo-4-(hydroxymethyl)cubane (3-6) from 4-iodocubanecarboxylic acid (3-5)



Borane-methyl sulfide complex (2.0mL, 21mmol) was added to a solution of 4iodocubanecarboxylic acid (**3-5**: 3.62g, 13.2mmol) dissolved in dry THF (125mL) under

 $N_2$  and cooled to 0°C. The mixture was stirred at 0°C for 20 minutes, then at room temperature for 4 hours. The solution was quenched with H<sub>2</sub>O (20mL) and stirred overnight. Ethyl acetate (75mL) was added and the solution was washed with H<sub>2</sub>O (2 X 50mL) and brine (50mL), dried with MgSO<sub>4</sub>, filtered, and evaporated to dryness. Column chromatography [CHCl<sub>3</sub>/EtOAc (1:1)] afforded 1-iodo-4-(hydroxymethyl)cubane (**3-6**: 3.25g, 95%) as a white solid; mp 109-111°C (Lit<sup>10</sup> mp 108-110°C).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.39 (t, 1H, OH), 3.78 (d, 2H, CH<sub>2</sub>), 4.05 (m, 3H, H-3,5,7), 4.21 (m, 3H, H-2,6,8).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 38.9 (C-1), 47.9 (C-2,6,8), 54.7 (C-3,5,7), 59.0 (C-4), 63.2 (CH<sub>2</sub>).

Cubylcarbinol (3-1) from cubanecarboxylic acid (3-4)



To a solution of cubanecarboxylic acid (3-4: 0.48g, 3.2mmol) dissolved in dry THF (50mL) under N<sub>2</sub> at 0°C, BH<sub>3</sub> SMe<sub>2</sub> (0.50mL, 5.3mmol) was added. After 20 minutes at 0°C, the solution was warmed and stirred for an addition 2 hours at room temperature. The solution was quenched with H<sub>2</sub>O (10mL) and stirred overnight. EtOAc (25mL) was added, the solution was washed with H<sub>2</sub>O (2 X 20mL) and brine (20mL), dried with

MgSO<sub>4</sub>, filtered, and evaporated to dryness. Column chromatography [hexanes/EtOAc (3:1)] afforded cubylcarbinol, (**3-1**: 0.42g, 94%); mp 61-62°C (Lit<sup>8</sup> mp 62-62.5°C).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.32 (t, 1H, OH), 3.72 (d, 2H, CH<sub>2</sub>), 3.89 (m, 6H, H-2,3,5,6,7,8), 4.21 (m, 1H, H-4).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 44.6, 47.9 (cubyl CH), 48.9 (C-4), 58.6 (C-1), 64.1 (CH<sub>2</sub>).

Cubylcarbinol (3-1) from 1-iodo-4-(hydroxymethyl)cubane (3-6)



1-Iodo-4-(hydroxymethyl)cubane (**3-6**: 0.32g, 1.2mmol) was dissolved in dry THF (50mL) under N<sub>2</sub> and cooled to  $-78^{\circ}$ C, whereupon 1.6M *n*-BuLi in hexanes (5.0mL, 8.0mmol) was added. After 25 minutes at  $-78^{\circ}$ C, cold MeOH (6mL) was added and the solution was allowed to warm to room temperature and stirred for 1 hour; 25wt% NaOMe in MeOH (5.6mL) was added and the mixture was refluxed for 1 hour. The solution was cooled, hexanes (25mL) were added, washed with H<sub>2</sub>O (2 X 25mL) and brine (25mL), dried with MgSO<sub>4</sub>, filtered, and evaporated. Column chromatography [hexanes/EtOAc (3:1)] afforded cubylcarbinol (**3-1**: 0.13g, 84%); mp 59-61°C (Lit<sup>8</sup> mp 62-62.5°C).

Cubylcarbinol (3-1) from 4-iodocubanecarboxylic acid (3-5)



Lithium aluminum hydride (16.62g, 438mmol) was added to a solution of 4iodocubanecarboxylic acid (**3-5**: 2.59g, 9.46mol) in dry THF (200mL) under N<sub>2</sub> and refluxed for 5 days. The solution was cooled to 0°C, and the mixture was *very*, *very* slowly quenched with cold MeOH. Once all the excess LAH was destroyed, the solution was acidified to pH<1 with conc. HCl. Hexanes (200mL) were added and the solution was washed with H<sub>2</sub>O (3 X 200mL) and brine (150mL), dried with MgSO<sub>4</sub>, filtered, and evaporated to dryness. Column chromatography [hexanes/EtOAc (3:1)] afforded cubylcarbinol (**3-1**: 1.16g, 91%); mp 62-63°C (Lit<sup>8</sup> mp 62-62.5°C).

#### **3-4 REFERENCES**

- 1. Cole, T. W. Jr. Ph. D. Dissertation, University of Chicago, 1966.
- 2. Hormann, R. E. Ph. D. Dissertation, University of Chicago, 1987.
- 3. Silverman, R. B., Zhou, J. P., Eaton, P. E. J. Am. Chem. Soc. 1993, 115, 8841.
- Zhou, J. J. P., Li, J., Upadhyaya, S., Eaton, P. E., Silverman, R. B. J. Med. Chem. 1997, 40, 1165.
- 5. Kalgutkar, A. S., Castagnoli, N. Jr., Testa, B. Med. Res. Rev. 1995, 15, 325.
- 6. Della, E. W., Hine, P. T., Patney, H. K. J. Org. Chem. 1977, 42, 2940.
- 7. Eaton, P. E., Nordari, N., Tsanaktsidis, J., Upadhyaya, S. P. Synthesis, 1995, 5, 501.
- 8. Eaton, P. E., Yip, Y. C. J. Am. Chem. Soc. 1991, 113, 7692.
- 9. Moriarty, R. M., Khosrowshahi, J. S., Dalecki, T. M. J. Chem. Soc., Chem. Commun. 1987, 675.
- 10. Eaton, P. E., Galoppini, E., Gilardi, R. J. Am Chem. Soc. 1994, 116, 7588.
- 11. Krishnamurthy, S., Brown, H. C. J. Org. Chem. 1982, 47, 276.
- 12. Ashby, E. C., Welder, C. O., Doctorovich, F. Tetrahedron Lett. 1993, 34, 7235.
- Ashby, E. C., DePriest, R. N., Goel, A. B., Wenderoth, B., Pham, T. N. J. Org. Chem. 1984, 49, 3545.
- 14. Luh, T.-Y., Stock, L. M. J. Org. Chem. 1978, 43, 3271.
- 15. Eaton, P. E. Angew. Chem, Int. Ed. Engl. 1992, 31, 1421.
- 16. Medrdad, M., Sanjani, N. S. Polym. Int. 2000, 49, 260.
- 17. Della, E. W., Head, N. J. J. Org. Chem. 1995, 60, 5303.
- Priefer, R., Lee, Y. J., Barrios, F., Wosnick, J. H., Lebuis, A.-M., Farrell, P. G., Harpp, D. N., Sun, A., Wu, S., Snyder, J. P. J. Am. Chem. Soc. 2002, 124, 5626.

- 19. Eaton, P. E., Stossel, D. J. Org. Chem. 1991, 56, 5138.
- 20. Eaton, P. E., Yang, C.-X., Xiong, Y. J. Am. Chem. Soc. 1990, 112, 3225.
- 21. Cole, T. W. Jr., Mayers, C. J., Stock, L. M. J. Am. Chem. Soc. 1974, 96, 4555.
- 22. Edward, J. T., Farrell, P. G., Langford, G. E. J. Am. Chem. Soc. 1976, 98, 3075.
- 23. Moriarty, R. M., Khosrowshahi, J. S. Synthetic Comm. 1989, 19, 1395.
- 24. Instead of preparing the anhydrous sodium salt of N-hydroxypyridine-2-thione from sodium omadine, we used commercially available 2-mercaptopyridine-N-oxide sodium salt hydrate.
- 25. Eaton, P. E., Cole, T. W. Jr. J. Am. Chem. Soc. 1964, 86, 962.

## **CHAPTER 4**

# Dialkoxy Disulfides from Cubylcarbinols

Some of the work in this chapter has been published: Ronny Priefer, Patrick G. Farrell, David N. Harpp *Tetrahedron Letters* **43**, 8781-8784, (2002)

Alkoxy disulfides, 4-1, have been known for over a century<sup>1</sup> but only recently have attracted significant attention<sup>2-7</sup> in spite of a seminal paper by Thompson in 1965.<sup>8</sup> Of particular interest is the unusually short S-S bond (*ca.* 1.95Å) in these compounds that raises the S-S bond rotational barrier to *ca.* 18 kcal/mol<sup>4,5</sup> from the usual barrier of *ca.* 6-10 kcal/mol in the corresponding disulfides.<sup>8-11</sup> In addition, benzylic dialkoxy disulfides (4-1) (R = 4-X-C<sub>6</sub>H<sub>4</sub>) have been shown to decompose smoothly under moderate heat to deliver a diatomic sulfur fragment that can be trapped by dienes<sup>7</sup> (Scheme 4-1).



Scheme 4-1: Intramolecular fragmentation of benzylic dialkoxy disulfides

### 4-2 SYNTHESIS AND STUDIES ON DIALKOXY DISULFIDES DERIVED FROM CUBYL CARBINOLS

Dialkoxy disulfides were synthesized from the corresponding cubyl carbinols (4-2 and 4-3) (Chapter 3) by reacting these with 0.5 equivalents of sulfur monochloride in the presence of  $Et_3N$ . The reactions affording the corresponding dialkoxy disulfides 4-4 and 4-5 in 85% and 89% respective yields.



Scheme 4-2: Synthetic pathway of dialkoxy disulfides from cubylcarbinols

The barrier of rotation for compound 4-5 was determined to be 18.7 kcal/mol from the coalescence of the proton AB quartet at  $98^{\circ}$ C (aldehyde and alcohol were detected starting at  $90^{\circ}$ C.) An accurate value for the barrier of rotation of 4-4 could not be obtained due to the overlap of the AB quartet with the cubyl signal in the <sup>1</sup>H-NMR in high boiling solvents.

The crystal structure of bis-(4-iodocubylmethyl)-dialkoxy disulfide 4-5 (Figure 4-1) revealed no unusual features. The O-S-S-O dihedral bond angle is 87.6° and the S-S

bond length is 1.97Å (Appendix C), which are comparable to values in other dialkoxy disulfides.<sup>12,13</sup>



Figure 4-1: X-ray structure of *bis*-(4-iodocubylmethyl)-dialkoxy disulfide (4-5)

To date, only benzylic dialkoxy disulfides have been reported to liberate trappable diatomic sulfur fragments upon heating.<sup>2,4,7,13</sup> If this decomposition occurs as proposed in **Scheme 4-1**, then it is possible that the relative ease of abstraction of the benzylic proton accounts for this moderate-temperature intramolecular rearrangement. Because of the relatively high s-character of the external bonds of cubanes,<sup>9,14,15</sup> we considered it possible that compounds **4-4** and **4-5** might similarly liberate S<sub>2</sub> on thermolysis. Since **4- 4** has a much lower melting point than **4-5** (49°-51°C compared with 119°-121°C) we expected that it would decompose more rapidly than **4-5** at a given temperature. This

however was not the case as in refluxing toluene compound **4-4** is stable for at least 4 days, whereas **4-5** decomposes completely within 24 hours.

Table 4-1 shows the data obtained for  $S_2$  trapping from 4-4 and 4-5 with both 2,3diphenyl (4-6) and 2,3-dimethyl-1,3-butadienes (4-7).



Averaged data: experiments performed in refluxing chlorobenzene for 24 hours with 3 eq. of diene a: NMR ratio before purification b: percent isolated yield c: reaction was performed in refluxing toluene for 24 hours.

#### **Table 4-1**: $S_2$ trapping by dienes

In general agreement with previous reports,<sup>7,13</sup> a larger amount of cyclic tetrasulfide (4-8) than cyclic disulfide (4-9) was obtained on heating 4-4 or 4-5 with excess 2,3-dimethyl-1,3-butadiene (4-7). However, proportionally more cyclic disulfide (4-10) than cyclic tetrasulfide (4-11) was obtained using excess 2,3-diphenyl-1,3-butadiene (4-6) with dialkoxy disulfide 4-4, in contrast to the results obtained with 4-5. In view of the thermal stabilities of the two products obtained from 2,3-diphenyl-1,3-

butadiene, no interconversion between them is probable<sup>16</sup> and we have no explanation for the differing product ratios obtained.

Upon attempted recrystallization of *bis*-cubylmethyl-dialkoxy disulfide 4-4<sup>17</sup>, *bis*cubylmethyl-sulfite 4-12 was formed (**Figure 4-2**). This was confirmed by X-ray crystallography, followed by independent synthesis. It was also observed that on standing, 4-4 was eventually completely converted to 4-2; thus it was suspected that it might be light sensitive. Lunazzi and Placucci<sup>6</sup> suggested that under photolytic conditions, dialkoxy disulfides undergo homolytic cleavage to give ROS<sup>\*</sup> that is quickly oxidized to ROS<sup>\*</sup>=O; this species was trapped with *t*-BuNO. When the photolysis was carried out at -100°C in the absence of a good oxidizing agent (possibly *t*-BuNO itself), sulfite and sulfoxylate (-OSO-) were detected.<sup>6</sup>



Figure 4-2: X-ray structure of *bis*-cubylmethylsulfite (4-12)
It was therefore necessary to perform two photolysis experiments with compound 4-4 in toluene: one under nitrogen and the other open to air. After 24 hours of irradiation with a sun lamp (GE-ultraviolet), the sample in the oxygen free environment contained dialkoxy disulfide, 4-4, and cubylcarbinol, 4-2 (~1:1 ratio), whereas the sample that was open to the atmosphere showed no trace of 4-4 but revealed both the sulfite 4-12 and the alcohol 4-2 (~2:3 ratio.) The sample that had been under nitrogen was photolyzed for an additional 24 hours after which time it was completely converted to alcohol 4-2, as was observed with the photolyzed sample that was open to the atmosphere for the full 48 hours.

What this may suggest is that in air the dialkoxy disulfide initially becomes oxidized to give 4-13, followed by photolytic S-S bond cleavage, affording both ROS<sup>\*</sup>=O (4-14) and ROS<sup>\*</sup> (4-15) (Scheme 4-3). Lunazzi and Placucci have suggested that ROS<sup>\*</sup> radicals can lose sulfur easily at temperatures above  $-100^{\circ}C^{6}$  (our reactions were performed at 50°C). Thus, 4-15 would likely yield the alkoxy radical (4-16), that can react with the more stable sulfinate radical (4-14) to afford the sulfite 4-12; this would eventually be completely converted to alcohol.



Scheme 4-3: Proposed photolytic fragmentation of dialkoxy disulfides in an oxygen environment

When the photolysis was performed in an inert atmosphere, slower homolytic S-S bond cleavage should take place to form **4-15**, which could lose sulfur to form the alkoxy radical **4-16**. This might explain why the only product that we observed in this experiment was cubylcarbinol (**Scheme 4-4**).





#### **4-3 EXPERIMENTAL**

*Bis*-cubylmethyldialkoxy disulfide (4-4)



To a solution of cubylcarbinol (4-2: 0.500g, 3.73mmol) dissolved in Et<sub>2</sub>O (30mL) and CH<sub>2</sub>Cl<sub>2</sub> (20mL) under N<sub>2</sub>, Et<sub>3</sub>N (0.520mL, 3.73mmol) was added and the mixture was cooled to 0°C. To this, freshly distilled S<sub>2</sub>Cl<sub>2</sub> (0.151mL, 1.88mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5mL) was cannulated in and stirred at room temperature for 1 hour. To the cloudy solution, H<sub>2</sub>O (25mL) was added. The layers were separated; the organic layer was washed with brine (2 x 50mL), dried with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure. Column chromatography [hexanes/CHCl<sub>3</sub> (1:1)] afforded *bis*-cubylmethyldialkoxy disulfide (4-4: 0.52g, 85%) as a white solid; mp 49-51°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.92 (m, 12H, H-2,3,5,6,7,8), 4.01 (m, 2H, H-4), 3.94, 4.03 (ABq, 4H, J = 10.8 Hz).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 44.7, 47.6 (C-2,3,5,6,7,8), 48.5 (C-4), 56.8 (C-1), 76.2 (CH<sub>2</sub>).

Elemental anal.: calcd. C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub>: C 65.42; H 5.49; found C 65.37; H 5.58.

Bis-(4-iodocubylmethyl)-dialkoxy disulfide (4-5)



To a solution of 1-iodo-4-(hydroxymethyl)cubane (4-3: 0.299g, 1.15mmol) dissolved in  $Et_2O$  (30mL) and  $CH_2Cl_2$  (20mL) under N<sub>2</sub>,  $Et_3N$  (0.160mL, 1.15mmol) was added and the mixture was cooled to 0°C. To this, freshly distilled S<sub>2</sub>Cl<sub>2</sub> (0.050mL, 0.58mmol) dissolved in  $CH_2Cl_2$  (5mL) was cannulated in and stirred at room temperature for 1 hour. To the cloudy solution, H<sub>2</sub>O (25mL) was added. The layers were separated; the organic layer was washed with brine (2 x 50mL), dried with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure. Column chromatography [hexanes/CHCl<sub>3</sub> (3:1)] followed by recrystallization (hexanes) afforded of *bis*-(4-iodocubylmethyl)-dialkoxy disulfide (4-5: 0.30g, 89%) as a white solid; mp 119-121°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.94, 4.04 (ABq, 4H, J = 11.2 Hz), 4.07 (m, 6H, H-2,4,8), 4.21 (m, 6H, H-3,5,7).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 38.3 (C-4), 48.5 (C-2,6,8), 54.8 (C-3,5,7), 57.4 (C-4), 75.5 (CH<sub>2</sub>).

Elemental anal.: calcd. C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub>I<sub>2</sub>: C 37.13; H 2.77; found C 37.12; H 2.47.

2,3-Diphenyl-1,3-butadiene (4-6)<sup>18-20</sup>



To a dry three-neck flask under N<sub>2</sub>, magnesium turnings (1.47g, 60.3mmol) were added followed by anhydrous Et<sub>2</sub>O (30mL). A few drops of  $\alpha$ -bromostyrene in Et<sub>2</sub>O were added. The solution began refluxing after the magnesium turnings were scratched with a glass rod. The remaining  $\alpha$ -bromostyrene (8.00mL, 5.55mmol) was added dropwise to the stirring, refluxing brown-red solution. The solution was refluxed for 1 hour and Et<sub>2</sub>O (10mL) was added. The mixture, once cooled, was cannulated into a vigorously stirring green solution containing (PPh<sub>3</sub>)<sub>2</sub>NiCl<sub>2</sub> (3.15g, 4.8mmol) and  $\alpha$ -bromostyrene (6.40mL, 44.4mmol) in dry Et<sub>2</sub>O (50mL) at 0°C under N<sub>2</sub>. The mixture was stirred for 15 minutes at 0°C and overnight at room temperature. The system was cooled to 0°C and 1.2M HCl (150mL) was slowly added. The mixture was separated and the aqueous layer was extracted with Et<sub>2</sub>O (4 x 50mL). The combined organic layer was washed with satd. NaHCO<sub>3</sub> (2 x 50mL), dried with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure. Column chromatograph [hexanes] of the red oil afforded 2,3-diphenyl-1,3-butadiene (4-6; 2.24g, 25%) as a white solid; mp 53-54°C (Lit<sup>19</sup> mp 52-54°C, 46-47°C<sup>20</sup>).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.30 (d, 2H, J = 1.60 Hz), 5.53 (d, 2H, J = 1.60 Hz), 7.25 (m, 6H), 7.37 (m, 4H).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 116.3, 127.5, 127.9, 128.2, 140.2, 149.9.

1,2-Dithia-4,5-dimethyl-4-4-cyclohexene (4-9) and 1,2,3,4-tetrathia-6,7-dimethyl-6-



cyclooctene (4-8)

Example procedure: Dialkoxy disulfide, 4-4 or 4-5

Dialkoxy disulfide (4-4: 0.051g, 0.15mmol; 4-5: 0.050g, 0.086mmol) and 2,3-diphenyl-1,3-butadiene (4-7) (3 eq.) were dissolved in chlorobenzene (10mL) and refluxed with stirring for 24 hours. (Dialkoxy disulfide, 4-5, was refluxed in toluene (10mL) for 24 hours.) After the mixture was cooled to room temperature, the stir bar was removed and the solvent was evaporated off under reduced pressure. Column chromatography [CHCl<sub>3</sub>/hexanes (1:49)] afforded initially 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene (4-8) followed by 1,2-dithia-4,5-dimethyl-4-4-cyclohexene (4-9) as yellow oils.

1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene (**4-8**);<sup>13, 21</sup>

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.78 (s, 6H), 3.62 (s, 4H).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 20.8, 34.2, 125.2.

1,2-dithia-4,5-dimethyl-4-4-cyclohexene (**4-9**);<sup>13, 21</sup>

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.74$  (s, 6H), 3.19 (s, 4H).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 20.6, 33.6, 124.7.

1,2-Dithia-4,5-diphenyl-4-4-cyclohexene (4-10) and 1,2,3,4-tetrathia-6,7-diphenyl-6-





Example procedure: Dialkoxy disulfide, 4-4 or 4-5

Dialkoxy disulfide (4-4: 0.048g, 0.14mmol; 4-5: 0.050g, 0.086mmol) and 2,3-diphenyl-1,3-butadiene (4-6) (3 eq.) were dissolved in chlorobenzene (10mL) and refluxed with stirring for 24 hours. After mixture was cooled to room temperature, stir bar was removed and solvent was evaporated off under reduced pressure. Column chromatography [Et<sub>2</sub>O/petroleum ether (1:99)] afforded initially 1,2,3,4-tetrathia-6,7diphenyl-6-cyclooctene (4-11) followed by 1,2-dithia-4,5-diphenyl-4-4-cyclohexene (4-10) as beige solids.

1,2-dithia-4,5-diphenyl-4-4-cyclohexene (4-10);

mp 100-102°C (Lit. mp 100-102°C<sup>13</sup>, 101-102°C<sup>21</sup>).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 3.67$  (s, 4H), 7.02 (m, 10H).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 34.7, 126.6, 127.9, 129.2, 134.8, 142.6.

1,2,3,4-tetrathia-6,7-diphenyl-6-cyclooctene (4-11);

mp 135-138°C (Lit. mp 136-139°C<sup>13</sup>, 137-139°C<sup>21</sup>).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.07 (s, 4H), 7.10 (m, 10H).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 42.9, 126.9, 127.9, 129.5, 138.0, 140.9.

*Bis*-cubylmethyldialkoxy disulfide (4-12)



To a solution of cubylcarbinol (4-2: 0.12g, 0.91mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20mL) under N<sub>2</sub>, pyridine (0.73mL, 0.90mmol) was added and the mixture was cooled to  $-10^{\circ}$ C. To this, thionyl chloride (0.03mL, 0.45mmol) was added. The mixture was warmed, and stirred at room temperature for 1 hour. Reaction was quenched with H<sub>2</sub>O (10mL), the layers were separated, the organic layer was washed with brine (2 x 25mL), dried with MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure. Column chromatography [hexanes/CHCl<sub>3</sub> (1:1)] afforded *bis*-cubylmethylsulfite (4-12: 0.12g, 87%) as a white solid; mp 93-96°C.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ = 3.91 (m, 12H, H-2,3,5,6,7,8), 4.01 (m, 2H, H-4), 4.05, 4.16 (ABq, 4H, J = 11.0 Hz).

<sup>13</sup>C-NMR (126.7 MHz, CDCl<sub>3</sub>):  $\delta$  = 44.5, 47.2 (C-2,3,5,6,7,8), 48.5 (C-4), 55.6 (C-1), 62.8 (CH<sub>2</sub>).

Elemental anal.: calcd. C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>S: C 68.77; H 5.77; found C 68.58; H 5.79.

#### **4-4 REFERENCES**

- 1. Legfeld, F. Chem. Ber. 1895, 28, 449.
- 2. Tardif, S. L., Harpp, D. N. J. Org. Chem. 2000, 65, 4791.
- 3. Cerioni, G., Plumitallo, A. Magnetic Resonance in Chemistry, 1998, 36, 461.
- Snyder, J. P., Nevins, N., Tardiff, S., Harpp, D. N. J. Am. Chem. Soc. 1997, 119, 12685.
- Borghi, R., Lunazzi, L., Placucci, G., Cerioni, G., Foresti, E., Plumitallo, A. J. Org. Chem. 1997, 62, 4924.
- Borghi, R., Lunazzi, L., Placucci, G., Cerioni, G., Plumitallo, A. J. Org. Chem. 1996, 61, 3327.
- 7. Tardif, S. L., Williams, C. R., Harpp, D. N. J. Am. Chem. Soc. 1995, 117, 9067.
- Thompson, Q. E., Crutchfield, M. M., Dietrich, M. W., Pierron, E. J. Org. Chem. 1965, 30, 2692.
- Priefer, R., Lee, Y. J., Barrios, F., Wosnick, J. H., Lebuis, A.-M., Farrell, P. G., Harpp, D. N., Sun, A., Wu, S., Snyder, J. P. J. Am. Chem. Soc. 2002, 124, 5626.
- Fraser, R. R., Boussard, G., Saunders, J. K., Lambert, J. B. J. Am. Chem. Soc. 1971, 93, 3822.
- 11. Kessler, H., Rundel, W. Chem. Ber. 1968, 101, 3350.
- 12. 85.4° and 1.96Å for (4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-O-S)<sub>2</sub> in ref 2d;
- 76.8° and 1.93Å for (4-Cl-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-O-S)<sub>2</sub> in Tardif, S. L. Ph. D. Dissertation, McGill University, **1997**.
- 14. Della, E. E., Hine, P. T., Patney, H. K. J. Org. Chem. 1977, 42, 2940.
- 15. Eaton, P. E., Cole, T. W. Jr. J. Am. Chem. Soc. 1964, 86, 962, 3157.

