X-RAY INVESTIGATION OF CERTAIN SUBSTITUTION PRODUCTS OF CYCLOHEXANE

THE X-RAY INVESTIGATION
OF
CERTAIN SUBSTITUTION PRODUCTS
OF
CYCLOHEXANE

A Thesis submitted to the Faculty of Graduate Studies & Research
of McGill University in part fulfilment of the requirements
for the Degree of Doctor of Philosophy

By

T. N. WHITE, M.Sc.

September, 1929.

Foreword and Acknowledgments

As an introduction, the writer would like to give a brief outline of the work which has been done in connection with the x-ray crystal structure laboratory of the Physics Department of this University since its beginning some three years ago. For, although this thesis deals chiefly with the more recent research of the writer, its value can perhaps be better estimated if it be considered in relation to the more general scheme of research which has gradually been evolved during the collaboration of Dr. A. L. Patterson and the writer.

In the spring of 1926 the writer was given the privilege of commencing the organization of this laboratory, and by the end of the following summer the nucleus of an effective set of apparatus had been formed. During the ensuing session it was possible to give some slight assistance to Dr. G. S. Whitby in his research on certain polymerised colloids, and the results of the x-ray investigation of one of these has been presented elsewhere (M.Sc. Thesis). During the summer of 1927 the writer concluded some minor investigations in the X-ray Division of the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology, and so had the opportunity of studying at close quarters the work which was being done there.

Prior to the commencement of this laboratory at McGill University, Dr. Patterson had taken up an investigation of the lower w - phenyl normal saturated fatty acids under Sir William Bragg at the Davy-Faraday Research Laboratory of the Royal Institution.

After the conclusion of his work there he spent a year at the Institut für Faserstoffchemie, during which, among other things, he devoted some time to the study of the problem of the determination of particle size.

On the resumption of x-ray work at McGill University, the question arose as to what substances might best be chosen as a field for research. Both Dr. Patterson and the writer had been interested in the problem of organic structure and a survey was made of the state of knowledge in this field at that time. It appeared that the aliphatic compounds were being studied with success by a particularly capable body of workers and that attention might better be turned in other directions. The most interesting highly complex substances, such as rubber and cellulose, were also being studied with as much success as such difficult problems admitted at that time, and it was felt that progress in that field, which had been of particular interest to both Dr. Patterson and the writer in their eariler work, might best be advanced by the study of compounds of intermediate complexity. Perhaps the most outstanding field which remained at that time consisted of the aromatic compounds. Here again, though progress was slow owing to the complexity of the problem, excellent work was being done. Most of the compounds which were being studied