- 16. Rys, A. Z., Harpp, D. N. Tetrahedron Lett. 1997, 38, 4931.
- 17. Recrystallization was performed with hexanes and the dissolved sample was allowed to stand on the bench for 2 days.
- 18. Fulcher, B. C., Hunter, M. L., Welker, M. L. Synth. Comm. 1993, 23, 217.
- 19. Lesté-Lasserre, P. B. F. Ph. D. Dissertation, McGill University, 2001.
- Dodson, R. M., Srinivasan, V., Sharma, K. S., Sauers, R. F. J. Org. Chem. 1972, 37, 2367.
- 21. Nicolaou, K. C., DeFrees, S. A., Hwang, C.-K., Stylianides, N., Carroll, P. J., Snyder, J. P. J. Am. Chem. Soc. 1990, 112, 3029.

# **CHAPTER 5**

# Synthesis of Cubane-Containing Polymers

#### **5-1 INTRODUCTION**

This chapter deals with studies of cubane-based polymer synthesis. The synthesis of cubane-based polymers has only received attention over the past 6 years.<sup>1-3</sup> It has been postulated that since cubane has a high strain energy,<sup>4</sup> "cubane-containing polymers may find applications as energetic binders for solid rocket propellants."<sup>1</sup> However, the literature concerning cubane-based polymers is rather minimal.

The first attempt at synthesizing a polymer containing cubane was the metathesis polymerization of the 1,4-bis(homoallyl)cubane, 5-1.<sup>1</sup> Chauvin reported that 5-1 with catalyst  $[(CF_3)_2MeCO](N-2,6-C_6H_3-i-Pr)Mo=CHC(Me)_2Ph$  afforded an oligomer with an average of 6.2 repeat units per chain.<sup>1</sup> In hopes of increasing the solubility of the growing polymer, and thus increase the chain length, Chauvin also carried out a co-polymerization of 5-1 and 1,5-hexadiene (1:1).<sup>1</sup> This synthetic procedure yielded a polymer with 14 repeat units (butenylene:cubylene = 0.56:1). Notably, the oligomer and copolymer were formed without rearrangement of the cube structure.<sup>1</sup>



Scheme 5-1: Metathesis polymerization of 1,4-bis(homoallyl)cubane (5-1)

In hopes to circumvent the problem of solubility, Kakuchi performed polycondensation reactions of cubane-1,4-dicarboxylic acid (5-2) to form polymer 5-3 using a range of aromatic diamines (5-4 to 5-7).<sup>2</sup> He envisioned that upon formation of

the polymer 5-3, it would be possible to react it with a rhodium catalyst (which is known to open the cage)<sup>5</sup> and with heating, could form the cyclooctatetraene<sup>6</sup> containing polymer. Grubbs has shown that cyclooctatetraene can open *via* a ring opening metathesis polymerized to form polyacetylene<sup>7</sup>; thus 5-3 could ultimately be converted to a grafted or network polymer.



Scheme 5-2: Polycondensation of cubane-1,4-dicarboxylic acid (5-2) and a variety of aromatic diamines (5-4 to 5-7)

It was reported that polymers containing diamines 5-6 and 5-7, were the only two that were soluble enough to run GPC.<sup>2</sup> (However still require DMF.) The polymer with diamine 5-6 had a  $M_n = 8.3 \times 10^3$  and a PDI of 3.60. This corresponds to a length of ~20 units. With diamine 5-7, they obtained a polymer with a  $M_n = 1.2 \times 10^4$  and PDI of 2.41. This corresponds to a length of ~25 units. In all the examples he reported, only concentrated H<sub>2</sub>SO<sub>4</sub> could solubilize all of the cubane-based polymers. In addition they were able to show that indeed the cubane moiety could be converted with a rhodium catalyst such that cyclooctatetraene units were then incorporated into the polymer.<sup>2</sup>

One final paper in the area of cubane polymer chemistry that has been published also deals with polycondensation. Mahkam reported five cubane-based polymers, derived from cubane-1,4-dicarboxylic acid (5-2), 1,4-diaminocubane (5-8), and a variety of different diacids and diamines to form polymers 5-9 to 5-13.<sup>3</sup> Scheme 5-3 illustrates that the number of monomer units reaches a maximum of 68 when monomers 5-8 and adipoyl chloride are reacted to form polymer 5-9. When the two cubane monomers (5-2 and 5-8) are reacted together, the polymer, 5-13, has 43 repeat units. None of the polymers were soluble in THF, and only partially soluble in DMF and DMSO. Solubility was only achieved in TFA and formic acid.<sup>3</sup>



Scheme 5-3: Polycondensation of cubane-1,4-dicarboxylic acid (5-2) and 1,4diaminocubane (5-8) with a variety of diacids and diamines As stated, solubility was an issue in the examples described above.<sup>1-3</sup> Here, it is postulated, that this problem is due to the lack of free rotation in the systems where the cube is part of the polymer chain. This promotes the polymer to come out of solution, and thus prematurely terminate the polymerization.<sup>8</sup> Therefore, it was envisioned that having the cube tethered to a polymer backbone (5-14) may increase the free rotation of cubane, and the increase in entropy would thus increase the solubility, allowing for homopolymer formation.



#### **5-2 SYNTHESIS OF VINYL CUBANE**

In order to synthesize the polymer **5-14**, it was necessary to initially synthesize the corresponding monomer. Eaton has reported that vinyl-cubane compounds can be synthesized from cubane aldehydes *via* a Wittig reaction.<sup>9</sup> Unfortunately, he did not state any uses for these compounds nor show any experimental or characterization data. This did, however, provide useful knowledge that the monomer was likely to be attainable.

Scheme 5-4 illustrates the synthetic pathway employed in making 4-iodo-1vinylcubane (5-15). Initially, 1-iodo-4-(hydroxymethyl)cubane (5-16) was converted to

the aldehyde (5-17) via a Swern oxidation<sup>10</sup> in 93% yield. (The Dess-Martin procedure was not as an efficient reaction.) A Wittig reaction on 5-17 ultimately afforded 5-15 as a white solid in 88% yield.



Scheme 5-4: Synthetic scheme for the synthesis of 4-iodo-1-vinylcubane (5-15)

### **5-3 ATTEMPTED CATIONIC POLYMERIZATION**

It is well-known that vinyl compounds can be polymerized using a variety of different techniques<sup>11</sup> one of which being cationic polymerization. The field of cationic polymerization has been studied for decades; many books have been written specifically on this area of chemistry.<sup>14-17</sup> The principle of cationic polymerization is illustrated in **Scheme 5-5**. Electron-rich alkenes react in the presence of a Lewis acid and a co-catalyst (*e.g.* water, methanol) to ultimately form the polymer.<sup>14-17</sup> It is believed that initially a Brönsted acid is formed from the Lewis acid, followed by subsequent attack by an alkene.<sup>14-17</sup>



Scheme 5-5: Proposed pathway for cationic polymerization

This technique has been used in the synthesis of many different polymers. One such example is the synthesis of poly(1-vinyladamantane).<sup>18,19</sup> Using AlBr<sub>3</sub> as the Lewis acid to catalyze this reaction, both Majerski and Dovgan were able to polymerize 1-vinyladamatane.<sup>18,19</sup> It was believed that perhaps the vinyl-cubane system may also be polymerized in this way.

The cationic polymerization of **5-15** was performed with  $AlBr_3$ ,  $AlCl_3$ , or  $BF_3$  as the Lewis acid. In all cases, at a variety of concentrations and temperatures, the reactions did not afford the desired polymer. This initially suggested that the monomer was not

100

electron-rich enough however, upon performing the reaction for an extended period of time, a new compound was produced.

#### **5-4 VINYL CUBANE REARRANGEMENT**

When the attempted polymerization of 4-iodo-1-vinylcubane (5-15) was performed by refluxing in toluene for 3 days with a Lewis acid, the result was the formation of an aromatic compound, which was isolated by column chromatography. This compound was identified as 4-vinyl-*trans*- $\beta$ -iodostyrene (5-18); this represents a new styrene derivative. However, it did offer a mystery as to the mechanism for its formation.

Eaton reported that cubane compounds could undergo cage opening with Rh(I) to afford syn-tricyclooctadiene,<sup>5</sup> which upon heating goes through an additional opening to  $cyclooctatetraene^{6}$  (Section 1-10). In addition, Konz noted that form bromocyclooctatetraene rearranges on heating at 80°C to give trans- $\beta$ -bromostyrene.<sup>20</sup> It was therefore postulated that with 5-15, a similar fragmentation must occur. Initially, it was believed that the Lewis acid initiates this rearrangement by pulling electron density away from the cage. However, upon performing a reaction with 5-15 in refluxing toluene for 5 days with no Lewis acid, complete conversion to 5-18 was achieved. Samples were removed periodically during the reaction for NMR analysis. The resulting spectra suggested that a cyclooctatetraene derivative was initially formed (signals correspond to cyclooctatetraene compounds)<sup>9</sup> which upon further heating was converted to 5-18. This represents the first reported example of a cubane compound going through this type of Although the pathway for this rearrangement without the assistance of Rh(I).

rearrangement has not been ascertained, Scheme 5-6 illustrates the initially proposed mechanism.



Scheme 5-6: Possible mechanism for the rearrangement of 4-iodo-1-vinylcubane (5-15) to 4-vinyl-*trans*-β-iodostyrene (5-18) with light

As illustrated in **Scheme 5-6**, the initial step is a 2+2 ring opening, which is thermally forbidden.<sup>21</sup> It was therefore postulated that the driving force for this reaction is the presence of ambient light during the reaction, as well as the resulting formation of a conjugated system. However, when the same reaction was performed in the absence of light, **5-18** was still formed. This suggests that the mechanism in **Scheme 5-6** was incorrect; therefore it was necessary to formulate an alternative mechanism for cage opening.

A possible mechanism for the fragmentation of 5-15 to 5-18 is illustrated in Scheme 5-7. It is reasonable to consider that 5-15 could possess zwitterion character thus inducing the molecule to unravel as indicated. The driving force would be strain relief. In addition, this mechanism does not require light. Another factor that suggests that this is a plausible process is that in the presence of a Lewis acid, the rearrangement is accelerated; possibly the Lewis acid induces the initial fragmentation and stabilizes the proposed charged intermediate thus speeding the process.



Scheme 5-7: Possible mechanism for the rearrangement of 4-iodo-1-vinylcubane (5-15) to 4-vinyl-*trans*-β-iodostyrene (5-18) employing the zwitterion transition state

#### 5-5 ATTEMPTED ANIONIC POLYMERIZATION

Although the initial attempt to polymerize **5-15** *via* cationic polymerization was unsuccessful, there were many other synthetic routes that could be explored.<sup>11</sup> One such method is anionic polymerization.<sup>11,23,24</sup> Typically, this reaction works on alkene monomers that are electron-poor.<sup>25</sup> Many different catalysts can be employed for this type of polymerization. Alkyl or aryl lithium, Grignard, or aluminum reagents are commonly used.<sup>25</sup> Typically, the anion attacks the double bond, and the newly formed alkyl anion can continue to attack additional monomers (**Scheme 5-8**).



Scheme 5-8: Proposed pathway for anionic polymerization

It was therefore necessary to choose an appropriate metal alkyl which could polymerize the alkene functionality, while leaving the iodine on the *para* position untouched. Kern has shown that with styrene, *n*-BuLi is an excellent catalyst for anionic polymerizations;<sup>26</sup> however, as mentioned in Section 1-8, BuLi can extract the iodine from the cube.<sup>27-30</sup> Another catalyst commonly employed in anionic polymerization is diphenylmethylpotassium (DPMP).<sup>31-33</sup> Initially, it was necessary to explore whether DPMP could extract iodine from iodocubane. To a solution of iodocubane in THF, under  $N_2$ , at -78°C; DPMP in THF was added and the system was slowly warmed to room temperature over 1 hour, whereupon MeOH was added to quench the system. Analysis of the resulting mixture showed only diphenylmethane, iodocubane, and no cubane. It was therefore concluded that DPMP would be an appropriate catalyst to attempt anionic polymerization.

When the polymerization of **5-15** was attempted with DPMP as the catalyst, no reaction occurred. In an additional effort, co-polymerization of **5-15** with styrene (10:1, styrene:**5-15**) was attempted, however, only polystyrene was observed, and **5-15** was recovered. This suggested that the vinyl group of **5-15** was not electron-poor enough for anionic polymerization to be successful.

#### **5-6 ATTEMPTED FREE RADICAL POLYMERIZATION**

Yet another attempt at polymerizing 4-iodo-1-vinylcubane (**5-15**) was made using the free radical approach. This technique, as in all polymerization methods, requires an initiation, propagation, and termination step.<sup>11,34-37</sup> Scheme 5-9 illustrates a free radical mechanism. The initiation step usually is accomplished by the homolytic cleavage of one or two sigma bonds to form two radical initiators.<sup>11,34-37</sup> Common free radical initiators are peroxides or azo compounds.<sup>11,34-37</sup> The radical initiator attacks the double bond of vinyl monomers forming a new radical species that can then attack additional monomers during the propagation steps.<sup>36,37</sup> Ultimately, the reaction is terminated when two radical species react with one another to either elongate the chain or react to form a saturated end group on one of the polymers and an unsaturated end group on the other.<sup>36,37</sup>

1. Initiation step



2. Propagation step



2. Termination step



Scheme 5-9: Proposed pathway for free radical polymerization

As in the case of anionic polymerization (Section 5-5), it was imperative to determine whether the iodine of 5-15 could react with the radical initiator. The initiator used in this reaction was 2,2'-azobisisobutyronitrile (AIBN). Mixing AIBN with iodocubane in THF, under N<sub>2</sub> and heating at 60°C for 24 hours, afforded no bicubyl or any other cubyl products, and iodocubane was recovered. This suggested that although the radical fragment of AIBN may extract the iodine of iodocubane (Section 1-7), it is in

equilibrium, and therefore it was possible to attempt the free radical polymerization of 5-15 with AIBN as the initiator.

In a similar approach to those taken with cationic and anionic polymerization, the synthesis of polystyrene was initially performed; this ensured that the technique was performed correctly and the catalyst was sufficiently pure. However, the reaction of **5-15** and AIBN in THF with either heat or UV-light did not proceed. Notably, the reaction that was heated did show the presence of 4-vinyl-*trans*- $\beta$ -iodostyrene (**5-18**) after 5 days. Additional efforts to co-polymerize **5-15** with styrene (10:1 styrene:**5-15**) yielded only a homopolymer of polystyrene, and cubane, **5-15** was recovered.

#### 5-7 ATTEMPTED PALLADIUM-CATALYZED CO-POLYMERIZATION

The results obtained to this point indicated that the polymerization of **5-15** could not be accomplished *via* any of the conventional methods. It was therefore necessary to examine other routes for polymerization. In the early 1950s, Reppe and Magin discovered that ethane could be co-polymerized with carbon monoxide to form a polyketone using the nickel-based catalyst, K<sub>2</sub>Ni(CN)<sub>4</sub>.<sup>38</sup> In the latter part of the 1960s Gough reported that a bis(tertiary phosphine) palladium dichloride catalyst yielded the polyketone at excellent rates.<sup>39</sup> However, extreme conditions were required (250°C, 2000 bar) and the yields were not high.<sup>39</sup> In the 1980s Sen published work that showed that this palladium-based catalyst could be improved by the addition of a weakly coordinating tetrafluoroborate anion.<sup>40,41</sup> The reactions could be carried out under milder conditions (120°C, 70 bar), but the yields were still low.<sup>40,41</sup> Finally, Drent at Shell Research in Amsterdam, reported that the co-polymerization could be accomplished under mild conditions (90°C, 45 bar) and in excellent yields with the use of bidentate tertiary phosphine ligands.<sup>42,43</sup> The evolution of a palladium catalysts for co-polymerization has continued, and Osakada has reported that the use of bidentate nitrogen ligands also afford excellent results.<sup>44,45</sup> Scheme 5-10 illustrates the co-polymerization mechanism of an alkene and carbon monoxide using the palladium-catalyst<sup>46</sup> that Osakada employed.



Scheme 5-10: Mechanism for co-polymerization of vinyl and carbon monoxide with Pd(Me)(bpy)(BARF) in acetonitrile

Using Osakada's methodology,<sup>44</sup> **5-15** in acetonitrile, under one atmosphere of carbon monoxide was reacted with Pd(Me)(bpy)(MeCN)(BARF). By <sup>1</sup>H-NMR, it was determined that there was an initial insertion of carbon monoxide, however, the reaction did not continue even upon heating at 40°C for 5 days. It was postulated that although acetonitrile is a weakly binding ligand,<sup>47</sup> if **5-15** is also weakly binding, then the vast excess of acetonitrile (acetonitrile was the solvent) would hinder the progression of the reaction. Thus, an additional reaction was performed with dichloromethane as the solvent, however, even after 5 days at 40°C, only the initial insertion of carbon monoxide was detected.

### 5-8 ATTEMPTED CYCLOADDITION OF VINYL CUBANE WITH CYCLOPENTADIENE

At this point, the attempted direct synthesis of a polymer from 4-iodo-1vinylcubane (5-15) was abandoned. It was postulated that, if the cube was attached to norbornene (5-19), ring opening metathesis polymerization (ROMP) could be attempted to afford polymer 5-20 (Scheme 5-11).



# Scheme 5-11: Proposed synthetic pathway towards cubane containing-norbornene based polymer, 5-20

Cubane 5-15, was reacted in a Diels-Alder fashion with freshly cracked cyclopentadiene. When this reaction was attempted in refluxing THF under N<sub>2</sub> for 24 hours, no reaction was observed. Performing this reaction in ether, under ~2.7 or ~3.8 atmospheres, under refluxing conditions for 24 hours, only afforded the dimerization of the cyclopentadiene and trace amounts of 4-vinyl-*trans*- $\beta$ -iodostyrene (5-18).

#### **5-9 SYNTHESIS OF CUBANE CONTAINING NORBORNENE MONOMERS**

Although the synthesis of the cubane containing-norbornene based polymer was unsuccessful due to the inability of **5-15** to react with cyclopentadiene, it was still envisioned that if cubane could be attached to norbornene *via* a linker, the ROMP polymerization could be carried out.

Commercially available 5-norbornene-2-carboxylic acid (5-21: mixture of *endo* and *exo*) was reacted initially *via* a Vilsmeier reaction<sup>48</sup> [(COCl)<sub>2</sub>, DMF] to form the acid chloride (5-22). This was subsequently reacted with either 5-16 or 5-23 to form the corresponding esters 5-24 and 5-25. The products existed as a mixture of *endo* and *exo* adducts, which could be separated *via* column chromatography. However, for the purpose of possible polymerization, the separation was not necessary and the purified mixture of diastereomers was used for polymerization.



Scheme 5-12: Synthesis of two cubane derivatives attached to norbornene *via* an ester linkage

## 5-10 SYNTHESIS OF CUBANE CONTAINING NORBORNENE POLYMERS

Two different cubane-containing norbornene derivatives were now available for performing ROMP reactions. Ring opening metathesis polymerization has been extensively investigated since its initial discovery by Eleuterio in 1957 with the successful preparation of polypentenamer and polynorbornene.<sup>49</sup> Since that time, key discoveries have been made in this area of polymer chemistry. In 1964, Natta and

Dall'Asta reported some highly active, soluble catalysts that could polymerize low-strain monomers under mild conditions.<sup>50</sup>

The work in this area of polymerization has produced many commercially available catalysts (*e.g.* **5-26** to **5-28**).<sup>51</sup> Molybdenum complex **5-26** is referred to as the Schrock catalyst;<sup>52</sup> ruthenium complexes **5-27** and **5-28** are referred to as Grubbs catalysts.<sup>53</sup>



Scheme 5-13: Commercially available ROMP catalysts

The reaction is generally believed to go through a 2+2 cycloaddition of the monomeric olefin (5-29) and the carbene attached to the metal of the catalyst (5-30), to form the metallacycle, 5-31 (Scheme 5-14).<sup>52-54</sup> The metallacycle then opens to form a new carbene center, which can react with an additional olefinic monomer and the reaction propagates until the monomer has been completely depleted.<sup>52-54</sup>



Scheme 5-14: Mechanism for ring opening metathesis polymerization (ROMP)

Reacting norbornene 5-24. with bis(tricyclohexylphosphine)benzylidine ruthenium (IV) dichloride (5-28) in THF, under N<sub>2</sub> for 24 hours at room temperature, polymer 5-32 was obtained upon precipitation with pentane. This reaction was repeated using norbornene 5-25, and polymer 5-33, was obtained. (Did not possess a detectable glass transition temperature.) In the synthesis of 5-32, a ratio of ~65:1 of monomer to catalyst (5-24:5-28) was used, and ultimately the polymer exhibited a weight (GPC using polystyrene standards) that corresponds to ~71 units. (Obtaining an exact amount of 5-28 is difficult as it is required to weigh in a glove box, and only 8mg were used.) In the formation of polymer, 5-33, a ratio of ~88:1 of monomer to catalyst (5-25:5-28) was used. This produced a polymer of ~143 units. These represent the first examples of polymers that have a cubane tethered to it. Also, these are the first examples of cubanecontaining polymers where solubility is not an issue. In addition, to determine if other

functional groups could be attached to the cube, polymer 5-32 was reacted with LDBB and quenched with MeOH, and the corresponding product was polymer 5-33 (Scheme 5-15). Thus it is believed that the addition of alternative electrophiles could ultimately deliver a range of cubane-containing norbornene-derived polymers.





#### **5-11 EXPERIMENTAL**





Dry DMSO (0.33mL, 4.7mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (5mL), under N<sub>2</sub>, was cannulated into a stirring solution of oxalyl chloride (0.20mL, 2.3mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (5mL), under N<sub>2</sub>, at -78°C. After 20 minutes at -78°C, 1-iodo-4-(hydroxymethyl)cubane (**5-16**: 0.50g, 1.9mmol) dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20mL), under N<sub>2</sub> was cannulated in and the system was maintained at -78°C for 1.5 hours whereby dry Et<sub>3</sub>N (1.2mL, 8.6mmol) was added *via* syringe. The cooling bath was removed and the mixture was allowed to warm to room temperature. The mixture was quenched with H<sub>2</sub>O (20mL) and separated. Aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 X 20mL), and the combined organic layer was washed with H<sub>2</sub>O (2 X 25mL) and brine (25mL), dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to dryness. Column chromatography [CH<sub>2</sub>Cl<sub>2</sub>] afforded 1-iodocubane-4-carboxaldehyde (**5-17**: 0.46g, 93%) as a white solid; mp 106-109°C (Lit<sup>10</sup> mp 108-110°C).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.29 (m, 3H), 4.51 (m, 3H), 9.73 (s, 1H). <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 35.7, 49.0, 54.8, 62.8, 197.0. 4-Iodo-1-vinylcubane (5-15)



To a suspension of methyltriphenylphosphonium bromide (0.76g, 2.2mmol) in dry THF (20mL), at -78°C, under N<sub>2</sub>, 2.50M *n*-BuLi in hexanes (0.60mL, 1.5mmol), was slowly added. The yellow mixture was stirred for 20 minutes, whereupon 1-iodocubane-4-carboxaldehyde (**5-17**: 0.26g, 1.0mmol) dissolved in dry THF (10mL), under N<sub>2</sub>, was cannulated in and maintained at -78°C for 1 hour. After an additional hour at room temperature the mixture was quenched with H<sub>2</sub>O (15mL). Hexanes (25mL) were added and the layers were separated. The aqueous layer was extracted with hexanes (2 X 25mL), and the combined organic layer was washed with H<sub>2</sub>O (2 X 25mL) and brine (25mL), dried with MgSO<sub>4</sub>, filtered, and evaporated to dryness. Column chromatography [hexanes] afforded 4-iodo-1-vinylcubane (**5-15**: 0.23g, 88%) as a white solid; mp 77-79°C.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 4.09 (m, 3H), 4.19 (m, 3H), 4.92 (dd, 1H, J = 1.95, 17.10Hz), 5.06 (dd, 1H, J = 1.95, 10.60Hz), 6.05 (dd, 1H, J = 10.60, 17.10Hz).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 39.2, 50.5, 54.3, 60.3, 113.2, 136.7.

Elemental anal.: calcd. C<sub>10</sub>H<sub>9</sub>I: C 46.90, H 3.54; found C 47.22, H 3.45.

4-Vinyl-*trans*-β-iodostyrene (5-18)



1-Iodo-4-vinylcubane (**5-15**: 0.050g, 0.20mmol) was refluxed in dry toluene, under N<sub>2</sub>, for 5 days. The mixture was cooled and evaporated to dryness. Column chromatography [hexanes] afforded 4-vinyl-*trans*- $\beta$ -iodostyrene (**5-18**: 0.050g, 94%) as a white solid; mp 101-102°C.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 5.27 (dd, 1H, J = 0.60, 10.80Hz), 5.75 (dd, 1H, J = 0.60, 17.10Hz), 6.67 (dd, 1H, J = 10.80, 17.10Hz), 6.81 (d, 1H, J = 14.70Hz), 7.24 (d, 2H, J = 8.40Hz), 7.35 (d, 2H, J = 8.40Hz), 7.39 (d, 1H, J = 14.70Hz).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 114.3, 126.0, 126.4, 136.1, 136.9, 137.4, 144.4, 149.7. Elemental anal.: calcd. C<sub>10</sub>H<sub>9</sub>I: C 46.90, H 3.54; found C 47.04, H 3.22.
(4'-Iodo-1'-cubylmethyl)-5-norbornene-2-carboxylate (5-24)



To 5-norbornene-2-carboxylic acid (5-21: 0.22g, 1.6mmol) dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (50mL) at 0°C, under N<sub>2</sub>, oxalyl chloride (0.50mL, 5.7mmol) then dry DMF (8µL, 0.10mmol) were added *via* syringe. After 5 minutes at 0°C, the system was warmed to room temperature and stirred for an additional hour, whereupon the mixture was evaporated to near-dryness. The white solid was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (50mL) under N<sub>2</sub>, and 1-iodo-4-(hydroxymethyl)cubane (5-16: 0.20g, 0.79mmol), Et<sub>3</sub>N (0.25mL, 1.8mmol), and DMAP (0.008g, 0.06mmol) were added and the system was stirred at room temperature for 1 hour. After quenching with H<sub>2</sub>O (25mL), the mixture was brought to pH~9 with satd. NaHCO<sub>3</sub>. Separation of layers, washing with H<sub>2</sub>O (2 X 25mL) and brine (25mL), followed by drying with Na<sub>2</sub>SO<sub>4</sub>, filtration, and evaporation, afforded a clear colorless oil. Column chromatography [hexanes/EtOAc (4:1)] yielded (4'-iodo-1'-cubylmethyl)-5-norbornene-2-carboxylate (5-24: 0.28g, 92%) as a white solid; mp 38-45°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.24$  (d, J = 8.40Hz), 1.28-1.44 (m), 1.48 (d, J = 8.00Hz), 1.90 (m), 2.23 (dd, J = 4.40, 10.00Hz), 2.90 (br. s), 2.94 (t, J = 3.20Hz), 2.96 (t, J = 4.00Hz), 2.98 (br. s), 3.16 (br. s), 3.99-4.06 (m), 4.13-4.34 (m), 5.84 (dd, J = 2.80, 5.80Hz), 6.10 (ddd, J = 2.80, 6.00, 12.8 Hz), 6.16 (dd, J = 3.20, 5.20Hz).

118

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): δ = 29.4, 30.5, 38.5, 41.7, 42.5, 43.2, 43.4, 45.8, 46.3, 46.9, 48.4, 49.7, 54.5, 54.6, 54.7, 56.8, 63.7, 63.8, 64.0, 66.6, 132.1, 135.5, 137.7, 137.9, 174.6, 176.2.

MS: calcd. MH<sup>+</sup> 381.0351; found: 381.0359.

Cubylmethyl-5-norbornene-2-carboxylate (5-25)



To 5-norbornene-2-carboxylic acid (5-21: 0.450g, 3.25mmol) dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (50mL) at 0°C, under N<sub>2</sub>, oxalyl chloride (1.10mL, 1.26mmol) then dry DMF (12 $\mu$ L, 0.16mmol) were added *via* syringe. After 5 minutes at 0°C, system was warmed to room temperature and stirred for an additional hour, whereupon the mixture was evaporated to near-dryness. The oil obtained was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (50mL) under N<sub>2</sub>, and cubylcarbinol (5-23: 0.20g, 1.5mmol), Et<sub>3</sub>N (0.50mL, 3.6mmol), and DMAP (0.010g, 0.083mmol) were added and the system was stirred at room temperature for 1.5 hours. After quenching with H<sub>2</sub>O (25mL), the mixture was brought to pH-9 with satd. NaHCO<sub>3</sub>. Separation of layers, washing with H<sub>2</sub>O (2 X 25mL) and brine (25mL), followed by drying with Na<sub>2</sub>SO<sub>4</sub>, filtration, and evaporation, afforded a clear colorless oil. Column chromatography [hexanes/EtOAc (4:1)] yielded cubylmethyl-5-norbornene-2-carboxylate (5-25: 0.36g, 94%) as a clear colorless oil.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.21$ -1-55 (m), 1.86-2.01 (m), 2.24 (dd, J = 4.40, 10.40Hz), 2.90 (br. s), 2.94-2.99 (m), 3.04-3.11 (m), 3.19 (br. s), 3.24 (br. s), 3.85-3.93 (m), 3.99-4.03 (m), 4.11 (d, J = 12.40Hz), 4.19-4.32 (m), 5.89 (dd, J = 3.20, 6.00Hz), 6.09-6.12 (m), 6.16 (dd, J = 2.80, 5.20Hz).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): δ = 29.4, 30.5, 38.5, 41.7, 42.6, 43.3, 43.4, 44.6, 45.8, 45.9, 46.4, 46.9, 47.4, 48.6, 49.6, 55.2, 56.0, 64.6, 64.9, 67.3, 131.8, 135.2, 137.5, 138.1, 174.8, 176.0.

MS: calcd. MH<sup>+</sup> 255.1385; found: 255.1394.

Poly((4'-iodo-1'-cubylmethyl)-5-norbornene-2-carboxylate) (5-32)



To a solution of (4'-iodo-1'-cubylmethyl)-5-norbornene-2-carboxylate (5-24: 0.230g, 0.613mmol) in dry THF (8mL), under N<sub>2</sub>; Grubbs catalyst (5-28: 0.008g, 0.01mmol) dissolved in dry THF (4mL), under N<sub>2</sub>, was cannulated in. The solution went from purple to brown over a period of 5 minutes. and the mixture was stirred at room temperature overnight. Ethyl vinyl ether (0.56mL, 5.9mmol) was added *via* syringe to

quench the reaction, and the mixture was allowed to stir for 10 minutes. Pentane (15mL) was slowly added to the solution, and a precipitate slowly formed. Vacuum filtration and washing with pentane (25mL) afforded poly((4'-iodo-1'-cubylmethyl)-5-norbornene-2-carboxylate) (5-32: 0.19g, 85%) as a white, fluffy, crystalline solid; mp. dec. 253°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.06-1.42 (br, 1H), 1.58-2.09 (br, 3H), 2.37-3.18 (br, 3H), 3.99 (br. s, 3H), 4.18 (br. s, 5H), 5.07-5.45 (br, 2H).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): δ = 35.9, 36.4, 38.3, 39.6, 40.8, 41.1, 41.9, 42.6, 42.9, 45.6, 45.9, 47.5, 48.3, 48.4, 49.4, 54.6, 56.3, 56.6, 63.9, 67.3, 129.2, 132.4, 133.1, 134.3, 174.4, 175.6.

IR (KBr pellet): 3083, 2990, 1729, 1195, 1160, 1028, 837, 799, 660.

GPC (THF, polystyrene standards):  $M_n = 2.7 \times 10^4$  (calculated  $M_n = 23989$ ) and PDI = 1.11. ~71 units.

Poly(cubylmethyl-5-norbornene-2-carboxylate) (5-33)





To a solution of cubylmethyl-5-norbornene-2-carboxylate (5-25: 0.21g, 0.82mmol) in dry THF (8mL), under N<sub>2</sub>; Grubbs catalyst (5-28: 0.008g, 0.01mmol) dissolved in dry THF (4mL), under N<sub>2</sub>, was cannulated in. The solution went from purple to brown over a period of 5 minutes and the mixture was stirred at room temperature overnight. Ethyl vinyl ether (0.56mL, 5.9mmol) was added *via* syringe to quench the reaction, and the mixture was allowed to stir for 10 minutes. Pentane (15mL) was slowly added to the solution, and a precipitate slowly formed. Vacuum filtration and washing with pentane (25mL) afforded poly(cubylmethyl-5-norbornene-2-carboxylate) (5-33: 0.18g, 88%) as a white, crystalline solid; mp. dec. 292°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.02-1.39 (br, 1H), 1.51-2.13 (br, 3H), 2.32-3.04 (br, 3H), 3.99 (br, 6H), 3.99 (br. s, 1H), 4.11-4.23 (br, 2H), 5.05-5.78 (br, 2H).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): δ = 36.0, 36.5, 37.7, 39.9, 40.2, 40.7, 41.1, 41.9, 42.7, 44.6, 45.9, 46.3, 47.4, 48.6, 49.7, 50.3, 55.6, 55.8, 55.9, 64.8, 131.1, 132.8, 134.7, 135.6, 174.7, 175.8.

IR (KBr pellet): 3013, 2980, 1728, 1451, 1356, 1167, 1030, 968, 728.

GPC (THF, polystyrene standards):  $M_n = 3.6 \times 10^4$  (calculated  $M_n = 21479$ ) and PDI = 1.26. ~143 units.

Poly(cubylmethyl-5-norbornene-2-carboxylate) (5-33)



To a solution of poly((4'-iodo-1'-cubylmethyl)-5-norbornene-2-carboxylate) (5-32: 0.12g, 0.0043mmol) dissolved in dry THF (10mL), under N<sub>2</sub>, and cooled to -78°C, a green solution of LDBB in THF was added dropwise *via* syringe, until the solution remained green. After 5 minutes at -78°C, reaction was quenched with MeOH (2mL) and warmed to room temperature. Pentane (25mL) was slowly added to the solution and a precipitate slowly formed. Vacuum filtration and washing with pentane (25mL) afforded poly(cubylmethyl-5-norbornene-2-carboxylate) (5-33: 0.07g, 87%) as a white, crystalline solid; mp. dec.  $284^{\circ}C$ .

IR (KBr pellet): 3021, 2979, 1728, 1450, 1354, 1167, 1034, 968, 725.

GPC (THF, polystyrene standards):  $M_n = 1.9 \times 10^4$  (calculated  $M_n = 17942$ ) and PDI = 1.31. ~71 units.

#### **5-12 REFERENCES**

- 1. Chauvin, Y., Saussine, L. Macromolecules, 1996, 29, 1163.
- 2. Kakuchi, T., Hirahata, W., Yano, S., Kaga, H. Polymer Bulletin, 1997, 38, 651.
- 3. Mahkam, M., Sanjani, N. S. Polym. Int. 2000, 49, 260.
- 4. Kybett, K. D., Carroll, S., Natalis, P., Bonnell, D. W., Margrave, J. L., Franklin, J.
  L. J. Am. Chem. Soc. 1966, 88, 626.
- 5. Cassar, L., Eaton, P. E., Halpern, J. J. Am. Chem. Soc. 1970, 92, 3515.
- Byrd, J. E., Cassar, L., Eaton, P. E., Halpern, J. J. Chem. Soc., Chem. Commun. 1971, 40.
- 7. Klavetter, F. L., Grubbs, R. H. J. Am. Chem. Soc. 1988, 110, 7807.
- 8. Gilson, D. F. R. Personal Communication.
- 9. Eaton, P. E., Stössel, D. J. Org. Chem. 1991, 56, 5138.
- 10. Eaton, P. E., Galoppini, E., Gilardi, R. J. Am. Chem. Soc. 1994, 116, 7588.
- Arshady, R. Desk Reference of Functional Polymers, Syntheses and Applications: American Chemical Society, Washington, DC. 1996.
- 12. Thomas, R. M.; Lightbrown, I. E.; Sparks, W. J.; Frolich, K. P.; Murphree, E. V. Ind. Eng. Chem. 1940, 32, 1283.
- 13. Evans, A. G.; Meadows, G. W.; Polanyi, M. Nature, 1946, 158, 94.
- Kennedy, J. P.; Marichal, E. Carbocationic Polymerization: Wiley Intersciences, New York, 1982.
- 15. Matyjaszewski, K. Cationic Polymerization; Mechanism, Synthesis and Applications: Marcel Dekker, Inc., New York, NY, **1996**.

- Goethals, E. J. Cationic Polymerization and Processes: Academic Press, London, UK, 1984.
- 17. Faust, R., Shaffer, T. D. Cationic Polymerization, Fundamentals and Applications: American Chemical Society, Washington, DC. 1997.
- Dovgan, N. L., Zosim, L. A., Yurchenko, A. G., Murzinova, Z. N., Krasutskii, P.
   A. Visn. Kiiv. Politekh. Inst. Ser. Khim. Mashinobuduv. Teknol. 1976, 13, 54.
- 19. Žuanić, M., Majerski, Z. J. Polym. Sci., Lett. Ed. 1981, 19, 387.
- 20. Huisgen, R., Konz, W. E. J. Am. Chem. Soc. 1970, 92, 4102, 4104, 4105.
- 21. Fleming, I. Frontier Orbitals and Organic Chemical Reactions: John Wiley & Sons, New York, NY, 1996, 210.
- March, J. Advanced Organic Chemistry, 3<sup>rd</sup> ed.: John Wiley & Sons, New York, NY, 1985, 227.
- 23. Tsuruta, T. Anionic Polymerization: Kagakudoujin, Tokyo, Japan, 1973.
- Morton, M. Anionic Polymerization; Principles and Practices: Academic, Orlando, FL, 1983.
- 25. Archer, R. D. Inorganic and Organometallic Polymers: Wiley-VCH, New York, NY, 2001, 68.
- 26. Kern, R. J. Nature, 1960, 187, 410.
- 27. Eaton, P. E., Galoppini, E., Gilardi, R. J. Am. Chem. Soc. 1994, 116, 7588.
- 28. Della, E. W., Head, N. J. J. Org. Chem. 1995, 60, 5303.
- 29. Eaton, P. E., Stossel, D. J. J. Org. Chem. 1991, 56, 5138.
- 30. Eaton, P. E., Yang, C.-X., Xiong, Y. J. Am. Chem. Soc. 1974, 96, 4555.

- 31. Hirao, A., Matsuo, A., Morifufi, K., Tokudo, Y., Hayashi, M. Polym. Adv. Technol. 2001, 12, 680.
- 32. Ishizone, T., Yoshimura, K., Hirao, A., Nakahama, S. *Macromolecules*, 1998, 31, 8706.
- 33. Marie, P., Lingelser, J. P., Gallot, Y. Makromol. Chem. 1982, 183, 2961.
- Moad, G., Solomon, D. H. *The Chemistry of Free Radical Polymerization*: Pergamon, Elsevier Science Ltd., Oxford, UK, 1995.
- 35. Mishra, M. K., Yagci, Y. Handbook of Radical Vinyl Polymerization: Marcel Dekker, Inc., New York, NY, **1998**.
- 36. Archer, R. D. Inorganic and Organometallic Polymers: Wiley-VCH, New York, NY, 2001, 60.
- 37. Cowie, J. M. G. Polymers; Chemistry & Physics of Modern Materials 2<sup>nd</sup> ed.:
   Blackie Academic & Professional, New York, NY, 1991, 52.
- 38. Reppe, W., Magin, A. Chem. Abstr. 1952, 46, 6143.
- 39. Gough, A. Chem Abstr. 1967, 67, 100569.
- 40. Sen, A., Lai, T.-W. J. Am. Chem. Soc. 1982, 104, 3520.
- 41. Sen, A., Lai, T.-W. Organometallics, 1984, 3, 866.
- 42. Drent, E. Chem Abstr. 1985, 102, 46423.
- 43. Drent, E., Van Broekhoven, J. A. M., Doyle, M. J. Organomet. Chem. 1991, 417, 235.
- 44. Kim, S., Takeuchi, D., Osakada, K. J. Am. Chem. Soc. 2002, 124, 762.
- 45. Takeuchi, D., Kim, S., Osakada, K. Angew. Chem., Int. Ed. 2001, 40, 2685.
- 46. Drent, E., Budzelaar, P. H. M. Chem. Rev. 1996, 96, 663.

- 47. Collman, J. P., Hegedus, L. S., Norton, J. R., Finke, R. G. Principals and Applications of Organotransition Metal Chemistry: University Science Books, Mill Valley, CA, 1987, 240.
- 48. Vilsmeier, A, Haack, A. Chem. Ber. 1927, 60, 119.
- 49. Eleuterio, H. S. U.S. Pat. 3,074,918, Jan. 22, 1963.
- 50. Natta, G, Dall'Asta, G., Mazzanti, G. Angew. Chem., Int. Ed. Engl. 1964, 3, 723.
- 51. Strem Chemicals, Inc., Newburyport, MA, U.S.A.
- 52. Schrock, R. R. The Strem Chemiker, Vol. XIV, Strem Chemicals, Newburgport, 1992, No. 1, 1.
- 53. Grubbs, R. H., Pine, S. H. Comprehensive Organic Synthesis, Vol. 5, Chapter 9.3: Pergamon, New York, NY, 1991.
- 54. Mijis, W. J. New Methods for Polymer Synthesis: Plenum Press, New York, NY, 1992.

# **CHAPTER 6**

Conclusions, Contributions to Original Knowledge, and Suggestions for Future Work

## 6-1 CONCLUSIONS, CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

i) The synthesis of cubanethiol was successfully accomplished. The compound is far more stable than was originally postulated. Unlike, other cubane compounds that possess an electron donating group bearing an acidic proton, attached directly to the cube, this cubane derivative has been shown to be relatively stable even when in solution.

i) The oxidation of cubanethiol to dicubyl disulfide was performed and this compound has the shortest C-S bond length of any reported molecule where the carbon is  $sp^3$  hybridized. It was found in collaboration with Dr. J. P. Snyder of Emory University, that this apparently results from the high s-character that the external bonds of cubane possess.

ii) The oxidation of dicubyl disulfide to four different derivatives, as well as the synthesis of two tritylmethyl polysulfides was accomplished.

iii) In order to decrease the cost of chemistry requiring cubylcarbinol as a precursor, new synthetic routes to this intermediate were discovered. The key pathway was a "twoin-one reaction" that performs the reduction of the carboxylic acid, as well as dehalogenation of 4-iodocubanecarboxylic acid using a single reagent to afford the cubylcarbinol. This has increased the overall yield from 66% to 77%, while decreasing the cost for the formation of cubylcarbinol. iv) The first examples of cubane-based dialkoxy disulfides were synthesized. It was found that they have the ability to deliver trappable  $S_2$ , which represents the only examples of non-benzylic dialkoxy disulfide that have this property.

v) A study on the previously unknown photo-induced rearrangement/oxidation of dialkoxy disulfides was undertaken by performing reactions under different atmospheres.

vi) The synthesis and attempted polymerization of a vinyl cubane derivative was performed. The polymerization of this derivative was unsuccessful, however the non rhodium-catalyzed cage opening and eventual rearrangement to a new styrene derivative was accomplished.

vii) The polymerization of a cubane derivative was ultimately achieved by the linkage of the cube moiety to a norbornene residue, followed by subsequent ring opening metathesis polymerization. This afforded two new cubane-based polymers, which represent the first examples of this type of polymer where solubility is not an issue. This was carried out by having the cubane functionality tethered off the backbone of the cube, and not incorporated within.

130

## **6-2 FUTURE WORK**

These studies have shown that the field of cubane chemistry can be further expanded from traditional patterns. Unlike sulfur-functionalized cubane, no reported results exist concerning selenium or telerium-functionalization of cubane. This work could also provide interesting insights, perhaps similar to those obtained for dicubyl disulfide.

The photo-induced rearrangement of *bis*-cubylmethyldialkoxy disulfide to *bis*cubylmethylsulfite is the first example of its kind. It would be interesting to determine if other dialkoxy disulfides participate in this type of rearrangement. In addition, the liberation of trappable  $S_2$  from cubane-based dialkoxy disulfides was successful due to (what is believed to be), the acidic nature of the methylene protons. A study to investigate the required acidity of these protons would also be of interest.

It has now been determined that it is possible to obtain a cubane-based polymer (not oligomer) using the technique of tethering the cube to the backbone of a polymer. The additional research that could be performed in this area could include formation of alternate polymer backbones, as well as derivatizing the existing cubane of the polymer for possible nitration or cross-linking.

# **APPENDIX** A

# X-RAY STRUCTURE OF S-CUBYL-N,N-DIMETHYLDITHIOCARBAMATE (2-7)

#### CRYSTAL AND MOLECULAR STRUCTURE OF

Cll H13 N S2 (harp64)

### Ron Priefer (David Harpp)

## Departement of chemistry, McGill University,

Otto Maass Chemistry Blg, 801 Sherbrooke St. W. Montreal, Canada, H3A 2K6

Structure solved by X-Ray crystallography laboratory, chemistry department, McGill University by Dr Anne-Marie Lebuis, November 14, 2001 Table 1. Crystal data and structure refinement for C11 H13 N S2.

Identification code harp64 Empirical formula C11 H13 N S2 Formula weight, Mr 223.34 Cell setting Monoclinic P2(1)/cSpace group Unit cell dimensions (A, deg) a = 15.2722(11)alpha = 90b = 6.0801(5)beta = 105.316(5)c = 11.9964(8)gamma = 90 Volume of unit cell, V (A^3) 1074.38(14) Formula units per cell, Z 4 Formula units per assymetric unit, Z' 1 Density calculated from formula and cell, Dx (Mg/m<sup>3</sup>) . 1.381 F(000) 472 Radiation type CuKa Wavelength, lambda (A) 1.54178 No. of reflections for cell measurement 1688 Theta range (deg) 3.0 to 69.9 Linear absorption coefficient, mu (mm^-1) 4.136 Measurement temperature (K) 293(2) Crystal shape very thin plate Colour colourless Size (mm) 0.74 x 0.36 x 0.01 Data collection Diffractometer type Bruker AXS Smart 2K/Platform Data-collection method phi scans Absorption correction type Multi scan

Max and min transmission values 0.98 and 0.52 No. of reflections measured 12012 No. of independent reflections 2051 Completeness of data to Theta max 1.000 No. of observed reflections 1729 Criterion for observed reflections >2sigma(I) Rint 0.1120 Theta range for data collection 3.00 to 70.21 deg. -18<=h<=18, -7<=k<=6, -14<=l<=14 Ranges of h,k,l No. of standard reflections 109 Intensity decay (%) none Refinement Refinement method Full-matrix on F<sup>2</sup> Final R indices, I>2sigma(I) R1 = 0.0551, wR2 = 0.1586R indices, all data R1 = 0.0603, WR2 = 0.1586Goodness-of-fit on F<sup>2</sup>, S 1.025  $R1 = sum (absabs Foabs -abs Fcabsabs )/sum (abs Foabs ), \\ wR2 = [sum [w(Fo^2^-Fc^2^)^2]/sum [w(Fo^2^-)^2]]^1*2^ and$  $GoF = [sum [w(Fo^2^-Fc^2)^2]/(No. of reflns - No. of params.)]^1*2^{-1}$ Data / restraints / parameters 2051 / 0 / 129 Method of refining and locating H atoms riding Weighting scheme based on measured s.u.'s Function minimized sum  $w(Fo^2^-Fc^2)$ calc w=1/[ $s^2$ (Fo<sup>2</sup>)+(0.1165P)<sup>2</sup>+0.0294P] where P=(Fo<sup>2</sup>+2Fc<sup>2</sup>)/3 Maximum shift/sigma 0.003 Largest diff. peak and hole 0.367 and -0.367 e.A<sup>\*3</sup>

135

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (A<sup>2</sup> x 10 <sup>2</sup>) for C11 H13 N S2.

verse construction of the second	x	У	Z	U(eq)	
				<u></u>	·····
S(1)	0.24769(5)	-0.07364(11)	0.62677(5)	6.26(3)	
S(2)	0.14657(5)	0.34910(10)	0.61632(6)	6.22(3)	
N(1)	0.11021(14)	0.0378(3)	0.45534(16)	5.44(5)	
C(1)	0.30692(16)	0.0734(4)	0.74999(19)	5.00(5)	
C(2)	0.39253(18)	-0.0427(5)	0.8307(2)	6.41(7)	
C(3)	0.44638(19)	0.1755(6)	0.8394(3)	8.01(9)	
C(4)	0.36180(18)	0.2922(5)	0.7586(2)	6.33(7)	
C(5)	0.27506(17)	0.1404(4)	0.8586(2)	5.32(6)	
C(6)	0.36023(19)	0.0266(5)	0.9381(2)	6.44(7)	
C(7)	0.41399(19)	0.2451(6)	0.9469(2)	7.45(8)	
C(8)	0.3287(2)	0.3584(4)	0.8660(2)	6.52(7)	
C(9)	0.16094(16)	0.1089(4)	0.55596(19)	4.79(5)	
C(10)	0.1236(2)	-0.1720(4)	0.4034(3)	7.07(7)	
C(11)	0.03610(18)	0.1704(5)	0.3848(2)	6.79(7)	

U-eq- = (1/3)sum-i-sum-j-U-ij-a^\*^-i-a^\*^-j-a-i-.a-j-.

S(1) - C(1)	1.760(2)	S(1) - C(9)	1.765(2)	
S(2)-C(9)	1.670(2)	N(1) - C(9)	1.323(3)	
N(1) - C(10)	1.458(3)	N(1) - C(11)	1.463(3)	
C(1)-C(5)	1.561(3)	C(1) - C(4)	1.561(3)	
C(1) - C(2)	1.574(3)	C(2) - C(3)	1.550(4)	
C(2) - C(6)	1.555(3)	C(2)-H(2)	0.9800	
C(3) - C(7)	1.557(4)	C(3) - C(4)	1.565(4)	
C(3)-H(3)	0.9800	C(4) - C(8)	1.556(4)	
C(4) - H(4)	0.9800	C(5) - C(8)	1.549(3)	
C(5)-C(6)	1.557(3)	C(5)-H(5)	0.9800	
C(6) - C(7)	1.551(4)	C(6)-H(6)	0.9800	
C(7) - C(8)	1.563(4)	C(7) - H(7)	0.9800	
C(8)-H(8)	0.9800	C(10) - H(10A)	0.9600	
C(10)-H(10B)	0.9600	C(10) - H(10C)	0.9600	
C(11) - H(11A)	0.9600	C(11) - H(11B)	0.9600	
C(11)-H(11C)	0.9600	- ( , , - , - , - , - , - , -		
C(1)-S(1)-C(9)	103.82(11)	C(9)-N(1)-C(10)	124.2(2)	
C(9) - N(1) - C(11)	121.6(2)	C(10) - N(1) - C(11)	114.2(2)	
C(5) - C(1) - C(4)	90.13(18)	C(5) - C(1) - C(2)	89.70(18)	
C(4) - C(1) - C(2)	89.83(19)	C(5) - C(1) - S(1)	129.02(18)	
C(4) - C(1) - S(1)	129.54(17)	C(2) - C(1) - S(1)	116.65(17)	
C(3) - C(2) - C(6)	89.5(2)	C(3) - C(2) - C(1)	89.8(2)	
C(6) - C(2) - C(1)	89.70(19)	C(3)-C(2)-H(2)	125.5	
C(6)-C(2)-H(2)	125.5	C(1) - C(2) - H(2)	125.5	
C(2) - C(3) - C(7)	90.5(2)	C(2) - C(3) - C(4)	90.6(2)	
C(7) - C(3) - C(4)	89.9(2)	C(2) - C(3) - H(3)	125.0	
C(7)-C(3)-H(3)	125.0	C(4) - C(3) - H(3)	125.0	
C(8) - C(4) - C(1)	89.40(17)	C(8)-C(4)-C(3)	90.0(2)	
C(1) - C(4) - C(3)	89.7(2)	C(8) - C(4) - H(4)	125.5	
C(1) - C(4) - H(4)	125.5	C(3) - C(4) - H(4)	125.5	
C(8) - C(5) - C(6)	90.1(2)	C(8) - C(5) - C(1)	89.68(17)	
C(6) - C(5) - C(1)	90.06(18)	C(8) - C(5) - H(5)	125.3	
C(6) - C(5) - H(5)	125.3	C(1) - C(5) - H(5)	125.3	
C(7) - C(6) - C(2)	90.6(2)	C(7)-C(6)-C(5)	90.1(2)	
C(2) - C(6) - C(5)	90.54(18)	C(7)-C(6)-H(6)	125.0	
C(2) - C(6) - H(6)	125.0	C(5)-C(6)-H(6)	125.0	
C(6) - C(7) - C(3)	89.4(2)	C(6)-C(7)-C(8)	89.8(2)	
C(3) - C(7) - C(8)	90.0(2)	C(6) - C(7) - H(7)	125.4	
C(3) - C(7) - H(7)	125.4	C(8)-C(7)-H(7)	125.4	
C(5) - C(8) - C(4)	90.78(19)	C(5) - C(8) - C(7)	90.0(2)	
C(4) - C(8) - C(7)	90.0(2)	C(5)-C(8)-H(8)	125.1	
C(4) - C(8) - H(8)	125.1	C(7) - C(8) - H(8)	125.1	
N(1) - C(9) - S(2)	124.69(18)	N(1) - C(9) - S(1)	114.69(18)	
S(2) - C(9) - S(1)	120.61(14)	N(1) - C(10) - H(10A)	109.5	
N(1) - C(10) - H(10B)	109.5	H(10A) - C(10) - H(10B)	109.5	
N(1) - C(10) - H(10C)	109.5	H(10A) -C(10) -H(10C)	109.5	
H(10B)-C(10)-H(10C)	109.5	N(1) - C(11) - H(11A)	109.5	
	100 5	U(11) - C(11) - U(11)	109 5	
N(1) - C(11) - H(11B)	109.5	$\mathbf{n}(\mathbf{TTW}) = \mathbf{C}(\mathbf{TT}) = \mathbf{n}(\mathbf{TTP})$	TO3'3	
N(1)-C(11)-H(11B) N(1)-C(11)-H(11C)	109.5	H(11A) - C(11) - H(11B) H(11A) - C(11) - H(11C)	109.5	

C(9) - S(1) - C(1) - C(5)	68.8(2)	C(9) - S(1) - C(1) - C(4)	-63.5(2)
C(9) - S(1) - C(1) - C(2)	-177.67(17)	C(5) - C(1) - C(2) - C(3)	-89.9(2)
C(4) - C(1) - C(2) - C(3)	0.3(2)	S(1) - C(1) - C(2) - C(3)	135.57(19)
C(5) - C(1) - C(2) - C(6)	-0.3(2)	C(4) - C(1) - C(2) - C(6)	89.8(2)
S(1) - C(1) - C(2) - C(6)	-134.91(19)	C(6) - C(2) - C(3) - C(7)	0.0(2)
C(1) - C(2) - C(3) - C(7)	89.6(2)	C(6) - C(2) - C(3) - C(4)	-90.0(2)
C(1) - C(2) - C(3) - C(4)	-0.3(2)	C(5) - C(1) - C(4) - C(8)	-0.60(19)
C(2) - C(1) - C(4) - C(8)	-90.3(2)	S(1) - C(1) - C(4) - C(8)	144.3(2)
C(5) - C(1) - C(4) - C(3)	89.4(2)	C(2) - C(1) - C(4) - C(3)	-0.3(2)
S(1) - C(1) - C(4) - C(3)	-125.7(2)	C(2) - C(3) - C(4) - C(8)	89.7(2)
C(7) - C(3) - C(4) - C(8)	-0.8(2)	C(2) - C(3) - C(4) - C(1)	0.3(2)
C(7) - C(3) - C(4) - C(1)	-90.2(2)	C(4) - C(1) - C(5) - C(8)	0.60(19)
C(2) - C(1) - C(5) - C(8)	90.4(2)	S(1) - C(1) - C(5) - C(8)	-144.6(2)
C(4) - C(1) - C(5) - C(6)	-89.49(19)	C(2) - C(1) - C(5) - C(6)	0.3(2)
S(1)-C(1)-C(5)-C(6)	125.3(2)	C(3) - C(2) - C(6) - C(7)	0.1(2)
C(1) - C(2) - C(6) - C(7)	-89.8(2)	C(3) - C(2) - C(6) - C(5)	90.2(2)
C(1) - C(2) - C(6) - C(5)	0.3(2)	C(8) - C(5) - C(6) - C(7)	0.6(2)
C(1) - C(5) - C(6) - C(7)	90.23(19)	C(8) - C(5) - C(6) - C(2)	-90.0(2)
C(1) - C(5) - C(6) - C(2)	-0.3(2)	C(2) - C(6) - C(7) - C(3)	0.0(2)
C(5) - C(6) - C(7) - C(3)	-90.6(2)	C(2) - C(6) - C(7) - C(8)	90.0(2)
C(5) - C(6) - C(7) - C(8)	-0.6(2)	C(2) - C(3) - C(7) - C(6)	0.1(2)
C(4) - C(3) - C(7) - C(6)	90.6(2)	C(2) - C(3) - C(7) - C(8)	-89.7(2)
C(4) - C(3) - C(7) - C(8)	0.8(2)	C(6) - C(5) - C(8) - C(4)	89.5(2)
C(1) - C(5) - C(8) - C(4)	-0.60(19)	C(6) - C(5) - C(8) - C(7)	-0.6(2)
C(1) - C(5) - C(8) - C(7)	-90.6(2)	C(1) - C(4) - C(8) - C(5)	0.60(19)
C(3) - C(4) - C(8) - C(5)	-89.1(2)	C(1) - C(4) - C(8) - C(7)	90.6(2)
C(3) - C(4) - C(8) - C(7)	0.8(2)	C(6) - C(7) - C(8) - C(5)	0.6(2)
C(3) - C(7) - C(8) - C(5)	89.9(2)	C(6) - C(7) - C(8) - C(4)	-90.23(19)
C(3) - C(7) - C(8) - C(4)	-0.8(2)	C(10) - N(1) - C(9) - S(2)	179.80(19)
C(11) - N(1) - C(9) - S(2)	1.5(3)	C(10) - N(1) - C(9) - S(1)	-0.9(3)
C(11) - N(1) - C(9) - S(1)	-179.18(18)	C(1) - S(1) - C(9) - N(1)	175.92(16)
C(1) - S(1) - C(9) - S(2)	-4.77(18)		
· · · · · · · · · · · · · · · · · · ·			

					-	
	x	У	Z	U~iso~		
H(2)	0.4153	-0.1885	0.8178	7.7		
H(3)	0.5088	0.1885	0.8327	9.6		
H(4)	0.3628	0.3890	0.6937	7.6		
H(5)	0.2129	0.1267	0.8662	6.4		
H(6)	0.3597	-0.0696	1.0035	7.7		
H(7)	0.4526	0.3081	1.0182	8.9		
H(8)	0.3056	0.5039	0.8790	7.8		
H(10A)	0.1704	-0.2536	0.4564	10.6		
H(10B)	0.1412	-0.1460	0.3334	10.6		
H(10C)	0.0681	-0.2545	0.3861	10.6		
H(11A)	0.0548	0.2341	0.3215	10.2		
H(11B)	0.0210	0.2854	0.4313	10.2		
H(11C)	-0.0161	0.0788	0.3553	10.2		

Table 5. Hydrogen coordinates and isotropic displacement parameters (A^2^ x 10 ^2^) for Cl1 H13 N S2.

Table 6. Anisotropic parameters (A<sup>2</sup> x 10<sup>2</sup>) for Cl1 H13 N S2.

The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a\*^2 U11 + ... + 2 h k a\* b\* U12 ]

		· · · · · · · · · · · · · · · · · · ·				
	Ull	U22	U33	U23	<b>U1</b> 3	U12
C (1)	7 65 (5)	5 10 (4)	5 00(4)	-0.58(2)	-0 14(3)	1 59(3)
S(1) C(2)	(-00)(5)	5.10(4)	5.00(4)	-0.58(2)	-0.14(3)	1.59(3) 1.05(3)
S(2)	5.99(3) 5 g1(12)	4.96(11)	4 81 (10)	-0.07(2)	0.33(3)	-0.71(8)
( <b>1</b> )	5.91(12)	4.90(II) 5.01(12)	4.01(10)	0.00(8)	0.30(9)	-0.71(0)
	= 00(14)	5.01(13)	4.33(11)	0.24(3)	0.03(9)	0.07(3)
C(2)	5.89(14)	10 1 (1)	5.30(13)	0.39(12)	0.02(11)	1.74(12)
C(3)	4.83(14)	12.1(3)	5.77(10)	1.11(10)	0.07(13)	-0.46(13
C(4)	5.97(14)	7.33(16)	5.58(14)	0.76(12)	1.35(11)	-1.16(13
C(5)	5.26(13)	5.68(14)	4.98(12)	-0.11(10)	1.26(10)	-0.08(10
C(6)	6.83(16)	7.72(18)	4.22(12)	0.51(12)	0.45(11)	0.04(13
C(7)	6.60(16)	9.2(2)	5.53(14)	-0.51(15)	-0.11(12)	-1.36(16
C(8)	7.16(16)	5.66(16)	6.33(15)	-1.00(12)	1.08(13)	-0.71(12
C(9)	5.25(12)	4.16(11)	4.70(11)	0.79(9)	0.85(9)	-0.28(9)
C(10)	8.53(19)	6.05(16)	5.69(15)	-0.57(12)	0.20(13)	-1.39(14
C(11)	5.68(14)	7.72(19)	5.99(15)	1.61(13)	-0.19(12)	-0.52(12

Table 7. Distances to the weighted least-squares planes for C11 H13 N S2.

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (\* indicates atom used to define plane)

### PLANE 1

-11.8717 (0.0150) x -2.6487 (0.0044) y +7.7141 (0.0235) z =2.0896 (0.0179)

\* 0.0000 (0.0000) S1 \* 0.0000 (0.0000) C9 \* 0.0000 (0.0000) S2 0.0144 (0.0059) N1 -0.1421 (0.0052) C1

Rms deviation of fitted atoms = 0.0000

#### PLANE 2

- 11.7535 (0.0350) x - 2.6657 (0.0109) y + 7.8098 (0.0187) z = 2.1600 (0.0132)

Angle to previous plane (with approximate esd) = 0.76 ( 0.34 )

\* 0.0000 (0.0000) N1
\* 0.0000 (0.0000) C9
\* 0.0000 (0.0000) S2
-0.0042 (0.0040) C10
-0.0335 (0.0069) C11
0.0201 (0.0082) S1

Rms deviation of fitted atoms = 0.0000

Discussion data collection, structure determination and refinement procedure

X-ray crystallographic data for I were collected from a single crystal sample, which was mounted on a glass fiber. Data were collected using a Bruker Platform diffractometer, equipped with a Bruker SMART 2K Charged-Coupled Device (CCD) Area Detector using the program SMART and normal focus sealed tube source graphite monochromated Cu-K\_ radiation. The crystal-to-detector distance was 4.908 cm, and the data collection was carried out in 512 x 512 pixel mode, utilizing 4 x 4 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 9.0 degree scan in 30 frames over four different parts of the reciprocal space (120 frames total). One complete sphere of data was collected, to better than 0.8\_A resolution. Upon completion of the data collection, the first 101 frames were recollected in order to improve the decay correction analysis.

Data reduction processing was carried out by the use of the program SAINT (Bruker, 1999), which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS (Sheldrick, 1996) was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The space group was confirmed by XPREP routine in SHELXTL program (Sheldrick, 1997). The structure was solved by direct method using SHELXS97 (Sheldrick, 1997) and difmap synthesis using SHELXL96 (Sheldrick, 1996). All non-hydrogen atoms anisotropic, hydrogen atoms isotropic. Hydrogen atoms constrained to the parent site using a riding model; SHELXL96 defaults, C-H 0.93 to 0.97 and O-H 0.82\_A. The isotropic factors, Uiso, were adjusted to a value 50% higher then U(eq) of the parent site (methyl and hydroxyl) and 20% higher (others).

A final verification of possible voids was performed using the VOID routine of the PLATON program (Spek, 1995).

#### REFERENCES

International Tables for Crystallography (1992). Vol. C. Tables 4.2.6.8 and 6.1.1.4, Dordrecht: Kluwer Academic Publishers.

SAINT (1999) Release 6.06; Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, WI 53719-1173.

Sheldrick, G.M. (1996). SADABS, Bruker Area Detector Absorption Corrections. Bruker AXS Inc., Madison, WI 53719-1173.

Sheldrick, G.M. (1997). SHELXS97, Program for the Solution of Crystal Structures. Univ. of Gottingen, Germany.

Sheldrick, G.M. (1997). SHELXL97, Program for the Refinement of Crystal Structures. Univ. of Gottingen, Germany.

SHELKTL (1997) Release 5.10; The Complete Software Package for Single Crystal Structure Determination. Bruker AXS Inc., Madison, WI 53719-1173.

SMART (1999) Release 5.059; Bruker Molecular Analysis Research Tool. Bruker AXS Inc., Madison, WI 53719-1173.

Spek, A.L. (1995. PLATON, Molecular Geometry Program, July 1995 version. University of Utrecht, Utrecht, Holland. (version 190499 at McGill)

XPREP (1997) Release 5.10; X-ray data Preparation and Reciprocal space Exploration Program. Bruker AXS Inc., Madison, WI 53719-1173.





# **APPENDIX B**

# X-RAY STRUCTURE OF DICUBYL DISULFIDE (2-2)

### CRYSTAL AND MOLECULAR STRUCTURE OF

C16 H14 S2 (harp59)

Ron Priefer (David N. Harpp)

Departement of chemistry, McGill University,

Otto Maass Chemistry Blg, 801 Sherbrooke St. W. Montreal, Canada, H3A 2K6

Structure solved by X-Ray crystallography laboratory, chemistry department, McGill University by Dr Anne-Marie Lebuis, date july 2001 Table 1. Crystal data and structure refinement for C16 H14 S2.

Identification code harp59 Empirical formula C16 H14 S2 Formula weight, Mr 270.39 Cell setting Triclinic P-1 Space group Unit cell dimensions (A, deg) a = 6.1315(1)alpha = 79.081(1)b = 9.2705(1)beta = 77.334(1)c = 11.2898(1)qamma = 88.980(1)Volume of unit cell, V (A<sup>3</sup>) 614.60(2) Formula units per cell, Z 2 Formula units per assymetric unit, Z' Density calculated from formula and cell, Dx (Mg/m<sup>3</sup>) 1.461 F(000) 284 Radiation type CuK\a Wavelength, lambda (A) 1.54178 No. of reflections for cell measurement 6674 Theta range (deg) 4.1 to 72.7 Linear absorption coefficient, mu (mm^-1) 3.706 Measurement temperature (K) 293(2) Crystal shape plate Colour colourless Size (mm) 0.76 x 0.50 x 0.03 Data collection Diffractometer type Bruker AXS SMART 2K/Platform Data-collection method omega scans Absorption correction type Semi-empirical from equivalents

Max and min transmission values 0.90 and 0.17 No. of reflections measured 7412 No. of independent reflections 2360 Completeness of data to Theta max 0.959 No. of observed reflections 2192 Criterion for observed. reflections >2sigma(I) 0.0606 Rint Theta range for data collection 4.09 to 72.93 deg. Ranges of h, k, l -6<=h<=7, -11<=k<=11, -13<=1<=13 No. of standard reflections 58 Intensity decay (%) ñ0,0 Refinement Refinement method Full-matrix on F<sup>2</sup> Final R indices, I>2sigma(I) R1 = 0.0666, wR2 = 0.1913 R indices, all data R1 = 0.0681, wR2 = 0.1913Goodness-of-fit on F<sup>2</sup>, S 1.083 R1 = sum (absabs Foabs - abs Fcabsabs )/sum (abs Foabs ),  $wR2 = [sum [w(Fo^2^-Fc^2^)^2]/sum [w(Fo^2^)^2]]^{1*2}$  and GoF = [sum [w(Fo<sup>2</sup>-Fc<sup>2</sup>)<sup>2</sup>]/(No. of reflns - No. of params.)]<sup>1</sup>\*2<sup>\*</sup> Data / restraints / parameters 2360 / 0 / 163 Method of refining and locating H atoms calculated Weighting scheme based on measured s.u.'s Function minimized sum  $w(Fo^2^-Fc^2^)$ calc w=1/[ $s^2^{(Fo^2^)}$ +(0.1485P)<sup>2</sup>+0.0717P] where P=(Fo<sup>2</sup>+2Fc<sup>2</sup>)/3 Maximum shift/sigma 0.001 Largest diff. peak and hole

148

	x	У	Z	U(eq)
S(1)	0.31346(11)	0.27473(6)	0.90630(5)	4.72(3)
S(2)	-0.01981(10)	0.31725(6)	0.92930(5)	4.50(3)
C(11)	-0.0815(4)	0.7012(2)	0.75998(19)	3.90(5)
C(2)	0.2170(4)	0.0049(2)	0.8201(2)	3.62(5)
C(9)	-0.0353(3)	0.4619(2)	0.80371(18)	3.40(5)
C(10)	0.1244(4)	0.5993(2)	0.75513(19)	3.67(5)
C(1)	0.3595(3)	0.1476(2)	0.80496(19)	3.52(5)
C(12)	-0.2428(3)	0.5645(2)	0.80914(19)	3.75(5)
C(15)	-0.0855(4)	0.6894(3)	0.6246(2)	4.47(6)
C (6)	0.2405(4)	0.0325(3)	0.6771(2)	3.94(5)
C (3)	0.4350(4)	-0.0858(2)	0.8073(2)	4.36(6)
C(14)	0.1211(4)	0.5868(3)	0.6196(2)	4.42(6)
C(7)	0.4579(4)	-0.0594(3)	0.6639(2)	4.66(6)
C(13)	-0.0405(4)	0.4498(3)	0.6683(2)	4.40(6)
C(4)	0.5794(4)	0.0563(3)	0.7916(2)	4.64(6)
C(5)	0.3839(4)	0.1755(2)	0.6612(2)	4.01(5)
C(16)	-0.2463(4)	0.5520(3)	0.6737(2)	4.56(6)
C(8)	0.6008(4)	0.0831(3)	0.6482(2)	4.97(6)

U~eq~ = (1/3)sum~i~sum~j~U~ij~a^\*^~i~a^\*^~j~a~i~.a~j~.

	gens (A) and any		
S(1) - C(1)	1.771(2) S(1)	-5(2) 2.0435(	9)
S(2) - C(9)	1.775(2) C(11	) = C(15) 1.558(3)	)
C(11) - C(12)	1.559(3) C(11	$) - C(10) \qquad 1.560(3)$	)
C(11) - H(11)	0.9800 $C(2)$	-C(1) 1.560(3	)
C(2) - C(6)	1.560(3) C(2)	-C(3) 1 561 (3	)
C(2) - H(2)	0.9800 $C(9)$	-C(10) 1 558(3	) )
C(2) - C(13)	1.561(3) C(9)	-C(12) 1.530(3	)
C(10) - C(14)	1.561(3) C(10	) - H(10) = 0.9800	,
C(1) = C(5)	1.568(3) . C(1)	-C(4) 1 573(3	)
C(12) = C(16)	1.560(3) $C(12)$	) - H(12) 0 9800	,
C(12) = C(16)	1.562(4) C(15	) = C(14) 1 567 (3	1
C(15) - H(15)	0.9800 C(5)	-C(7) 1 563 (3	)
C(6) = C(5)	1.564(3) C(6)	-H(6) 0.9800	1
C(3) = C(4)	1.560(3) $C(3)$	-C(7) 1 566 (3)	\ \
C(3) - H(3)	0.9800 + C(14)	(13) = 0(13)	) )
C(34) = H(14)	0.9800 C(1)	-C(8) 1.501(4	/ · · · · · · · · · · · · · · · · · · ·
C(14) = H(7)	0.9800 C(13	C(16) 1.550 (4)	)
C(13) - H(13)	0.9800 C(4)	-C(8) = 1.562(3)	)
C(4) - H(4)	0.9800 - C(5)	-C(8) - 1 = 63(3)	) N
C(4) = H(5)	0.9800 C(16	-E(0) 1.505(5) -H(16) 0.9800	)
C(3) - H(3)		)-H(10) 0.9800	
C(0) $H(0)$	0.000		
C(1) = S(1) = S(2)	104 55(7)	C(9) - S(2) - S(1)	101 29(7)
C(15) - C(11) - C(12)	89 99(17)	C(15) = C(11) = C(10)	89 87 (15)
C(12) - C(11) - C(10)	90.35(15)	C(15) - C(11) - H(11)	125.2
C(12) - C(11) - H(11)	125 2	C(10) = C(11) = H(11)	125.2
C(1) - C(2) - C(6)	89.52(15)	C(10) = C(2) = C(3)	89 68 (16)
C(6) = C(2) = C(3)	90,30(15)	C(1) = C(2) = H(2)	125 4
C(6) - C(2) - H(2)	125.4	C(3) - C(2) - H(2)	125.4
C(10) - C(9) - C(13)	90.46(16)	C(10) - C(9) - C(12)	89 94 (15)
C(13) - C(9) - C(12)	90.21(15)	C(10) = C(9) = S(2)	126 35 (15)
C(13) - C(9) - S(2)	127.93(15)	C(12) - C(9) - S(2)	120.05(15) 120.87(14)
C(9) - C(10) - C(11)	90.09(16)	C(9) - C(10) - C(14)	89 68 (17)
C(11) - C(10) - C(14)	90.39(15)	C(9) - C(10) - H(10)	125 2
C(11) - C(10) - H(10)	125.2	C(14) - C(10) - H(10)	125.2
C(2) - C(1) - C(5)	90.60(15)	C(2) - C(1) - C(4)	90 32 (16)
C(5) - C(1) - C(4)	90.00(15)	C(2) - C(1) - S(1)	125 58(15)
C(5) - C(1) - S(1)	129.34(14)	C(4) - C(1) - S(1)	119.89(16)
C(11) - C(12) - C(16)	90.14(17)	C(11) = C(12) = C(9)	89 62 (15)
C(16) - C(12) - C(9)	89.40(15)	C(11) - C(12) - H(12)	125 5
C(16) - C(12) - H(12)	125.5	C(9) - C(12) - H(12)	125.5
C(11) - C(15) - C(16)	90.09(16)	C(11) = C(15) = C(14)	90 25 (16)
C(16) - C(15) - C(14)	90.02(18)	C(11) - C(15) - H(15)	125 2
C(16) - C(15) - H(15)	125.2	C(14) - C(15) - H(15)	125.2
C(2) - C(6) - C(7)	89,89(16)	C(2) - C(6) - C(5)	90 78 (16)
C(7) - C(6) - C(5)	90.04(17)	C(2) - C(6) - H(6)	125 1
C(7) - C(6) - H(6)	125.1	C(5) - C(6) - H(6)	125 1
C(4) - C(3) - C(2)	90.76(15)	C(4) - C(3) - C(7)	89 79 (1.2)
C(2) - C(3) - C(7)	89,80(15)	C(4) - C(3) - H(3)	125.2
C(2) - C(3) - H(3)	125.2	C(7) - C(3) - H(3)	125 2
C(10) - C(14) - C(13)	90.31(16)	C(10) - C(14) - C(15)	89 49 (16)
C(13) - C(14) - C(15)	89.78(18)	C(10) - C(14) - H(14)	125.4
C(13) - C(14) - H(14)	125.4	C(15) - C(14) - H(14)	125.4

Table 3. Bond lengths (A) and angles (deg) for C16 H14 S2



C(8) - C(7) - C(6)	89.95(17)	C(8) - C(7) - C(3)	90.24(18)	
C(6) - C(7) - C(3)	90.01(16)	C(8)-C(7)-H(7)	125.2	
C(6) - C(7) - H(7)	125.2	C(3) - C(7) - H(7)	125.2	
C(9) - C(13) - C(14)	89.55(16)	C(9) - C(13) - C(16)	89.75(15)	
C(14) - C(13) - C(16)	90.24(17)	C(9)-C(13)-H(13)	125.4	
C(14)-C(13)-H(13)	125.4	C(16)-C(13)-H(13)	125.4	
C(3) - C(4) - C(8)	90.14(18)	C(3) - C(4) - C(1)	89.24(17)	
C(8) - C(4) - C(1)	89.65(16)	C(3) - C(4) - H(4)	125.5	
C(8) - C(4) - H(4)	125.5	C(1) - C(4) - H(4)	125.5	
C(8) - C(5) - C(6)	89.77(16)	C(8) - C(5) - C(1)	89.92(16)	
C(6) - C(5) - C(1)	89.10(15)	C(8) - C(5) - H(5)	125.5	
C(6)-C(5)-H(5)	125.5	C(1) - C(5) - H(5)	125.5	
C(12) - C(16) - C(15)	89.79(17)	C(12)-C(16)-C(13)	90.63(16)	
C(15)-C(16)-C(13)	89.96(18)	C(12) - C(16) - H(16)	125.2	
С(15)-С(16)-Н(16)	125.2	C(13)-C(16)-H(16)	125.2	
C(7) - C(8) - C(5)	90.24(17)	C(7) - C(8) - C(4)	89.83(18)	
C(5) - C(8) - C(4)	90.42(16)	C(7) - C(8) - H(8)	125.2	
C(5)-C(8)-H(8)	125.2	C(4) - C(8) - H(8)	125.2	



Table 4. Torsion angles (deg) for C16 H14 S2.

C(1) - S(1) - S(2) - C(9)	-86.49(10)	S(1) - S(2) - C(9) - C(10)	-42.79(18)
S(1) - S(2) - C(9) - C(13)	83.08(19)	S(1) - S(2) - C(9) - C(12)	-158.79(15)
C(13) - C(9) - C(10) - C(11)	89.99(15)	C(12) - C(9) - C(10) - C(11)	-0.22(15)
S(2) - C(9) - C(10) - C(11)	-129.74(16)	C(13)-C(9)-C(10)-C(14)	-0.40(15)
C(12) - C(9) - C(10) - C(14)	-90.61(15)	S(2) - C(9) - C(10) - C(14)	139.88(16)
C(15) - C(11) - C(10) - C(9)	-89.76(16)	C(12) - C(11) - C(10) - C(9)	0.22(15)
C(15) - C(11) - C(10) - C(14)	-0.08(19)	C(12) - C(11) - C(10) - C(14)	89.90(16)
C(6) - C(2) - C(1) - C(5)	-0.10(14)	C(3) - C(2) - C(1) - C(5)	90.21(15)
C(6) - C(2) - C(1) - C(4)	-90.11(15)	C(3) - C(2) - C(1) - C(4)	0.20(16)
C(6) - C(2) - C(1) - S(1)	141.81(16)	C(3) - C(2) - C(1) - S(1)	-127.88(17)
S(2) - S(1) - C(1) - C(2)	-49.24(17)	S(2) - S(1) - C(1) - C(5)	77.86(18)
S(2) - S(1) - C(1) - C(4)	-164.02(15)	C(15) - C(11) - C(12) - C(16)	0.25(15)
C(10)-C(11)-C(12)-C(16)	-89.62(15)	C(15) - C(11) - C(12) - C(9)	89.65(15)
C(10) - C(11) - C(12) - C(9)	-0.22(15)	C(10) - C(9) - C(12) - C(11)	0.22(15)
C(13) - C(9) - C(12) - C(11)	-90.23(17)	S(2) - C(9) - C(12) - C(11)	133.84(16)
C(10) - C(9) - C(12) - C(16)	90.36(17)	C(13) - C(9) - C(12) - C(16)	-0.09(18)
S(2) - C(9) - C(12) - C(16)	-136.02(17)	C(12) - C(11) - C(15) - C(16)	-0.25(15)
C(10) - C(11) - C(15) - C(16)	90.11(16)	C(12) - C(11) - C(15) - C(14)	-90.27(17)
C(10)-C(11)-C(15)-C(14)	0.08(18)	C(1) - C(2) - C(6) - C(7)	90.14(17)
C(3) - C(2) - C(6) - C(7)	0.47(18)	C(1) - C(2) - C(6) - C(5)	0.10(14)
C(3) - C(2) - C(6) - C(5)	-89.57(16)	C(1) - C(2) - C(3) - C(4)	-0.20(16)
C(6) - C(2) - C(3) - C(4)	89.31(17)	C(1) - C(2) - C(3) - C(7)	-89.98(17)
C(6) - C(2) - C(3) - C(7)	-0.47(18)	C(9) - C(10) - C(14) - C(13)	0.40(15)
C(11) - C(10) - C(14) - C(13)	-89.69(16)	C(9) - C(10) - C(14) - C(15)	90.17(18)
C(11) - C(10) - C(14) - C(15)	0.08(18)	C(11) - C(15) - C(14) - C(10)	-0.08(18)
C(16) - C(15) - C(14) - C(10)	-90.17(18)	C(11)-C(15)-C(14)-C(13)	90.23(17)
C(16) - C(15) - C(14) - C(13)	0.14(16)	C(2) - C(6) - C(7) - C(8)	-90.71(17)
C(5) - C(6) - C(7) - C(8)	0.07(16)	C(2) - C(6) - C(7) - C(3)	-0.47(18)
C(5) - C(6) - C(7) - C(3)	90.31(17)	C(4) - C(3) - C(7) - C(8)	-0.34(16)
C(2) - C(3) - C(7) - C(8)	90.42(17)	C(4) - C(3) - C(7) - C(6)	-90.30(17)
C(2) - C(3) - C(7) - C(6)	0.47(18)	C(10) - C(9) - C(13) - C(14)	0.40(15)
C(12) - C(9) - C(13) - C(14)	90.34(16)	S(2) - C(9) - C(13) - C(14)	-138.86(18)
C(10) - C(9) - C(13) - C(16)	-89.85(18)	C(12) - C(9) - C(13) - C(16)	0.09(18)
S(2) - C(9) - C(13) - C(16)	130.89(18)	C(10) - C(14) - C(13) - C(9)	-0.40(15)
C(15) - C(14) - C(13) - C(9)	-89.89(16)	C(10) - C(14) - C(13) - C(16)	89.35(15)
C(15) = C(14) = C(13) = C(16)	-0.14(16)	C(2) - C(3) - C(4) - C(8)	-89.45(16)
C(7) - C(3) - C(4) - C(8)	0.34(16)	C(2) - C(3) - C(4) - C(1)	0.20(16)
C(7) = C(3) = C(4) = C(1)	89.99(16)	C(2) - C(1) - C(4) - C(3)	-0.20(16)
C(5) - C(1) - C(4) - C(3)	-90.80(16)	S(1) - C(1) - C(4) - C(3)	132.20(17)
C(2) = C(1) = C(4) = C(8)	89.95(17) 127.CE(17)	C(5) - C(1) - C(4) - C(8)	-0.65(18)
S(1) = C(1) = C(4) = C(8)	-137.65(17)	C(2) - C(6) - C(5) - C(8)	89.82(16)
C(7) = C(6) = C(5) = C(8)	-0.07(16)	C(2) = C(6) = C(5) = C(1)	-0.10(14)
C(1) - C(6) - C(5) - C(1)	-69.99(15)	C(2) = C(1) = C(5) = C(8) C(1) = C(1) = C(5) = C(8)	-89.67(17)
C(4) = C(1) = C(3) = C(3)	0.05(10)	S(1) = C(1) = C(5) = C(8) C(4) = C(3) = C(6)	130.78(19)
C(2) = C(1) = C(3) = C(8)	120.46(10)	C(4) - C(1) - C(5) - C(6) C(11) - C(12) - C(16) - C(16)	90.42(16)
S(1) = C(1) = C(3) = C(3)	-139.40(10)	C(11) - C(12) - C(16) - C(13)	-0.25(15)
C(9) = C(12) = C(16) = C(13)	(01)00.20 <sup>-</sup>	C(11) = C(15) = C(16) = C(13)	0 3E (1E)
C(14) = C(15) = C(16) = C(12)	90.49(16)	C(11) - C(15) - C(16) - C(12)	-90 39(16)
C(14) = C(15) = C(16) = C(12)	-0.14(16)	C(9) - C(13) - C(16) - C(13)	-0 00(10) -0 00(10)
C(14) - C(13) - C(16) - C(12)	-89.65(17)	C(9) - C(13) - C(16) - C(15)	89 69 (17)
C(14) - C(13) - C(16) - C(15)	0.14(16)	C(6) - C(7) - C(8) - C(5)	-0.07(16)
C(3) = C(7) = C(8) = C(5)	-90.08(16)	C(6) - C(7) - C(8) - C(4)	90 35 (16)
C(0) C(1) C(0) C(0)	20.00(10)		

i i i i i i i i i i i i i i i i i i i	$\sim \sim (1 c)$	$\sigma(c) = \sigma(c) = \sigma(c) = \sigma(c)$	0, 07(1c)
C(3) - C(7) - C(8) - C(4)	0.34(16)	C(6) = C(5) = C(8) = C(7)	0.0/(18)
C(1) - C(5) - C(8) - C(7)	89.17(17)	C(6) - C(5) - C(8) - C(4)	-89.76(18)
C(1) - C(5) - C(8) - C(4)	-0.66(18)	C(3) - C(4) - C(8) - C(7)	-0.34(16)
C(1) - C(4) - C(8) - C(7)	-89.58(17)	C(3) - C(4) - C(8) - C(5)	89.89(17)
C(1) - C(4) - C(8) - C(5)	0.65(18)		
Table 5. Hydrogen coordinates and isotropic displacement parameters (A^2^ x 10 ^2^) for C16 H14 S2.

	x	У	Z	U~iso~	
u(11)	-0 0960	0 7973	0 7978	A · 7	
H(2)	0.0780	-0.0234	0.8820	4.3	
H(10)	0.2585	0.6162	0.7850	4.4	
H(12)	-0.3739	0.5559	0.8779	4.5	
H(15)	-0.1034	0.7720	0.5594	5.4	
H(6)	0.1185	0.0234	0.6354	4.7	
H(3)	0.4538	-0.1803	0.8597	5.2	
H(14)	0.2524	0.5955	0.5509	5.3	
H(7)	0.4927	-0.1348	0.6129	5.6	
H(13)	-0.0260	0.3587	0.6354	5.3	
H(4)	0.7017	0.0656	0.8330	5.6	
H(5)	0.3652	0.2700	0.6088	4.8	
H(16)	-0.3806	0.5353	0.6440	5.5	
H(8)	0.7395	0.1108	0.5859	5.0	

Table 6. Anisotropic parameters (A<sup>2</sup> x 10<sup>2</sup>) for Cl6 H14 S2. The anisotropic displacement factor exponent takes the form:

-2 pi<sup>2</sup> [ h<sup>2</sup> a\*<sup>2</sup> U11 + ... + 2 h k a\* b\* U12 ]

	Ull	U22	U33	U23	U13	U12
S(1)	6.53(5)	3.78(4)	4.98(4)	-1.57(3)	-3.08(3)	0.74(3)
S(2)	6.23(5)	3.42(4)	3.43(4)	-0.59(3)	-0.29(3)	0.74(3)
C(11)	4.68(12)	3.29(10)	3.72(11)	-0.79(8)	-0.83(8)	0.33(9)
C(2)	3.82(11)	3.35(10)	3.72(11)	-0.67(8)	-0.93(8)	0.24(8)
C(9)	4.11(11)	3.15(10)	3.02(10)	-0.99(8)	-0.63(8)	0.33(8)
C(10)	3.66(10)	4.20(11)	3.21(10)	-0.72(8)	-0.87(8)	0.11(8)
C(1)	3.89(11)	3.10(10)	3.81(10)	-0.66(8)	-1.33(8)	0.25(8)
C(12)	3.61(11)	3.93(11)	3.69(11)	-1.33(9)	-0.24(8)	0.28(8)
C(15)	4.32(12)	5.33(13)	3.46(11)	-0.22(9)	-0.83(9)	1.19(10)
C(6)	4.16(11)	4.31(11)	3.79(11)	-1.24(9)	-1.44(9)	0.57(9)
C(3)	5.00(13)	3.50(11)	4.78(13)	-0.69(9)	-1.68(10)	1.24(9)
C(14)	3.98(11)	6.16(14)	2.85(10)	-0.73(9)	-0.35(8)	1.43(10)
C(7)	4.96(13)	4.81(13)	4.45(12)	-1.72(10)	-0.94(10)	1.28(10)
C(13)	5.19(13)	5.07(13)	3.76(11)	-2.36(10)	-1.53(9)	1.40(10)
C(4)	3.81(12)	5.06(13)	5.50(14)	-1.02(11)	-2.02(10)	0.75(10)
C(5)	4.25(12)	3.79(11)	3.77(11)	-0.11(9)	-0.95(9)	0.18(9)
C(16)	3.99(12)	6.07(14)	4.47(13)	-2.26(11)	-1.71(9)	0.96(10)
C(8)	3.53(11)	6.07(15)	4.96(13)	-0.83(11)	-0.39(9)	0.29(10)

Discussion data collection, structure determination and refinement procedure

X-ray crystallographic data for I were collected from a single crystal sample, which was mounted on a glass fiber. Data were collected using a Bruker Platform diffractometer, equipped with a Bruker SMART 2K Charged-Coupled Device (CCD) Area Detector using the program SMART and normal focus sealed tube source graphite monochromated Cu-K\_ radiation.

The crystal-to-detector distance was 4.908 cm, and the data collection was carried out in 512 x 512 pixel mode, utilizing 4 x 4 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 9.0 degree scan in 30 frames over four different parts of the reciprocal space (120 frames total). One complete sphere of data was collected, to better than 0.8 A resolution. Upon completion of the data collection, the first 101 frames were recollected in order to improve the decay correction analysis.

Data reduction processing was carried out by the use of the program SAINT (Bruker, 1999), which applied Lorentz and polarization corrections to threedimensionally integrated diffraction spots.

The program SADABS (Sheldrick, 1996) was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The space group was confirmed by XPREP routine in SHELXTL program (Sheldrick, 1997). The structure was solved by direct method using SHELXS97 (Sheldrick, 1997). All non-hydrogen atoms are anisotropic, hydrogen atoms are isotropic. Hydrogen atoms constrained to the parent site using a riding model; SHELXL96 defaults, C-H 0.93 to 0.97Å. The isotropic factors, Uiso, were adjusted to a value 20% higher then U(eq) of the parent.

A final verification of possible voids was performed using the VOID routine of the PLATON program (Spek, 1995).

#### REFERENCES

International Tables for Crystallography (1992). Vol. C. Tables 4.2.6.8 and 6.1.1.4, Dordrecht: Kluwer Academic Publishers.

SAINT (1999) Release 6.06; Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, WI 53719-1173.

Sheldrick, G.M. (1996). SADABS, Bruker Area Detector Absorption Corrections. Bruker AXS Inc., Madison, WI 53719-1173.

SHELXTL (1997) Release 5.10; The Complete Software Package for Single Crystal Structure Determination. Bruker AXS Inc., Madison, WI 53719-1173.

SMART (1999) Release 5.059; Bruker Molecular Analysis Research Tool. Bruker AXS Inc., Madison, WI 53719-1173.

Spek, A.L. (1995b). PLUTON Molecular Graphics Program, July 1995 version. University of Utrecht, Utrecht, Holland.

Spek, A.L. (1995. PLATON, Molecular Geometry Program, July 1995 version. University of Utrecht, Utrecht, Holland. (version 190499 at McGill)

XPREP (1997) Release 5.10; X-ray data Preparation and Reciprocal space Exploration Program. Bruker AXS Inc., Madison, WI 53719-1173.



# **APPENDIX C**

# X-RAY STRUCTURE OF *BIS*-(4-IODOCUBYLMETHYL)-DIALKOXY DISULFIDE (4-5)

# CRYSTAL AND MOLECULAR STRUCTURE OF

C18 H16 I2 O2 S2 (harp65)

## Ron Priefer

# Department of chemistry, McGill University,

Otto Maass Chemistry Blg, 801 Sherbrooke St. W. Montreal, Canada, H3A 2K6

Structure solved by X-Ray crystallography laboratory, chemistry department, McGill University by Dr Anne-Marie Lebuis, may 2002

Table 1. Crystal data and structure refinement for C18 H16 I2 O2 S2.

Identification code harp65 C18 H16 I2 O2 S2 Empirical formula 582.254 Formula weight, Mr Triclinic Cell setting P-1 Space group Unit cell dimensions (A, deg) a = 7.0804(2)alpha = 66.455(2)a = 7.0001(2)b = 11.8075(4)beta = 76.659(2)c = 12.9297(4)gamma = 74.542(2)Volume of unit cell, V (A^3) 945.61(5) Formula units per cell, Z 2 Formula units per assymetric unit, Z' 1 Density calculated from formula and cell, Dx (Mg/m^3) 2.045 556 F(000) Cu K∖a Radiation type Wavelength, lambda (A) 1.54178 No. of reflections for cell measurement 997 4.1 to 71.6 Theta range (deg) Linear absorption coefficient, 28.526  $mu (mm^{-1})$ Measurement temperature (K) 293(2)Crystal shape triangular Colour colourless .464 x .220 x .122 Size (mm) Data collection Diffractometer type Bruker SMART2K Platform with CCD detector Data-collection method omega scans Absorption correction type Semi-empirical from equivalents

Max and min transmission values 0.20 and 0.03 No. of reflections measured 11489 No. of independent reflections 3610 Completeness of data to Theta max 0.962 No. of observed reflections 3155 Criterion for observed reflections >2sigma(I) 0.0744 Rint Theta range for data collection 3.77 to 72.55 deg. Ranges of h, k, l -8<=h<=8, -14<=k<=14, -15<=l<=15 No. of standard reflections 997 Intensity decay (%) none Refinement Refinement method Full-matrix on F^2 Final R indices, I>2sigma(I) R1 = 0.0718, wR2 = 0.2022 R indices, all data R1 = 0.0752, wR2 = 0.2022Goodness-of-fit on F^2, S 1.037 R1 = sum (absabs Foabs -abs Fcabsabs )/sum (abs Foabs ),  $wR2 = [sum [w(Fo^{2}-Fc^{2})^{2}]/sum [w(Fo^{2})^{2}]^{1*2^{a}} and$ GoF = [sum [w(Fo^2^-Fc^2^)^2^]/(No. of reflns - No. of params.)]^1\*2^ Data / restraints / parameters 3610 / 0 / 218 Method of refining and locating H atoms calculated Weighting scheme based on measured s.u.'s Function minimized sum  $w(Fo^2^-Fc^2^)$ calc w=1/[\s^2^(Fo^2^)+(0.1618P)^2^] where  $P=(Fo^2^+2Fc^2^)/3$ Maximum shift/sigma 0.001 Largest diff. peak and hole 1.885 and -2.894 e.A^\*3 Secondary extinction value 0.0011(4)

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (A^2^  $\times$  10 ^2^) for C18 H16 I2 O2 S2.

	X	У	Z	U(eq)	
I(1)	0.88113(7)	0.34799(5)	0.02386(4)	6.11(3)	
I(2)	-0.83213(7)	0.94740(5)	0.15203(4)	6.15(3)	
S(1)	0.0428(3)	0.1884(2)	0.52060(15)	6.54(6)	
S(2)	0.0910(3)	0.3618(2)	0.4484(2)	6.90(6)	
0(1)	0.0781(7)	0.1295(5)	0.4201(5)	5.47(12)	
0(2)	-0.1186(9)	0.4550(5)	0.4096(5)	6.31(14)	
C(1)	0.4124(9)	0.1272(6)	0.3173(6)	4.00(12)	
C(2)	0.6115(10)	0.0635(6)	0.2633(6)	5.00(15)	
C(3)	0.7214(9)	0.1555(7)	0.2741(6)	4.65(14)	
C(4)	0.5235(9)	0.2200(7)	0.3279(6)	4.57(14)	
C(5)	0.3686(10)	0.2225(7)	0.1957(6)	5.24(16)	
C(6)	0.5647(11)	0.1569(8)	0.1429(6)	5.43(16)	
C(7)	0.6750(9)	0.2499(6)	0.1521(6)	4.41(13)	
C(8)	0.4771(9)	0.3149(6)	0.2064(7)	4.91(15)	
C(9)	0.2695(10)	0.0533(6)	0.4048(7)	4.95(15)	
C(11)	-0.3212(11)	0.5804(6)	0.2682(6)	4.90(15)	
C(12)	-0.5323(11)	0.5981(7)	0.3373(6)	4.98(15)	
C(13)	-0.6241(11)	0.6508(7)	0.2246(7)	5.39(16)	
C(14)	-0.4138(11)	0.6325(7)	0.1555(6)	5.50(17)	
C(15)	-0.3082(11)	0.7172(7)	0.2511(7)	5.33(16)	
C(16)	-0.5170(10)	0.7339(7)	0.3210(6)	5.00(15)	
C(17)	-0.6062(10)	0.7850(6)	0.2076(6)	4.39(13)	
C(18)	-0.3961(10)	0.7685(7)	0.1384(6)	5.32(16)	
C(19)	-0.1603(12)	0.4669(7)	0.3015(7)	5.53(17)	

 $U \sim eq \sim = (1/3) sum \sim i \sim sum \sim j \sim U \sim ij \sim a^{*} \sim i \sim a^{*} \sim j \sim a^{-}i \sim .a^{-}j^{-}.$ 

Table 3. Bond 1	engths (A) and	angles (deg) for C18	H16 12 02 S2.	Mt.
I(1) - C(7) S(1) - O(1) S(2) - O(2) O(2) - C(19) C(1) - C(2) C(1) - C(4) C(2) - C(3) C(3) - C(4) C(3) - H(3) C(4) - H(4) C(5) - C(8) C(6) - C(7) C(7) - C(8) C(6) - C(7) C(7) - C(8) C(9) - H(9A) C(11) - C(19) C(11) - C(12) C(12) - C(13) C(12) - H(12) C(13) - C(14) C(15) - C(18) C(15) - H(15) C(16) - H(16) C(19) - H(19B)	2.114(7) 1.647(6) 1.642(6) 1.439(9) 1.562(8) 1.570(8) 1.558(10) 1.559(8) 0.9800 1.555(10) 1.565(8) 0.9700 1.565(8) 0.9700 1.559(10) 1.563(9) 1.559(10) 0.9800 1.559(10) 0.9800 0.9900 0.900 0.90	$\begin{array}{c} (2) - C(17) & 2 \\ (1) - S(2) & 1 \\ (1) - C(9) & 1 \\ (1) - C(9) & 1 \\ (1) - C(5) & 1 \\ (2) - C(6) & 1 \\ (2) - H(2) & 0 \\ (3) - C(7) & 1 \\ (4) - C(8) & 1 \\ (5) - C(6) & 1 \\ (5) - H(5) & 0 \\ (6) - H(6) & 0 \\ (6) - H(6) & 0 \\ (6) - H(8) & 0 \\ (11) - C(14) & 1 \\ (11) - C(15) & 1 \\ (12) - C(16) & 1 \\ (13) - C(17) & 1 \\ (13) - H(13) & 0 \\ (14) - H(14) & 0 \\ (15) - C(16) & 1 \\ (16) - C(17) & 1 \\ (17) - C(18) & 1 \\ (19) - H(19A) & 0 \\ \end{array}$	133(7) 970(3) 433(8) 489(9) 569(9) 556(10) 9800 574(9) 571(10) 551(10) 9800 9800 9800 9700 563(11) 566(9) 563(10) 547(9) 9800 9800 9800 553(9) 559(10) 556(8) 9700	
O(1) - S(1) - S(2) $C(9) - O(1) - S(1)$ $C(9) - C(1) - C(2)$ $C(2) - C(1) - C(5)$ $C(2) - C(1) - C(4)$ $C(6) - C(2) - C(3)$ $C(3) - C(2) - C(1)$ $C(3) - C(2) - H(2)$ $C(2) - C(3) - C(4)$ $C(4) - C(3) - C(4)$ $C(4) - C(3) - H(3)$ $C(3) - C(4) - C(1)$ $C(1) - C(4) - C(1)$ $C(1) - C(4) - C(1)$ $C(1) - C(4) - C(8)$ $C(1) - C(4) - H(4)$ $C(6) - C(5) - C(8)$ $C(8) - C(5) - H(5)$ $C(5) - C(6) - C(2)$ $C(2) - C(6) - H(5)$ $C(5) - C(6) - C(2)$ $C(2) - C(6) - H(6)$ $C(6) - C(7) - C(8)$ $C(8) - C(7) - C(3)$ $C(8) - C(7) - C(3)$ $C(8) - C(7) - I(1)$ $C(5) - C(8) - C(7)$ $C(7) - C(8) - C(4)$ $C(7) - C(8) - C(4)$ $C(7) - C(8) - H(8)$ $O(1) - C(9) - C(1)$	108.2(2) $115.4(4)$ $122.5(5)$ $90.1(5)$ $89.7(5)$ $91.1(5)$ $90.2(5)$ $125.1$ $90.2(5)$ $125.5$ $89.6(5)$ $125.5$ $89.9(5)$ $89.4(5)$ $125.3$ $91.0(5)$ $90.0(5)$ $125.2$ $91.0(5)$ $89.5(5)$ $125.3$ $90.3(5)$ $124.3(5)$ $89.5(5)$ $125.4$ $112.6(5)$	O(2) - S(2) - S(1) $C(19) - O(2) - S(2)$ $C(9) - C(1) - C(5)$ $C(9) - C(1) - C(4)$ $C(5) - C(1) - C(4)$ $C(6) - C(2) - C(1)$ $C(6) - C(2) - H(2)$ $C(1) - C(2) - H(2)$ $C(1) - C(2) - H(2)$ $C(2) - C(3) - H(3)$ $C(7) - C(3) - H(3)$ $C(7) - C(3) - H(3)$ $C(3) - C(4) - C(8)$ $C(3) - C(4) - H(4)$ $C(6) - C(5) - H(5)$ $C(1) - C(5) - H(5)$ $C(1) - C(5) - H(5)$ $C(5) - C(6) - C(7)$ $C(5) - C(6) - H(6)$ $C(7) - C(6) - H(6)$ $C(6) - C(7) - I(1)$ $C(5) - C(8) - C(4)$ $C(5) - C(8) - H(8)$ $C(4) - C(8) - H(8)$ $C(4) - C(8) - H(8)$ $C(4) - C(8) - H(8)$	107.4(3) $115.7(4)$ $124.8(6)$ $128.4(6)$ $90.1(5)$ $89.5(5)$ $125.1$ $125.1$ $89.0(5)$ $125.5$ $125.5$ $90.6(5)$ $125.2$ $125.2$ $89.4(5)$ $125.2$ $89.5(5)$ $125.3$ $125.3$ $90.4(5)$ $126.3(5)$ $124.5(4)$ $90.6(5)$ $125.4$ $125.4$	

Table 3. Bond lengths (A) and angles (deg) for C18 H16



C(1) - C(9) - H(9A)	109.1	O(1) - C(9) - H(9B)	109.1
C(1) - C(9) - H(9B)	109.1	H(9A)-C(9)-H(9B)	107.8
C(19) - C(11) - C(14)	125.1(6)	C(19) - C(11) - C(12)	125.5(7)
C(14) - C(11) - C(12)	90.2(5)	C(19) - C(11) - C(15)	125.3(7)
C(14) - C(11) - C(15)	90.1(6)	C(12) - C(11) - C(15)	89.6(5)
C(13) - C(12) - C(16)	90.4(5)	C(13) - C(12) - C(11)	89.6(5)
C(16) - C(12) - C(11)	90.0(5)	C(13) - C(12) - H(12)	125.2
C(16) - C(12) - H(12)	125.2	C(11) - C(12) - H(12)	125.2
C(17) - C(13) - C(12)	89.6(6)	C(17) - C(13) - C(14)	89.6(5)
C(12) - C(13) - C(14)	90.5(5)	C(17)-C(13)-H(13)	125.3
C(12)-C(13)-H(13)	125.3	C(14)-C(13)-H(13)	125.3
C(13) - C(14) - C(11)	89.6(5)	C(13) - C(14) - C(18)	90.3(5)
C(11) - C(14) - C(18)	89.3(5)	C(13)-C(14)-H(14)	125.4
C(11)-C(14)-H(14)	125.4	C(18)-C(14)-H(14)	125.4
C(18) - C(15) - C(16)	91.9(5)	C(18)-C(15)-C(11)	89.9(6)
C(16) - C(15) - C(11)	90.3(5)	C(18)-C(15)-H(15)	124.8
C(16)-C(15)-H(15)	124.8	C(11)-C(15)-H(15)	124.8
C(15) - C(16) - C(17)	88.3(5)	C(15)-C(16)-C(12)	90.1(5)
C(17) - C(16) - C(12)	89.0(5)	C(15)-C(16)-H(16)	125.9
C(17)-C(16)-H(16)	125.9	C(12)-C(16)-H(16)	125.9
C(13) - C(17) - C(18)	91.1(5)	C(13) - C(17) - C(16)	91.0(5)
C(18) - C(17) - C(16)	91.2(5)	C(13) - C(17) - I(2)	123.5(5)
C(18) - C(17) - I(2)	123.1(5)	C(16) - C(17) - I(2)	126.8(4)
C(15)-C(18)-C(17)	88.6(5)	C(15) - C(18) - C(14)	90.7(5)
C(17) - C(18) - C(14)	89.0(5)	C(15) - C(18) - H(18)	125.7
C(17)-C(18)-H(18)	125.7	C(14)-C(18)-H(18)	125.7
O(2) - C(19) - C(11)	106.3(6)	O(2)-C(19)-H(19A)	110.5
C(11)-C(19)-H(19A)	110.5	O(2)-C(19)-H(19B)	110.5
C(11)-C(19)-H(19B)	110.5	H(19A)-C(19)-H(19B)	108.7

O(1) - S(1) - S(2) - O(2)	87.6(3)	S(2) - S(1) - O(1) - C(9)	96.9(5)
S(1) - S(2) - O(2) - C(19)	-83.7(6)	C(9) - C(1) - C(2) - C(6)	131.8(7)
C(5) - C(1) - C(2) - C(6)	-1.0(5)	C(4) - C(1) - C(2) - C(6)	-91.0(5)
C(9) - C(1) - C(2) - C(3)	-137.1(6)	C(5) - C(1) - C(2) - C(3)	90.2(5)
C(4) - C(1) - C(2) - C(3)	0.1(5)	C(6) - C(2) - C(3) - C(4)	89.4(5)
C(1) = C(2) = C(3) = C(4)	-0.1(5)	C(6) - C(2) - C(3) - C(7)	-0.2(5)
C(1) = C(2) = C(3) = C(7)	-89.7(5)	C(2) - C(3) - C(4) - C(1)	0.1(5)
C(1) = C(2) = C(3) = C(4) = C(1)	89.1(5)	C(2) - C(3) - C(4) - C(8)	-89.3(5)
C(7) = C(3) = C(4) = C(8)	-0.3(5)	C(9) - C(1) - C(4) - C(3)	132.9(7)
C(2) = C(1) = C(4) = C(3)	-0.1(5)	C(5) - C(1) - C(4) - C(3)	-90.2(5)
C(2) = C(1) = C(4) = C(8)	-136.5(6)	C(2) - C(1) - C(4) - C(8)	90.5(5)
C(5) = C(1) = C(4) = C(8)	0 4 (5)	C(9) - C(1) - C(5) - C(6)	-130.0(6)
C(3) = C(1) = C(4) = C(6)	1 0(5)	C(4) = C(1) = C(5) = C(6)	90.6(5)
C(2) = C(1) = C(3) = C(3)	138 9/6)	C(2) = C(1) = C(5) = C(8)	-90.1(5)
C(9) = C(1) = C(3) = C(0)	-0.4(5)	C(2) = C(1) = C(3) = C(2)	89 0(6)
C(4) = C(1) = C(3) = C(3)	-0.4(5)	C(8) - C(5) - C(6) - C(7)	-0.5(5)
C(1) = C(5) = C(6) = C(2)	-1.0(3)	C(3) = C(3) = C(6) = C(5)	-89.3(5)
C(1) = C(5) = C(6) = C(7)	-90.3(3)	C(3) = C(2) = C(6) = C(7)	0 2 (5)
C(1) - C(2) - C(6) - C(5)	1.0(5)	C(5) = C(2) = C(0) = C(7)	0.2(5)
C(1) - C(2) - C(6) - C(7)	90.4(5)	C(5) = C(6) = C(7) = C(3)	0.5(5)
C(2) = C(6) = C(7) = C(8)	-90.5(5)	C(5) = C(6) = C(7) = T(1)	-134.2(5)
C(2) - C(6) - C(7) - C(3)	-0.2(3)	C(3) = C(3) = C(7) = C(1)	-134.2(3)
C(2) - C(6) - C(7) - I(1)	134.8(5)	C(2) = C(3) = C(7) = C(8)	0.2(5)
C(4) - C(3) - C(7) - C(6)	-90.0(5)	C(2) = C(3) = C(7) = C(8)	90.0(5)
C(4) - C(3) - C(7) - C(8)	0.3(5)	C(2) = C(3) = C(7) = 1(1)	-130.0(3)
C(4) - C(3) - C(7) - I(1)	133.7(5)	C(6) - C(5) - C(8) - C(7)	0.5(5)
C(1) - C(5) - C(8) - C(7)	90.0(5)	C(6) - C(5) - C(8) - C(4)	-89.0(5)
C(1) - C(5) - C(8) - C(4)	0.4(5)	C(6) - C(7) - C(8) - C(5)	-0.5(5)
C(3) - C(7) - C(8) - C(5)	-90.9(5)	1(1) - C(7) - C(8) - C(5)	135.5(5)
C(6) - C(7) - C(8) - C(4)	90.1(5)	C(3) = C(7) = C(8) = C(4)	-0.3(5)
I(1) - C(7) - C(8) - C(4)	-133.9(5)	C(3) - C(4) - C(8) - C(5)	89.4(5)
C(1) - C(4) - C(8) - C(5)	-0.4(5)	C(3) = C(4) = C(8) = C(7)	0.3(5)
C(1) - C(4) - C(8) - C(7)	-89.5(5)	S(1) = O(1) = C(9) = C(1)	-92.1(6)
C(2) - C(1) - C(9) - O(1)	-164.6(6)	C(5) = C(1) = C(9) = O(1)	-48.2(9)
C(4) - C(1) - C(9) - O(1)	/5.5(8)	C(19) = C(11) = C(12) = C(13)	-135.4(7)
C(14) - C(11) - C(12) - C(13)	-0.3(5)	C(15) = C(11) = C(12) = C(13)	89.8(6)
C(19) - C(11) - C(12) - C(16)	134.2(7)	C(14) = C(11) = C(12) = C(16)	-90.7(5)
C(15) - C(11) - C(12) - C(16)	-0.6(6)	C(16) - C(12) - C(13) - C(17)	0.7(5)
C(11) - C(12) - C(13) - C(17)	-89.3(5)	C(16) = C(12) = C(13) = C(14)	90.4(5)
C(11) - C(12) - C(13) - C(14)	0.3(5)	C(17) - C(13) - C(14) - C(11)	89.3(6)
C(12) - C(13) - C(14) - C(11)	-0.3(5)	C(17) - C(13) - C(14) - C(18)	0.0(6)
C(12) - C(13) - C(14) - C(18)	-89.6(6)	C(19) = C(11) = C(14) = C(13)	135.8(8)
C(12) - C(11) - C(14) - C(13)	0.3(5)	C(15) - C(11) - C(14) - C(13)	-89.3(5)
C(19) - C(11) - C(14) - C(18)	-134.0(7)	C(12) - C(11) - C(14) - C(18)	90.6(5)
C(15) - C(11) - C(14) - C(18)	1.0(5)	C(19) = C(11) = C(15) = C(18)	133.8(/)
C(14) - C(11) - C(15) - C(18)	-1.0(5)	C(12) - C(11) - C(15) - C(18)	-91.2(5)
C(19) - C(11) - C(15) - C(16)	-134.3(7)	C(14) - C(11) - C(15) - C(16)	90.9(5)
C(12) - C(11) - C(15) - C(16)	0.6(6)	U(18) - U(15) - U(16) - U(17)	. 0.3(5)
C(11) - C(15) - C(16) - C(17)	-89.7(5)	C(18) - C(15) - C(16) - C(12)	89.3(5)
C(11) - C(15) - C(16) - C(12)	-0.6(6)	C(13) - C(12) - C(16) - C(15)	-89.0(6)
C(11) - C(12) - C(16) - C(15)	U.6(6)	C(13) - C(12) - C(16) - C(17)	-0.7(5)
C(11) - C(12) - C(16) - C(17)	88.9(5)	C(12) = C(13) = C(17) = C(18)	90.5(5)
C(14) - C(13) - C(17) - C(18)	0.0(6)	U(12) - U(13) - U(17) - U(16)	-0.7(5)
C(14) - C(13) - C(17) - C(16)	-91.2(5)	-C(12) - C(13) - C(17) - I(2)	-137.6(5)

Table 4. Torsion angles (deg) for C18 H16 I2 O2 S2.

~~~~~~	

C(14) - C(13) - C(17) - I(2)	131.9(5)	C(15) - C(16) - C(17) - C(13)	90.9(5)
C(12) - C(16) - C(17) - C(13)	0.7(5)	C(15) - C(16) - C(17) - C(18)	-0.3(5)
C(12) - C(16) - C(17) - C(18)	-90.4(5)	C(15) - C(16) - C(17) - I(2)	-134.5(5)
C(12) - C(16) - C(17) - I(2)	135.3(5)	C(16) - C(15) - C(18) - C(17)	-0.3(5)
C(11) - C(15) - C(18) - C(17)	90.0(5)	C(16) - C(15) - C(18) - C(14)	-89.3(5)
C(11) - C(15) - C(18) - C(14)	1.0(5)	C(13) - C(17) - C(18) - C(15)	-90.7(5)
C(16) - C(17) - C(18) - C(15)	0.3(5)	I(2)-C(17)-C(18)-C(15)	137.1(5)
C(13) - C(17) - C(18) - C(14)	0.0(6)	C(16) - C(17) - C(18) - C(14)	91.0(5)
I(2) - C(17) - C(18) - C(14)	-132.2(5)	C(13) - C(14) - C(18) - C(15)	88.6(5)
C(11) - C(14) - C(18) - C(15)	-1.0(5)	C(13) - C(14) - C(18) - C(17)	0.0(6)
C(11) - C(14) - C(18) - C(17)	-89.6(5)	S(2)-O(2)-C(19)-C(11)	-164.1(5)
C(14) - C(11) - C(19) - O(2)	178.9(7)	C(12) - C(11) - C(19) - O(2)	-60.6(10)
C(15) - C(11) - C(19) - O(2)	59.0(9)		



Table 5. Hydrogen coordinates and isotropic displacement parameters (A^2^ x 10 ^2^) for C18 H16 I2 O2 S2.

	X	У	Z	U~iso~	
ц (2)	0 6593	-0 0276	0 2840	6.0	
л(2) ц/2)	0.0335	0.1318	0.2015	5.6	
п()) п()	0.5073	0.2423	0.3952	5.5	
п(4). п(5)	0.2409	0.2423	0.1678	6.3	
H(6)	0.5804	0.1340	0.0761	6.5	
H(8)	0.4296	0.4060	0.1856	5.9	
H(9A)	0.2563	-0.0130	0.3822	5.9	
H(9B)	0.3215	0.0138	0.4769	5.9	
H(12)	-0.5805	0.5358	0.4090	6.0	
H(13)	-0.7406	0.6281	0.2148	6.5	
H(14)	-0.3766	0.5955	0.0962	6.6	
H(15)	-0.1928	0.7409	0.2609	6.4	
H(16)	-0.5552	0.7712	0.3801	6.0	
H(18)	-0.3479	0.8308	0.0667	6.4	
H(19A)	-0.2032	0.3924	0.3083	6.6	
H(19B)	-0.0432	0.4775	0.2449	6.6	

Table 6. Anisotropic parameters (A^2  $\times$  10^2) for C18 H16 I2 O2 S2.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [ h^2 a\*^2 U11 + ... + 2 h k a\* b\* U12 ]

U11	U22	CCII			
		055	023	U13	U12
3.93(3) 4.48(4)	8.28(4) 6.31(4)	5.28(4) 5.98(4)	-1.95(3) -2.23(3)	0.20(2) -0.27(2)	-1.32(2) 1.25(2)
5.48(11)	7.19(12)	4.49(8)	-1.38(8)	0.08(7)	0.93(9)
3.2(2)	5.7(3)	7.6(3)	-2.7(3)	-0.7(2)	-0.5(2)
3.2(2) 5.6(3) 2.8(3) 3.9(3) 2.5(3) 2.9(3) 3.1(3) 4.6(4) 2.7(3) 2.3(3) 3.4(3)	5.7(3) 6.3(3) 3.8(3) 4.6(3) 5.8(4) 5.7(4) 6.2(4) 7.0(4) 5.3(4) 4.4(3) 4.3(3)	7.6(3) 6.9(3) 5.4(3) 6.0(4) 5.2(3) 5.5(3) 5.5(3) 5.5(3) 5.5(3) 5.0(3) 6.6(4) 6.6(4)	$\begin{array}{c} -2.7(3) \\ -4.1(3) \\ -2.1(3) \\ -2.6(3) \\ -2.3(3) \\ -3.0(3) \\ -1.4(3) \\ -3.2(3) \\ -2.0(3) \\ -1.7(3) \\ -1.6(3) \end{array}$	$\begin{array}{c} -0.7(2) \\ -0.9(3) \\ -0.7(2) \\ 0.0(3) \\ -0.9(2) \\ 0.1(3) \\ -1.3(3) \\ -0.6(3) \\ -0.6(2) \\ 0.1(3) \\ -0.9(3) \end{array}$	-0.5(2) 1.6(2) 0.4(2) 0.5(3) 0.6(3) -0.5(3) -1.1(3) -0.2(2) 0.4(2) -0.2(3)
3.9(3)	4.7(3) 5.5(4)	5,7(3)	-2.5(3) -1.4(3)	0.4(3)	0.0(3) -0.6(3)
4.2(4) 4.6(4) 3.9(4) 3.9(3) 3.4(3) 3.6(3) 4.9(4)	5.6(4) 6.1(4) 4.5(3) 5.9(4) 4.1(3) 5.2(4) 5.3(4)	6.3(4) 5.8(4) 7.2(4) 5.3(3) 5.0(3) 5.6(4) 5.8(4)	$\begin{array}{c} -2.6(3) \\ -3.4(3) \\ -2.3(3) \\ -3.3(3) \\ -2.0(3) \\ -1.9(3) \\ -2.7(3) \end{array}$	-0.5(3) -0.2(3) -0.5(3) -0.3(3) 0.4(3) 0.8(3) -0.5(3)	-0.5(3) 0.6(3) -0.2(3) 0.4(3) 0.0(2) 0.5(3) 0.9(3)
	3.93(3) 4.48(4) 5.48(11) 5.40(11) 3.2(2) 5.6(3) 2.8(3) 3.9(3) 2.5(3) 2.9(3) 3.1(3) 4.6(4) 2.7(3) 2.3(3) 3.4(3) 3.9(3) 3.8(3) 4.2(4) 4.6(4) 3.9(4) 3.9(3) 3.4(3) 3.4(3) 3.6(3) 4.9(4)	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	3.93(3) $8.28(4)$ $5.28(4)$ $4.48(4)$ $6.31(4)$ $5.98(4)$ $5.48(11)$ $7.19(12)$ $4.49(8)$ $5.40(11)$ $6.85(12)$ $10.12(15)$ $3.2(2)$ $5.7(3)$ $7.6(3)$ $5.6(3)$ $6.3(3)$ $6.9(3)$ $2.8(3)$ $3.8(3)$ $5.4(3)$ $3.9(3)$ $4.6(3)$ $6.0(4)$ $2.5(3)$ $5.8(4)$ $5.2(3)$ $2.9(3)$ $5.7(4)$ $5.5(3)$ $3.1(3)$ $6.2(4)$ $5.8(4)$ $4.6(4)$ $7.0(4)$ $5.5(3)$ $2.7(3)$ $5.3(4)$ $5.0(3)$ $2.3(3)$ $4.4(3)$ $6.6(4)$ $3.9(3)$ $4.7(3)$ $5.7(3)$ $3.8(3)$ $5.5(4)$ $4.5(3)$ $4.2(4)$ $5.6(4)$ $6.3(4)$ $3.9(4)$ $4.5(3)$ $7.2(4)$ $3.9(3)$ $5.9(4)$ $5.3(3)$ $3.4(3)$ $4.1(3)$ $5.0(3)$ $3.4(3)$ $4.1(3)$ $5.0(3)$ $3.6(3)$ $5.2(4)$ $5.8(4)$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Discussion data collection, structure determination and refinement procedure

X-ray crystallographic data for I were collected from a single crystal sample, which was mounted on a glass fiber. Data were collected using a Bruker Platform diffractometer, equipped with a Bruker SMART 2K Charged-Coupled Device (CCD) Area Detector using the program SMART and normal focus sealed tube source graphite monochromated Cu-KD radiation. The crystal-to-detector distance was 4.908 cm, and the data collection was carried out in 512 x 512 pixel mode, utilizing 4 x 4 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 9.0 degree scan in 30 frames over four different parts of the reciprocal space (120 frames total). One complete sphere of data was collected, to better than 0.8DA resolution. Upon completion of the data collection, the first 101 frames were recollected in order to improve the decay correction analysis.

Data reduction processing was carried out by the use of the program SAINT (Bruker, 1999), which applied Lorentz and polarization corrections to threedimensionally integrated diffraction spots. The program SADABS (Sheldrick, 1996) was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections.

The space group was confirmed by XPREP routine in SHELXTL program (Sheldrick, 1997). The structure was solved by direct method using SHELXS97 (Sheldrick, 1997) and difmap synthesis using SHELXL96 (Sheldrick, 1996). All non-hydrogen atoms are anisotropic, hydrogen atoms isotropic. Hydrogen atoms constrained to the parent site using a riding model; SHELXL96 defaults, C-H 0.93 to 0.97. The isotropic factors, Uiso, were adjusted to a value 20% higher then U(eq) of the parent site.

A final verification of possible voids was performed using the VOID routine of the PLATON program (Spek, 1995).

### REFERENCES

International Tables for Crystallography (1992). Vol. C. Tables 4.2.6.8 and 6.1.1.4, Dordrecht: Kluwer Academic Publishers.

SAINT (1999) Release 6.06; Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, WI 53719-1173.

Sheldrick, G.M. (1996). SADABS, Bruker Area Detector Absorption Corrections. Bruker AXS Inc., Madison, WI 53719-1173.

Sheldrick, G.M. (1997). SHELXS97, Program for the Solution of Crystal Structures. Univ. of Gottingen, Germany.

Sheldrick, G.M. (1996). SHELXL96, Program for the Refinement of Crystal Structures. Univ. of Gottingen, Germany.

SHELXTL (1997) Release 5.10; The Complete Software Package for Single Crystal Structure Determination. Bruker AXS Inc., Madison, WI 53719-1173.

SMART (1999) Release 5.059; Bruker Molecular Analysis Research Tool. Bruker AXS Inc., Madison, WI 53719-1173.

Spek, A.L. (1995. PLATON, Molecular Geometry Program, version 190499. University of Utrecht, Utrecht, Holland.

XPREP (1997) Release 5.10; X-ray data Preparation and Reciprocal space Exploration Program. Bruker AXS Inc., Madison, WI 53719-1173.





# **APPENDIX D**

# X-RAY STRUCTURE OF *BIS*-CUBYLMETHYLSULFITE (4-12)

## Structure of HARP68

DAVID N. HARPP,<sup>a</sup> Ronny Priefer<sup>a</sup> and Francine Bélanger-Gariépy<sup>b</sup>

<sup>a</sup> Department of Chemistry, Otto Maass Chemistry Building, 801 Sherbrooke St. West, Montréal, Québec, Canada H3A 2K6, and <sup>b</sup> Département de Chimie, Université de Montréal, C.P. 6128, Succ. Centre-ville, Montréal, Québec, Canada H3C 3J7. E-mail: harpp@chemistry.mcgill.ca

#### Abstract

The crystal stucture of the title compound, recrystallized from ...

#### Comment

comment

#### Experimental

Synthesis was carried out by reaction of ...

Crystal data  $C_{18}H_{18}O_{3}S$   $M_{\tau} = 314.384$ Monoclinic C2/c a = 25.4005 (2) Å b = 6.5411 (1) Å c = 8.9505 (1) Å  $\beta = 104.169 (1)^{\circ}$   $V = 1441.86 (3) Å^{3}$  Z = 4  $D_{x} = 1.4483 \text{ Mg m}^{-3}$   $D_{m}$  not measured  $Cu \ K\alpha$  radiation  $\lambda = 1.54178 Å$ 

Cell parameters from 7329 reflections  $\theta = 3.59-72.88^{\circ}$   $\mu = 2.084 \text{ mm}^{-1}$  T = 220 (2) KBlock Colourless  $0.42 \times 0.15 \times 0.13 \text{ mm}$ Crystal source: synthesized by the authors, see text Data collection Bruker AXS SMART 2K/Platform diffractometer

 $\omega \operatorname{scan}$ 

Absorption correction: multi-scan SADABS (Sheldrick, 1996)

 $T_{\rm min} = 0.5200, T_{\rm max} = 0.7400$ 

8302 measured reflections

1430 independent reflections

Refinement

Refinement on  $F^2$ 

 $R[F^2 > 2\sigma(F^2)] = 0.0443$ 

 $wR(F^2) = 0.1164$ 

S = 1.155

1430 reflections

105 parameters

H-atom parameters constrained

1361 reflections with  $> 2\sigma(I)$   $R_{int} = 0.1070$   $\theta_{max} = 72.87^{\circ}$   $h = -31 \rightarrow 31$   $k = -6 \rightarrow 7$   $l = -11 \rightarrow 10$ 72 standard reflections every ? reflections

intensity decay: no docay, variation 0.0%

$$\begin{split} & w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 1.7296P] \\ & \text{where } P = (F_o^2 + 2F_c^2)/3 \\ & (\Delta/\sigma)_{\text{max}} = 0.000 \\ & \Delta\rho_{\text{max}} = 0.267 \text{ c} \text{ Å}^{-3} \\ & \Delta\rho_{\text{min}} = -0.330 \text{ c} \text{ Å}^{-3} \end{split}$$

Extinction correction: none

Scattering factors from International Tables for Crystallography (Vol. C)

## Table 1. Selected geometric parameters $(A, \circ)$

S1	O2 <sup>i</sup>	1.403 (3)	C2	C3	1.565 (2)
<b>S</b> 1	O2	1.403 (3)	C2	C6	1.565 (3)
S1 .	01 <sup>i</sup>	1.6147 (13)	C3	C7	1.564 (3)
S1	01	1.6147 (13)	C3	C4	1.567 (2)
01	C9	1.463 (2)	C4	C8	1.563 (2)
<b>C</b> 1	C9	1.485 (2)	C5	C8	1.565 (3)
Cl	C5	1.563 (2)	C5	C6	1.565 (3)
C1	C4	1.566 (2)	C6	C7	1.564 (3)
$C_1$	C2	1.568 (2)	C7	C8	1.564 (3)

02 <sup>i</sup>	· S1	O2	123.8 (3)	C2	C3	C4		90.41 (13)
02 <sup>i</sup>	51	01 <sup>i</sup>	104.51 (14)	CS	C4	Cl		89.76 (13)
02	<b>S</b> 1	Oli	110.93 (13)	C8	.C4	C3	•	90.02 (13)
02 <sup>i</sup>	<b>S</b> 1	01	110.94 (13)	Cl	C4	C3		89.65 (13)
02	<b>S</b> 1	01	104.51 (14)	Cl	C5	C8		89.80 (13)
01 <sup>i</sup>	S1	01	99.69 (10)	Cl	C5	C6		90.00 (13)
C9	01	S1	116.09 (10)	C8	C5	C6		90.00 (14)
C9	C1	C5	123.29 (15)	C7	C6	C5		89.94 (14)
C9	Cl	C4	125.05 (15)	C7	C6	C2		89.92 (14)
C5	C1	C4	90.19 (13)	C5	C6	C2		90.13 (13)
C9	C1	C2	126.99 (15)	C8	C7	C6		90.10 (14)
C5	Cl	C2	90.07 (13)	C8	C7	C3		90.11 (14)
C4	C1	C2	90.32 (13)	C6	C7	C3		90.14 (14)
C3	C2	C6	90.02 (14)	C4	C8	C7		90.00 (13)
C3	C2.	C1	89.62 (13)	C4	C8	C5		90.24 (13)
C6	C2	C1	89.80 (13)	C7	C8	C5		89.95 (14)
C7	C3	C2	89.92 (14)	01	C9	C1		106.96 (13)
C7	C3	C4	89.86 (13)					

02 <sup>i</sup>	S1	01	C9	43.4 (2)	C1	C5	C6	C2	0.22 (13)	
02	<b>S</b> 1	01	C9	178.91 (17)	C8	C5	C6	C2	90.02 (14)	
οıi	<b>S</b> 1	oʻi	C9	-66.35 (11)	C3	C2	Cfi	C7	0.11 (14)	
C9	С1	C2	C3	-136.28 (18)	C1	C2	C6	C7	89.73 (14)	
C5	Cl	$C_2$	C3	90.24 (13)	C3	C2	C6	C5	-89.83 (13)	
C4	Cl	C2	C3	0.05 (13)	Cl	C2	C6	C5	-0.22 (13)	
C9	C1	C2	C6	133.70 (18)	C5	C6	<b>C</b> 7	C8	-0.10 (14)	
C5	CI	C2	C6	0.22 (13)	C2	C6	C7	C8	-90.23 (14)	
C4	Cl	C2	C6	-89.97 (13)	C5	C6	C7	C3	90.02 (14)	
C6	C2	C3	C7	-0.11 (14)	C2	C6	C7	C3	-0.11 (14)	
C1	C2	<b>C</b> 3	C7	-89.91 (14)	C2	C3	C7	C8	90.21 (13)	
C6	C2	СЗ	C4	89.75 (13)	. C4	СЗ	C7	C8	-0.20 (13)	
C1	$C_2$	C3	C4	-0.05 (13)	C2	C3	C7	C6	0.11 (14)	
C9	C1	C4	C8	-132.39 (17)	C4	C3	C7	C6	-90.30 (13)	
C5	Cl	C4	C8	-0.10 (13)	C1	C4	C8	C7	-89.85 (13)	
C2	Cı	C4	C8	89.97 (13)	C3	C4	C8	C7 .	-0.20 (13)	
C9	Cl	C4	-C3-	137.60 (17)	C1	C4	- C8	C5	0.10 (13)	
C5	Cl	C4	СЗ	-90.12 (13)	C3	C4	C8	C5	89.76 (14)	
C2	C1	C4	C3	-0.05 (13)	C6	C7	C8	C4	90.34 (14)	
C7	C3	C4	C8	0.20 (13)	C3	C7	C8	C4	0.20 (13)	
C2	C3	C4	C8	-89.72 (13)	C6	C7	C8	C5	0.10 (14)	
C7	C3	C4	C1	89.96 (13)	. C3	C7	C8	C5	-90.04 (14)	
C2	C3	C4	Cl	0.05 (13)	C1	C5	C8	C4	-0.10 (13)	
C9	Cl	C5	C8	133.67 (17)	C6	C5	C8	C4	-90.10 (14)	
C4	Cl	C5	C8	0.10 (13)	<b>C</b> 1	C5	C8	C7	89.90 (14)	
C2	Cl	C5 -	C8	-90.22 (13)	C6	C5	C8	C7	-0.10 (14)	
C9	Cl	C5	C6	-136.33 (17)	S1	01	<b>C</b> 9	C1	-178.47 (11)	
C4	Cl	C5	C6	90.11 (13)	C5	C1	C9	01	177.91 (15)	
C2	Cl	C5	C6	-0.22(13)	C4	Cl	C9	01	-64.3 (2)	
Cl	C5	C6	C7	-89.70 (14)	C2	Cl	<b>C</b> 9	01	58.1 (2)	
C8	C5	C6	C7	0.10 (14)						

Symmetry codes: (i)  $-x, y, \frac{3}{2} - z$ .

Data collection: SMART (Bruker, 1999). Cell refinement: SAINT (Bruker, 1999). Data reduction: SAINT (Bruker, 1999). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *SHELXTL* (Bruker, 1997). Software used to prepare material for publication: *SHELXL*96 (Sheldrick, 1996).

The financial support from the Natural Sciences and Engineering Research Council of Canada and from the Fonds FCAR du Ministère de l'Éducation du Québec is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: ). Services for accessing these data are described at the back of the journal.

#### References

- International Tables for Crystallography (1992). Vol. C. Tables 4.2.6.8 and 6.1.1. 4, Dordrecht: Kluwer Academic Publishers.
- SAINT (1999) Release 6.06; Integration Software for Single Crystal Data, Bruker AXS Inc., Madison, WI 53719-1173.
- Sheldrick, G. M. (1996). SADABS, Bruker Area Detector Absorption Corrections, Bruker AXS Inc., Madison, WI 53719-1173.

Sheldrick, G. M. (1997). SHELX597. Program for the Solution of Crystal Structures. University of Gottingen, Germany.

Sheldrick, G. M. (1996). SHELXL96. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

SHELXTL (1997) Release 5.10; The Complete Software Package for Single Crystal Structure Determination, Bruker AXS Inc., Madison, WI 53719-1173.

SMART (1999) Release 5.059; Bruker Molecular Analysis Research Tool, Bruker AXS Inc., Madison, WI 53719-1173.

Spck, A. L. (1995). July 1995 version; *PLATON*, Molecular Geometry Program, University of Utrecht, Utrecht, Holland.

XPREP (1997) Release 5.10; X-ray data Preparation and Reciprocal space Exploration Program, Bruker AXS Inc., Madison, WI 53719-1173.

Fig. 1 ORTEP (SHELXTL, 1999) drawing of the molecule. Ellipsoids correspond to 30% probability. Data reduction processing was carried out by the use of the program SAINT (Bruker, 1999), which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS (Sheldrick, 1996) was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The space group was confirmed by XPREP routine in *SHELXTL* program (Sheldrick, 1997). The structure was solved by direct method using *SHELXS*97 (Sheldrick, 1997) and difmap synthesis using *SHELXL*96 (Sheldrick, 1996). All non-H atoms anisotropic, hydrogen atoms isotropic. H atoms constrained to the parent site using a riding model; *SHELXL*96 defaults, C—H 0.98 to 0.99 Å. The isotropic factors, U<sub>iso</sub>, were adjusted to 20% higher value of the parent site. A final verification of possible voids was performed using the VOID routine of the *PLATON* program (Spek, 1995).

Data collection: SMART (Bruker, 1999). Cell refinement: SAINT (Bruker, 1999). Data reduction: SAINT (Bruker, 1999). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *SHELXTL* (Bruker, 1997). Software used to prepare material for publication: *SHELXL*96 (Sheldrick, 1996).

# 180

# Supplementary data

The tables of data shown below are not normally printed in Acta Cryst. Section C but the data will be available electronically via the online contents pages at

## http://journals.iucr.org/c/journalhomepage.html

Table S1. Fractional atomic coordinates and equivalent isotropic displacement parameters  $(A^2)$ 

# $U_{\rm eq} = (1/3) \Sigma_i \Sigma_j U^{ij} a^i a^j \mathbf{a}_{i.\mathbf{a}_j}.$

	Occupanc	y x	y	z	$U_{\rm eq}$
31	1	0.0000	0.23042(10)	0.7500	0.0345(2)
D1	1	0.04946(5)	0.3896 (2)	0.80647 (14)	0.0309(3)
02	0.50	-0.00410(12)	0.1293 (5)	0.8850(4)	0.0472(8)
C1	1	0.11031(7)	0,6441(3)	0.76238(19)	0.0263(4)
C2	. 1	0.16705 (7)	0.5691(3)	0.8595 (2)	0.0299(4)
H2	1	0.1776	0.4246	0.8825	0.036
C3	1	0.16576 (8)	0.7382(3)	0.9822(2)	0.0300(4)
H3	1	0.1756	0.7174	1.0952	0.036
C4	1	0.10909 (7)	0.8133 (3)	0.88521(19)	0.0278(4)
H4	1	0.0775	0.8468	0.9271	0.033
C5	1	0.13905 (8)	0.7957 (3)	0.6729(2)	0.0316(4)
H5	1	0.1292	0.8164	0.5599	0.038
C6	1	0.19570 (8)	0.7216 (3)	0.7701(2)	0.0345(4)
H6	. 1	0.2273	0.6888	0.7281	0.041
C7	1	0.19448 (8)	0.8903 (3)	0.8930(2)	0.0339(4)
H7	1	0.2253	0.9806	0.9409	0.041
C8	1	0.13793 (8)	0.9646(3)	0.7958(2)	0.0324(4)
H8	1	0.1275	1.1091	0.7725	0.039
C9	1	0.06339(7)	0.5147(3)	0.6861(2)	0.0307(4)
H9A	1	0.0325	0.6004	0.6358	0.037
H9B	1	0.0731	0.4273	0.6080	0.037

# Table S2. Anisotropic displacement parameters $(Å^2)$

	$U_{11}$	$U_{22}$	$U_{33}$	U <sub>12</sub>	$U_{13}$	$U_{23}$
S1	0.0256(4)	0.0263(4)	0.0488 (4)	0.000	0.0040 (3)	0.000
01	0.0247 (7)	0.0326(7)	0.0319 (7)	-0.0029 (5)	0.0003 (5)	0.0022(5)
O2	0.0380 (16)	0.0362 (16)	0.067 (2)	0.0052 (12)	0.0112 (14)	0.0181 (14)
C1	0.0238(9)	0.0277(9)	0.0255 (8)	-0.0002 (7)	0.0025(6)	-0.0013(7)
C2	0.0247(9)	0.0294(9)	0.0330 (9)	0.0022(7)	0.0019(7)	-0.0020 (7)
C3	0.0287(9)	0.0332 (10)	0.0252 (8)	-0.0020(7)	0.0010 (7)	-0.0024(7)
C4	0.0272(9)	0.0276(9)	0.0286(9)	0.0006 (7)	0.0065 (7)	-0.0013(7)
C5	0.0335(10)	0.0354(10)	0.0260 (9)	-0.0021 (8)	0.0075(7)	0.0005(7)
C6	0.0261 (10)	0.0408(10)	0.0375 (10)	-0.0021 (8)	0.0094(8)	-0.0047(8)
C7	0.0293(10)	0.0350(10)	0.0362 (10)	-0.0083(7)	0.0055 (7)	-0.0052 (8)
C8	0.0360(10)	0.0265 (9)	0.0344 (9)	-0.0016(7)	0.0082 (8)	0.0011(7)
C9	0.0283 (9)	0.0334 (10)	0.0280 (9)	-0.0038 (7)	0.0019 (7)	-0.0011(7)

S1 O2<sup>i</sup> S1 O2 S1 O1<sup>i</sup> S1 O1 O1 C9 C3C7C3 C4 O2<sup>i</sup> S1 O2 O2 S1 O1 01<sup>i</sup> S1 O1 C9 O1 S1 C9 C1C5C1 C4 C1 C4 C1 C4 C1 C2 C9 C5 C9  $\begin{array}{ccc} C1 & C2 \\ C1 & C2 \\ C1 & C2 \\ C2 & C6 \end{array}$ C5C1 C7 C2 C7 C2 C7 C2 C2 C4 C8 C2 H2 C3 C2 C3 C4 C3 C4 C3 H3 C3 H3 C3 H3 C4 C1 Ċ8 C4 C3 C1 C4 C3 C8 C4 H4 C1 C4 H4

C3 C4 H4

Table S3. Geometric parameters $(\mathring{A}, \circ)$ 1.403 (3)       C3       H3         1.403 (3)       C4       C8         1.6147 (13)       C4       H4         1.6147 (13)       C4       H4         1.6147 (13)       C4       H4         1.6147 (13)       C4       H4         1.6147 (13)       C5       C8         1.463 (2)       C5       C6         1.463 (2)       C5       H5         1.565 (2)       C7       H7         1.565 (2)       C7       H7         1.565 (3)       C8       H8         0.9900       C9       H9A         1.565 (2)       C1       C5         1.667 (2)       C6       C6         110.91 (13)       C1       C5         104.51 (14) <th>• • • • • • • • • •</th> <th></th>	• • • • • • • • • •	
1.403 (3)C3H3 $1.403 (3)$ C4C8 $1.6147 (13)$ C4H4 $1.6147 (13)$ C5C8 $1.463 (2)$ C5C6 $1.485 (2)$ C5H5 $1.563 (2)$ C6C7 $1.566 (2)$ C6H6 $1.565 (2)$ C7H8 $0.9900$ C9H9A $1.564 (3)$ C9H9B $1.567 (2)$ C7C8 $104.51 (14)$ C1C5C6 $110.93 (13)$ C8C5H5 $99.69 (10)$ C6C5H5 $104.51 (14)$ C1C5C6 $110.94 (13)$ C1C5C6 $110.94 (13)$ C1C5C6 $122.29 (15)$ C7C6C2 $125.05 (15)$ C5C6C2 $90.19 (13)$ C7C6H6 $90.07 (13)$ C2C6H6 $90.02 (14)$ C8C7C3 $99.89 (13)$ C6C7H7 $125.4$ C6C7H7 $125.4$ C4C8C5 $89.80 (13)$ C7C8H8 $125.2$ C7C8H8 $125.2$ C7C8H8 $125.2$ C7C8H8 $125.4$ C1C9H9A $90.02 (13)$ C1C9H9A $90.02 (13)$ C1C9H9B $125.4$ C1C9H9B $125.4$ C1C9H9B<	Table S3. Geometric pare	ameters $(\AA, \circ)$
1.403 (3)C4C8 $1.6147$ (13)C4H4 $1.6147$ (13)C5C8 $1.463$ (2)C5C6 $1.463$ (2)C5H5 $1.563$ (2)C6C7 $1.566$ (2)C6H6 $1.568$ (2)C7K8 $1.565$ (2)C7H7 $1.565$ (3)C8H8 $0.9900$ C9H9A $1.564$ (3)C9H9B $1.567$ (2)C7C6 $10.451$ (14)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C3C5 $110.94$ (13)C1C5 $123.29$ (15)C7C6 $126.99$ (10)C6C7 $125.05$ (15)C5C6 $90.02$ (13)C4C8 $90.02$ (14)C8C7 $0.02$ (14)C8C7 $0.02$ (13)C6C7 $0.11$ (13)C4C8 $125.4$ C4C8 $125.4$ C4C8 $125.4$ C4C8 $125.4$ C1C9 $1998$ C1C9 $1925.4$ C1	1.403 (3)	C3 H3
1.6147 (13)C4H4 $1.6147$ (13)C5C8 $1.463$ (2)C5C6 $1.485$ (2)C5H5 $1.563$ (2)C6H6 $1.566$ (2)C6H6 $1.566$ (2)C7C8 $1.565$ (3)C8H8 $0.9900$ C9H9A $1.567$ (2)C7H7 $1.567$ (2)C7H7 $1.567$ (2)C1C5 $123.8$ (3)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C8C5 $104.51$ (14)C8C5 $110.94$ (13)C1C5 $123.29$ (15)C7C6 $123.29$ (15)C7C6 $126.99$ (10)C7C6 $126.99$ (15)C5C6 $126.99$ (15)C5C6 $90.02$ (14)C8C7 $90.02$ (14)C8C7 $99.80$ (13)C8C7 $89.80$ (13)C7C8 $89.80$ (13)C7C8 $89.86$ (13)C7C7 $89.86$ (13)C7C8 $90.41$ (13)C4C8 $125.4$ C4C8 $125.4$ C4C8 $125.2$ C7C8 $18$ C7C8 $18$ C7 $125.4$ C4C8 $125.2$ C7C8 $90.02$ (13)C1C9 $1998$ C9 $125.4$ C1<	1.403 (3)	C4 C8
1.6147 (13)C5C8 $1.463$ (2)C5C6 $1.485$ (2)C5H5 $1.563$ (2)C6C7 $1.566$ (2)C6H6 $1.568$ (2)C7C8 $1.565$ (3)C8H8 $0.9900$ C9H9A $1.567$ (2)C1C5 $12.3.8$ (3)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C8C5 $116.09$ (10)C7C6 $12.29$ (15)C7C6 $12.29$ (15)C7C6 $126.99$ (15)C5C6 $126.99$ (15)C5C6 $90.02$ (14)C8C7 $90.02$ (14)C8C7 $99.80$ (13)C7C6 $90.02$ (14)C8C7 $99.92$ (14)C4C8 $125.4$ C6C7 $125.4$ C4C8 $125.2$ C7C8 $18$ (13)C7C8 $125.2$ C7C8 $99.66$ (13)C1C9 $19.76$ (13)C1 </td <td>1.6147 (13)</td> <td>C4 H4</td>	1.6147 (13)	C4 H4
1.463(2)C5C6 $1.485(2)$ C5H5 $1.563(2)$ C6C7 $1.566(2)$ C6H6 $1.565(2)$ C7H7 $1.565(3)$ C8H8 $0.9900$ C9H9A $1.564(3)$ C9H9B $1.567(2)$ TC5 $123.8(3)$ C1C5 $104.51(14)$ C1C5 $104.51(14)$ C1C5 $104.51(14)$ C1C5 $99.69(10)$ C6C5 $116.09(10)$ C7C6 $123.29(15)$ C7C6 $126.99(15)$ C7C6 $126.99(15)$ C5C6 $90.07(13)$ C2C6 $90.02(14)$ C8C7 $90.42(13)$ C6C7 $89.80(13)$ C8C7 $125.4$ C6C7 $89.92(14)$ C4C8 $125.2$ C7C8 $89.86(13)$ C7 $125.4$ C4 $125.2$ C7 $89.86(13)$ C7 $125.4$ C4 $125.2$ C7 $125.4$ C4 $125.2$ C7 $125.4$ C4 $125.2$ C7 $125.4$ C4 $125.2$ C7 $125.4$ C4 $1$	1.6147 (13)	C5 C8
1.485 (2)C5H5 $1.563$ (2)C6C7 $1.565$ (2)C7C8 $1.565$ (2)C7H7 $1.565$ (3)C8H8 $0.9900$ C9H9A $1.564$ (3)C9H9B $1.567$ (2)123.8 (3)C1C5 $123.8$ (3)C1C5C6 $110.93$ (13)C8C5C6 $110.94$ (13)C1C5K6 $104.51$ (14)C1C5C6 $110.94$ (13)C1C5H5 $90.69$ (10)C6C5H5 $99.69$ (10)C6C5H5 $99.69$ (10)C7C6C2 $123.29$ (15)C7C6C2 $125.05$ (15)C5C6H6 $90.07$ (13)C2C6H6 $90.02$ (14)C8C7C3 $89.62$ (13)C6C7H7 $125.4$ C3C7H7 $125.4$ C4C8C5 $89.86$ (13)C7C8H8 $125.2$ C7C8H8 $125.2$ C7C8H8 $125.2$ C7C8H8 $125.2$ C1C9H9A $90.02$ (13)C1C9H9A $90.02$ (13)C1C9H9A $90.02$ (13)C1C9H9A $90.02$ (13)C1C9H9B $125.4$ C1C9H9B $125.4$ C1C9H9B </td <td>1.463 (2)</td> <td>C5 C6</td>	1.463 (2)	C5 C6
1.563 (2)C6C7 $1.566$ (2)C6H6 $1.565$ (2)C7K8 $1.565$ (2)C7H7 $1.565$ (3)C8H8 $0.9900$ C9H9A $1.564$ (3)C9H9B $1.567$ (2)T $123.8$ (3)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C1C5 $104.51$ (14)C3C5 $104.51$ (14)C3C5 $104.51$ (14)C3C5 $9.69$ (10)C6C5 $116.09$ (10)C7C6 $122.29$ (15)C7C6 $125.99$ (15)C5C6 $126.99$ (15)C5C6 $126.99$ (15)C5C6 $90.02$ (14)C8C7 $90.02$ (14)C8C7 $89.62$ (13)C6C7 $89.92$ (14)C4C8 $125.4$ C6C7 $90.41$ (13)C4C8 $125.2$ C7C8 $89.86$ (13)C7C7 $89.92$ (14)C4C8 $125.2$ C7C8 $90.41$ (13)C1 $C9$ H9A $90.02$ (13)C1C9 $91.41$ (24C8 $125.4$ C1 $125.4$ C1 $125.4$ C1 $125.4$ C1 $125.4$ C1 $125.4$ C1 $125.4$	1.485(2)	C5 H5
1.566 (2)C6H61.568 (2)C7C81.565 (2)C7H71.565 (3)C8H80.9900C9H9A1.564 (3)C9H9B1.567 (2)123.8 (3)C1123.8 (3)C1C5123.8 (3)C1C5104.51 (14)C1C5104.51 (14)C1C5104.51 (14)C8C5104.51 (14)C8C5160.9 (10)C7C6123.29 (15)C7C6124.09 (10)C7C6125.05 (15)C5C6126.99 (15)C5C6126.99 (15)C5C6126.99 (15)C5C690.02 (14)C8C725.4C6C7125.4C6C7125.4C4C8125.2C7C813)C7C690.41 (13)C4C8125.2C7C890.41 (13)C4C8125.2C7C890.41 (13)C4C8125.2C7C890.41 (13)C4C8125.2C7C890.41 (13)C491.76 (13)C191.76 (13)C191.76 (13)C191.76 (13)C191.76 (13)C191.76 (13)C191.76 (13)C191.76 (13)C191.76 (13)	1.563(2)	C6 C7
1.568 (2)C7C81.565 (2)C7H71.565 (3)C81.565 (3)C81.565 (3)C91.565 (3)C91.565 (3)C91.565 (3)C91.565 (3)C91.565 (3)C91.565 (3)C91.565 (3)C91.567 (2)123.8 (3)C11.567 (2)123.8 (3)C110.93 (13)C8C5C6110.94 (13)C1C5K6104.51 (14)C8C5C5123.29 (15)C7C6C2125.05 (15)C5C6126.09 (15)C5C690.02 (14)C8C7C725.4C6C789.80 (13)C7C8C789.80 (13)C7C889.80 (13)C7C889.86 (13)C7C789.86 (13)C7C789.76 (13)C1C9H9A90.02 (13)C1C9H9B125.4C1C910C1C7C8C8C7C8C8C7C8C9C9C9C9C9 <t< td=""><td>1.566 (2)</td><td>C6 H6</td></t<>	1.566 (2)	C6 H6
1.565(2)C7H7 $1.565(2)$ C7H7 $1.565(3)$ C8H8 $0.9900$ C9H9A $1.567(2)$ 123.8 (3)C1C5 $123.8(3)$ C1C5C6 $110.93(13)$ C8C5C6 $110.94(13)$ C1C5H5 $104.51(14)$ C8C5H5 $104.51(14)$ C8C5H5 $104.51(14)$ C8C5H5 $104.51(14)$ C8C5H5 $104.51(14)$ C8C5H5 $116.09(10)$ C7C6C2 $125.05(15)$ C5C6C2 $90.19(13)$ C7C6H6 $90.07(13)$ C2C6H6 $90.02(14)$ C8C7C3 $89.62(13)$ C6C7H7 $125.4$ C6C7H7 $125.4$ C6C7H7 $125.4$ C4C8C5 $89.86(13)$ C7C8K5 $89.86(13)$ C7C8K5 $90.41(13)$ C4C8H8 $125.2$ C1C9H9A $90.02(13)$ C1C9H9A $90.02(13)$ C1C9H9B $125.4$ C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B	1.568 (2)	C7 C8
1.565(3) $C8$ $H8$ $0.9900$ C9 $H9A$ $1.564(3)$ C9 $H9B$ $1.567(2)$ 123.8 (3)C1C5 $123.8(3)$ C1C5C6 $110.93(13)$ C8C5C6 $110.94(13)$ C1C5H5 $104.51(14)$ C3C5H5 $104.51(14)$ C3C5H5 $104.51(14)$ C3C5H5 $99.69(10)$ C6C5H5 $116.09(10)$ C7C6C2 $123.29(15)$ C7C6C2 $125.05(15)$ C5C6H6 $90.07(13)$ C2C6H6 $90.02(14)$ C8C7C3 $89.62(13)$ C6C7C3 $89.80(13)$ C8C7H7 $125.4$ C4C8C5 $89.92(14)$ C4C8C5 $90.41(13)$ C4C8H8 $125.2$ C7C8H8 $125.2$ C7C8H8 $125.2$ C1C9H9A $90.02(13)$ C1C9H9A $90.02(13)$ C1C9H9A $90.02(13)$ C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B $125.4$ H9AC9H9B	1 565 (2)	C7 H7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 565 (3)	C9 119
1.654 (3) $C9$ $H9B$ $1.667$ (2) $123.8$ (3) $C1$ $C5$ $C8$ $104.51$ (14) $C1$ $C5$ $C6$ $110.93$ (13) $C8$ $C5$ $C6$ $110.94$ (13) $C1$ $C5$ $H5$ $104.51$ (14) $C8$ $C7$ $C6$ $90.69$ (10) $C6$ $C5$ $H5$ $116.09$ (10) $C7$ $C6$ $C2$ $125.05$ (15) $C5$ $C6$ $C2$ $90.19$ (13) $C7$ $C6$ $H6$ $90.07$ (13) $C2$ $C6$ $H6$ $90.02$ (14) $C8$ $C7$ $C3$ $89.60$ (13) $C7$ $C8$ $C5$ $90.41$ (13) $C4$ $C8$ $C7$ $125.4$ $C4$ $C8$ $C5$ $90.41$ (13) $C4$ $C8$ $H8$ $125.2$ $C1$ $C9$ $H9A$ $90.02$ (13) $C1$ $C9$ $H9A$ $90.02$ (13) $C1$ $C9$ $H9B$ $125.4$ $C1$ $C9$ $H9B$ $125.4$ </td <td>0.0000</td> <td>C0 110</td>	0.0000	C0 110
1.004 (3)C9 H951.567 (2)123.8 (3)C1 C5 C8104.51 (14)C1 C5 C6110.93 (13)C8 C5 C6110.94 (13)C1 C5 H5104.51 (14)C8 C5 H599.69 (10)C6 C5 H5116.09 (10)C7 C6 C5123.29 (15)C7 C6 C6126.99 (15)C7 C6 H690.07 (13)C2 C6 H690.02 (14)C8 C7 C389.62 (13)C6 C7 H7125.4C6 C7 H7125.4C4 C8 C599.92 (14)C4 C8 C599.92 (14)C4 C8 H8125.2C7 C8 H8125.2C7 C8 H8125.2C7 C8 H8125.4C1 C9 H9A90.02 (13)C1 C9 H9A90.02 (14)C4 C8 H8125.4C5 C6 H8125.4C4 C8 H8125.4C7 C8 H8125.4C7 C8 H8125.4C7 C8 H8125.4C7 C8 H8125.4C7 C8 H8125.2C7 C8 H8125.4C1 C9 H9A90.02 (13)C1 C9 H9A90.02 (14)C4 C8 H8125.4C1 C9 H9B125.4C1 C9 H9B125.4C1 C9 H9B125.4C1 C9 H9B125.4H9A C9 H9B125.4H9A C9 H9B	1.564 (2)	C0 1102
1.301 (2) $123.8 (3)$ C1C5C8 $104.51 (14)$ C1C5C6 $110.93 (13)$ C8C5C6 $110.94 (13)$ C1C5H5 $104.51 (14)$ C8C5H5 $99.69 (10)$ C6C5H5 $116.09 (10)$ C7C6C2 $125.05 (15)$ C7C6C2 $90.19 (13)$ C7C6H6 $126.99 (15)$ C5C6H6 $90.07 (13)$ C2C6H6 $90.02 (14)$ C8C7C3 $89.62 (13)$ C6C7H7 $125.4$ C6C7H7 $125.4$ C4C8C7 $89.92 (14)$ C4C8C5 $89.86 (13)$ C7C8K8 $125.2$ C7C8H8 $125.2$ C7C8H8 $125.2$ C1C9C1 $89.76 (13)$ O1C9H9A $90.02 (13)$ C1C9H9B $125.4$ C1C9H9B $125.4$ C1C9H9B	1.004 (3)	Co Hab
123.8 (3)C1C5C8 $104.51$ (14)C1C5C6 $110.93$ (13)C8C5C6 $110.94$ (13)C1C5H5 $104.51$ (14)C8C5H5 $104.51$ (14)C8C5H5 $116.09$ (10)C7C6C5 $123.29$ (15)C7C6C2 $125.05$ (15)C5C6H6 $90.07$ (13)C2C6H6 $90.02$ (14)C8C7C3 $89.62$ (13)C6C7C3 $89.80$ (13)C8C7H7 $125.4$ C6C7H7 $125.4$ C4C8C7 $89.86$ (13)C7C8C5 $90.41$ (13)C4C8H8 $125.2$ C7C8H8 $125.2$ C7C8H8 $125.2$ C1C9H9A $90.02$ (13)C1C9H9A $90.02$ (14)C4C8C7	1.007 (2)	
104.51 $(14)$ $C1$ $C5$ $C6$ $110.93$ $(13)$ $C8$ $C5$ $C6$ $110.94$ $(13)$ $C1$ $C5$ $H5$ $104.51$ $(14)$ $C8$ $C5$ $H5$ $99.69$ $(10)$ $C6$ $C5$ $H5$ $116.09$ $(10)$ $C7$ $C6$ $C2$ $123.29$ $(15)$ $C7$ $C6$ $C2$ $125.05$ $(15)$ $C5$ $C6$ $C2$ $90.19$ $(13)$ $C7$ $C6$ $H6$ $90.07$ $(13)$ $C2$ $C6$ $H6$ $90.07$ $(13)$ $C2$ $C6$ $H6$ $90.02$ $(14)$ $C8$ $C7$ $C3$ $89.62$ $(13)$ $C6$ $C7$ $C3$ $89.80$ $(13)$ $C8$ $C7$ $H7$ $125.4$ $C3$ $C7$ $C8$ $C5$ $89.80$ $(13)$ $C7$ $C8$ $C5$ $89.92$ $(14)$ $C4$ $C8$ $C7$ $89.92$ $(14)$ $C4$ $C8$ $C5$ $90.41$ $(13)$ $C4$ $C8$ $H8$ $125.2$ $C7$ $C8$ $H8$ $125.2$ $C1$ $C9$ $H9A$ $90.02$ $(13)$ $C1$ $C9$ $H9A$ $90.02$ $(13)$ $C1$ $C9$ $H9B$ $125.4$ $C1$ $C9$ $H9B$ $125.4$ $H9A$ $C9$ $H9B$	123.8 (3)	C1 C5 C8
110.93 $(13)$ $C8$ $C5$ $C6$ $110.94$ $(13)$ $C1$ $C5$ $H5$ $104.51$ $(14)$ $C8$ $C5$ $H5$ $99.69$ $(10)$ $C6$ $C5$ $H5$ $116.09$ $(10)$ $C7$ $C6$ $C5$ $123.29$ $(15)$ $C7$ $C6$ $C2$ $22.05$ $(15)$ $C5$ $C6$ $C2$ $90.19$ $(13)$ $C7$ $C6$ $H6$ $90.07$ $(13)$ $C2$ $C6$ $H6$ $90.07$ $(13)$ $C2$ $C6$ $H6$ $90.02$ $(14)$ $C8$ $C7$ $C3$ $89.62$ $(13)$ $C8$ $C7$ $H7$ $125.4$ $C6$ $C7$ $H7$ $125.4$ $C4$ $C8$ $C5$ $89.80$ $(13)$ $C7$ $C8$ $C5$ $89.92$ $(14)$ $C4$ $C8$ $C5$ $90.41$ $(13)$ $C4$ $C8$ $H8$ $125.2$ $C7$ $C8$ $H8$ $125.2$ $C1$ $C9$ $H9A$ $90.02$ $(13)$ $C1$ $C9$ $H9A$ $90.02$ $(13)$ $C1$ $C9$ $H9B$ $125.4$ $C1$ $C9$ $H9B$ $125.4$ $H9A$ $C9$ $H9B$	104.51 (14)	C1 C5 C6
110.94 (13)C1C5H5 $104.51$ (14)C8C5H5 $99.69$ (10)C6C5H5 $116.09$ (10)C7C6C5 $123.29$ (15)C7C6C2 $125.05$ (15)C5C6C2 $90.19$ (13)C7C6H6 $126.99$ (15)C5C6H6 $90.07$ (13)C2C6H6 $90.02$ (14)C8C7C3 $89.62$ (13)C6C7C3 $89.80$ (13)C8C7H7 $125.4$ C6C7H7 $125.4$ C4C8C5 $89.92$ (14)C4C8C5 $90.41$ (13)C4C8H8 $125.2$ C7C8H8 $125.2$ C1C9C1 $89.76$ (13)O1C9H9A $90.02$ (13)C1C9H9B $125.4$ C1C9H9B $125.4$ C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B	110.93 (13)	C8 C5 C6
104.51 $(14)$ $C8$ $C5$ $H5$ $99.69$ $(10)$ $C6$ $C5$ $H5$ $116.09$ $(10)$ $C7$ $C6$ $C5$ $123.29$ $(15)$ $C7$ $C6$ $C2$ $125.05$ $(15)$ $C5$ $C6$ $C2$ $90.19$ $(13)$ $C7$ $C6$ $H6$ $90.07$ $(13)$ $C2$ $C6$ $H6$ $90.02$ $(13)$ $C8$ $C7$ $C3$ $89.62$ $(13)$ $C6$ $C7$ $C3$ $89.62$ $(13)$ $C6$ $C7$ $H7$ $125.4$ $C6$ $C7$ $H7$ $125.4$ $C4$ $C8$ $C7$ $89.92$ $(14)$ $C4$ $C8$ $C5$ $90.41$ $(13)$ $C4$ $C8$ $H8$ $125.2$ $C7$ $C8$ $H8$ $125.2$ $C7$ $C8$ $H8$ $125.2$ $C1$ $C9$ $H9A$ $90.02$ $(13)$ $C1$ $C9$ $H9B$ $125.4$ $C1$ $C9$ $H9B$ $125.4$ $C1$ $C9$ $H9B$	110.94 (13)	C1 C5 H5
99.69(10)C6C5H5 $116.09(10)$ C7C6C5 $123.29(15)$ C7C6C2 $125.05(15)$ C5C6C2 $90.19(13)$ C7C6H6 $126.99(15)$ C5C6H6 $90.07(13)$ C2C6H6 $90.02(14)$ C8C7C3 $89.62(13)$ C6C7C3 $89.80(13)$ C8C7H7 $125.4$ C6C7H7 $125.4$ C4C8C7 $89.92(14)$ C4C8C7 $89.92(14)$ C4C8C5 $89.86(13)$ C7C8C5 $90.41(13)$ C4C8H8 $125.2$ C7C8H8 $125.2$ C1C9H9A $90.02(13)$ C1C9H9A $90.02(13)$ C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B $125.4$ H9AC9H9B	104.51 (14)	C8 C5 H5
116.09(10)C7C6C5 $123.29(15)$ C7C6C2 $125.05(15)$ C5C6C2 $90.19(13)$ C7C6H6 $126.99(15)$ C5C6H6 $90.07(13)$ C2C6H6 $90.07(13)$ C2C6H6 $90.02(14)$ C8C7C3 $89.62(13)$ C6C7C3 $89.80(13)$ C8C7H7 $125.4$ C6C7H7 $125.4$ C4C8C7 $89.92(14)$ C4C8C5 $89.86(13)$ C7C8C5 $90.41(13)$ C4C8H8 $125.2$ C7C8H8 $125.2$ C1C9C1 $89.76(13)$ O1C9H9A $90.02(13)$ C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B $125.4$ H9AC9H9B	99.69 (10)	C6 C5 H5
123.29 (15)C7C6C2 $125.05$ (15)C5C6C2 $90.19$ (13)C7C6H6 $126.99$ (15)C5C6H6 $90.07$ (13)C2C6H6 $90.07$ (13)C8C7C6 $90.02$ (14)C8C7C3 $89.62$ (13)C6C7C3 $89.80$ (13)C8C7H7 $125.4$ C3C7H7 $125.4$ C4C8C7 $89.92$ (14)C4C8C5 $89.86$ (13)C7C8C5 $90.41$ (13)C4C8H8 $125.2$ C7C8H8 $125.2$ C1C9C1 $89.76$ (13)O1C9H9A $90.02$ (13)C1C9H9B $125.4$ C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B	116.09 (10)	C7 C6 C5
125.05(15)C5C6C2 $90.19(13)$ C7C6H6 $126.99(15)$ C5C6H6 $90.07(13)$ C2C6H6 $90.02(13)$ C8C7C6 $90.02(14)$ C8C7C3 $89.62(13)$ C6C7C3 $89.80(13)$ C8C7H7 $125.4$ C6C7H7 $125.4$ C4C8C7 $89.92(14)$ C4C8C5 $89.86(13)$ C7C8C5 $90.41(13)$ C4C8H8 $125.2$ C7C8K8 $125.2$ C7C8K8 $125.2$ C1C9C1 $89.76(13)$ O1C9H9A $90.02(13)$ C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B $125.4$ H9AC9H9B	123.29 (15)	C7 C6 C2
90.19 (13)C7C6H6 $126.99$ (15)C5C6H6 $90.07$ (13)C2C6H6 $90.32$ (13)C8C7C6 $90.02$ (14)C8C7C3 $89.62$ (13)C6C7C3 $89.62$ (13)C6C7H7 $125.4$ C6C7H7 $125.4$ C4C8C7 $89.92$ (14)C4C8C5 $89.86$ (13)C7C7C8 $125.2$ C7C8H8 $125.2$ C5C8H8 $125.2$ C1C9C1 $89.76$ (13)O1C9H9A $90.02$ (13)C1C9H9B $125.4$ C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B $125.4$ H9AC9H9B	125.05 (15)	C5 C6 C2
126.99(15)C5C6H6 $90.07(13)$ C2C6H6 $90.32(13)$ C8C7C6 $90.02(14)$ C8C7C3 $89.62(13)$ C6C7C3 $89.62(13)$ C6C7C3 $89.80(13)$ C8C7H7 $125.4$ C6C7H7 $125.4$ C4C8C7 $89.92(14)$ C4C8C5 $89.86(13)$ C7C8C5 $90.41(13)$ C4C8H8 $125.2$ C7C8H8 $125.2$ C5C8H8 $125.2$ C1C9C1 $89.76(13)$ O1C9H9A $90.02(13)$ C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B $125.4$ H9AC9H9B	90.19 (13)	C7 C6 H6
90.07 (13)C2C6H690.32 (13)C8C7C690.02 (14)C8C7C3 $89.62$ (13)C6C7C3 $89.62$ (13)C6C7C3 $89.80$ (13)C8C7H7 $125.4$ C6C7H7 $125.4$ C4C8C7 $89.92$ (14)C4C8C5 $89.92$ (14)C4C8C5 $99.41$ (13)C4C8K5 $125.2$ C7C8H8 $125.2$ C7C8H8 $125.2$ C1C9C1 $89.76$ (13)C1C9H9A $90.02$ (13)C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B $125.4$ H9AC9H9B $125.4$ H9AC9H9B	126.99 (15)	C5 C6 H6
90.32 (13) $C3$ $C6$ $C7$ $C6$ $90.02$ (14) $C8$ $C7$ $C3$ $89.62$ (13) $C6$ $C7$ $C3$ $89.80$ (13) $C8$ $C7$ $H7$ $125.4$ $C6$ $C7$ $H7$ $125.4$ $C6$ $C7$ $H7$ $125.4$ $C4$ $C8$ $C7$ $89.92$ (14) $C4$ $C8$ $C7$ $89.92$ (14) $C4$ $C8$ $C5$ $89.86$ (13) $C7$ $C8$ $C5$ $90.41$ (13) $C4$ $C8$ $H8$ $125.2$ $C7$ $C8$ $H8$ $125.2$ $C1$ $C9$ $H9A$ $90.02$ (13) $C1$ $C9$ $H9A$ $90.02$ (13) $C1$ $C9$ $H9B$ $125.4$ $C1$ $C9$ $H9B$ $125.4$ $H9A$ $C9$ $H9B$	90.07 (13)	C2 C6 H6
90.02 (14)C8C7C3 $90.02 (14)$ C8C7C3 $89.62 (13)$ C6C7C3 $89.80 (13)$ C8C7H7 $125.4$ C6C7H7 $125.4$ C3C7H7 $125.4$ C4C8C7 $89.92 (14)$ C4C8C5 $89.86 (13)$ C7C8C5 $90.41 (13)$ C4C8H8 $125.2$ C7C8H8 $125.2$ C1C9C1 $89.76 (13)$ O1C9H9A $90.02 (13)$ C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B $125.4$ H9AC9H9B	90.32 (13)	C8 C7 C6
89.62 (13) $C6$ $C7$ $C3$ $89.80$ (13) $C6$ $C7$ $C3$ $125.4$ $C6$ $C7$ $H7$ $125.4$ $C3$ $C7$ $H7$ $125.4$ $C3$ $C7$ $H7$ $125.4$ $C4$ $C8$ $C7$ $89.92$ (14) $C4$ $C8$ $C5$ $89.92$ (14) $C4$ $C8$ $C5$ $90.41$ (13) $C4$ $C8$ $H8$ $125.2$ $C7$ $C8$ $H8$ $125.2$ $C1$ $C9$ $C1$ $89.76$ (13) $O1$ $C9$ $H9A$ $90.02$ (13) $C1$ $C9$ $H9B$ $125.4$ $C1$ $C9$ $H9B$ $125.4$ $H9A$ $C9$ $H9B$	90.02 (14)	C8 C7 C3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	80.62 (13)	C6 C7 C3
33.80 (13) $C3$ $C7$ $H7$ $125.4$ $C6$ $C7$ $H7$ $125.4$ $C3$ $C7$ $H7$ $125.4$ $C4$ $C8$ $C7$ $89.92$ (14) $C4$ $C8$ $C5$ $89.86$ (13) $C7$ $C8$ $C5$ $90.41$ (13) $C4$ $C8$ $H8$ $125.2$ $C7$ $C8$ $H8$ $125.2$ $C5$ $C8$ $H8$ $125.2$ $C1$ $C9$ $C1$ $89.76$ (13) $O1$ $C9$ $H9A$ $90.02$ (13) $C1$ $C9$ $H9B$ $125.4$ $C1$ $C9$ $H9B$ $125.4$ $H9A$ $C9$ $H9B$ $125.4$ $H9A$ $C9$ $H9B$ $125.4$ $H9A$ $C9$ $H9B$	80.80 (12)	
125.4CoC7 $H7$ $125.4$ C3C7H7 $125.4$ C4C8C7 $89.92$ (14)C4C8C5 $89.86$ (13)C7C8C5 $90.41$ (13)C4C8H8 $125.2$ C7C8H8 $125.2$ C7C8H8 $125.2$ C1C9C1 $89.76$ (13)C1C9H9A $90.02$ (13)C1C9H9A $89.65$ (13)O1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B $125.4$ H9AC9H9B $125.4$ C1C9H9B	105.00 (13)	
125.4C3C7H7 $125.4$ C4C8C7 $89.92$ (14)C4C8C7 $89.92$ (14)C4C8C7 $89.92$ (14)C4C8C7 $89.92$ (13)C7C8C5 $90.41$ (13)C4C8K8 $125.2$ C7C8H8 $125.2$ C7C8H8 $125.2$ O1C9C1 $89.76$ (13)O1C9H9A $90.02$ (13)C1C9H9B $125.4$ C1C9H9B $125.4$ H9AC9H9B $125.4$ H9AC9H9B $125.4$ C1C9H9B	195 4	C0 C7 H7
125.4       C4       C8       C7         89.92 (14)       C4       C8       C7         89.92 (14)       C4       C8       C5         89.92 (14)       C4       C8       C5         89.92 (14)       C4       C8       C5         89.86 (13)       C7       C8       C5         90.41 (13)       C4       C8       H8         125.2       C7       C8       H8         125.2       C5       C8       H8         125.2       O1       C9       C1         89.76 (13)       O1       C9       H9A         90.02 (13)       C1       C9       H9A         90.02 (13)       O1       C9       H9B         125.4       C1       C9       H9B         125.4       H9A       C9       H9B         125.4       H9A       C9       H9B	120.4	
89.92 (14)       C4       C8       C5         89.86 (13)       C7       C8       C5         90.41 (13)       C4       C8       H8         125.2       C7       C8       H8         125.2       C5       C8       H8         125.2       O1       C9       C1         89.76 (13)       O1       C9       H9A         90.02 (13)       C1       C9       H9A         89.65 (13)       O1       C9       H9B         125.4       C1       C9       H9B         125.4       H9A       C9       H9B	120.4	04 08 07
89.86 (13)       C7       C8       C5         90.41 (13)       C4       C8       H8         125.2       C7       C8       H8         125.2       C5       C8       H8         125.2       C1       C9       C1         89.76 (13)       O1       C9       H9A         90.02 (13)       C1       C9       H9A         89.65 (13)       O1       C9       H9B         125.4       C1       C9       H9B         125.4       H9A       C9       H9B	89.92 (14)	C4 C8 C5
90.41 (13)       C4       C8       H8         125.2       C7       C8       H8         125.2       C5       C8       H8         125.2       C1       C9       C1         89.76 (13)       O1       C9       H9A         90.02 (13)       C1       C9       H9A         89.65 (13)       O1       C9       H9B         125.4       C1       C9       H9B         125.4       H9A       C9       H9B	89.86 (13)	C7 C8 C5
125.2       C7       C8       H8         125.2       C5       C8       H8         125.2       O1       C9       C1         89.76       (13)       O1       C9       H9A         90.02       (13)       C1       C9       H9B         125.4       C1       C9       H9B         125.4       H9A       C9       H9B	90.41 (13)	C4 C8 H8
125.2       C5       C8       H8         125.2       O1       C9       C1         89.76       (13)       O1       C9       H9A         90.02       (13)       C1       C9       H9A         89.65       (13)       O1       C9       H9B         125.4       C1       C9       H9B         125.4       H9A       C9       H9B	125.2	C7 C8 H8
125.2       O1       C9       C1         89.76       (13)       O1       C9       H9A         90.02       (13)       C1       C9       H9A         89.65       (13)       O1       C9       H9B         125.4       C1       C9       H9B         125.4       H9A       C9       H9B	125.2	C5 C8 H8
89.76 (13)       O1       C9       H9A         90.02 (13)       C1       C9       H9A         89.65 (13)       O1       C9       H9B         125.4       C1       C9       H9B         125.4       H9A       C9       H9B         125.4       H9A       C9       H9B         125.4       H9A       C9       H9B	125.2	O1 C9 C1
90.02 (13)       C1       C9       H9A         89.65 (13)       O1       C9       H9B         125.4       C1       C9       H9B         125.4       H9A       C9       H9B	89.76 (13)	O1 C9 H9A
89.65 (13)         O1         C9         H9B           125.4         C1         C9         H9B           125.4         H9A         C9         H9B           125.4         H9A         C9         H9B           125.4         H9A         C9         H9B	90.02 (13)	C1 C9 H9A
125.4         C1         C9         H9B           125.4         H9A         C9         H9B           125.4         H9A         C9         H9B	89.65 (13)	O1 C9 H9B
125.4 H9A C9 H9B 125.4	125.4	C1 C9 H9B
125.4	125.4	H9A C9 H9B
	125.4	

181

0.9900

0.9900 1.564 (3) 0.9900 1.564 (3) 0.9900 0.9900 0.9900 0.9800

0.9800

125.3

125.3

125.3

125.3

 $125.2 \\ 125.2 \\ 125.2 \\ 125.2$ 

 $\begin{array}{c} 125.2 \\ 125.2 \end{array}$ 

125.2 106.96 (13)

110.3

110.3

110.3 110.3 108.6

89.80 (13)

90.00 (13) 90.00 (14) 125.3

89.94 (14)

89.92 (14)

90.13 (13) 125.3

90.10 (14) 90.11 (14) 90.14 (14)

90.00 (13)

90.24 (13) 89.95 (14)

1.563 (2) 0.9900 1.565 (3) 1.565 (3)

															182
$O2^{i}$	S1	01	C9		43.4 (2)		C1	C5	C6	$C2^{\circ}$			0.22	(13)	
02	S1	01	C9		178.91 (17	)	C8	C5	C6	C2		1	90.02	(14)	
01 <sup>i</sup>	S1	01	C9		-66.35 (11	ý	C3	C2.	C6	C7			0.11	(14)	
C9	C1 .	C2	C3		-136.28 (18	) ·	C1	C2	C6	C7			89.73	(14)	
C5	C1	C2	C3		90.24 (13	; )	C3	C2	C6	C5			89.83	(13)	
C4	C1	C2	Ċ3		0.05 (13	j	C1	C2	C6	C5		-	-0.22	(13)	
C9	C1	C2	C6		133.70 (18	) · · · ·	C5	C6	C7	C8			-0.10	(14)	
C5	Cl	C2	C6		0.22 (13	)	C2	C6	C7	C8		••••	90.23	(14)	
C4	C1	C2	C6		-89.97 (13	)	C5	C6	C7	C3	-		90.02	(14)	
C6	C2	C3	C7		-0.11 (14	)	C2	C6	C7	C3			-0.11	(14)	
C1	C2	C3	C7		-89.91(14)	) -	$C_2$	C3	C7	C8			90.21	(13)	
C6	C2	C3	C4		89.75 (13	)	C4	C3	C7	C8		-	-0.20	(13)	
C1	C2	C3	C4		-0.05 (13)	)	_C2	C3	C7	C6			0.11	(14)	
. C9	C1	C4	C8.		-132.39 (17	)	C4	C3	C7	C6			90.30	(13)	
C5	C1	C4	C8		-0.10 (13	)	C1	C4	C8	C7		·	89.85	(13)	
C2	C1	C4	C8		89.97 (13	)	C3	C4	C8	C7		-	-0.20	(13)	
C9	C1	C4	$C_3$		137.60 (17	)	C1	C4	C8	$C_{2}$			0.10	(13)	
C5	C1	C4	C3		-90.12 (13)	)	C3	C4	C8	C5			89.76	(14)	
C2	C1	C4	C3		-0.05 (13	)	C6	C7	C8	C4			90.34	(14)	
C7	C3	C4	C8		0.20 (13	)	C3	C7	C8	C4			0.20	(13)	
$C_2$	C3	C4	C8		-89.72 (13	)	C6	C7	C8	C5 -			0.10	(14)	
C7	C3	C4	C1		89.96 (13	)	- C3	C7	C8	C5			90.04	(14)	
C2	C3	C4	Cl		0.05 (13	)	C1	C5	C8	C4		-	-0.10	(13)	
C9	C1	$C_{2}$	C8		133.67 (17	)	C6	C5	C8	C4		-	90.10	(14)	
C4	C1	C5	C8		0.10 (13	)	C1	C5	.C8	C7			89.90	(14)	
$C_2$	C1	C5	C8		-90.22 (13	) .	C6	C5	C8	C7			-0.10	(14)	
C9	C1	C5	C6		-136.33 (17)	) '' ''	S1	01	C9	C1		-1	78.47	(11)	
C4	C1	C5	C6		90.11 (13	)	C5	C1	C9	01		1	77.91	(15)	
C2	C1	C5	C6		-0.22 (13)	)	C4	C1	C9	01			64.3	(2)	
C1	C5	C6	C7		-89.70 (14	)	$C_2$	C1	C9	01			58.1 (	(2)	
C8	C5	C6	C7		0.10 (14	.)									
Syn	metr	у сос	les: (i)	$(-x,y,\frac{3}{2}-z)$	•										





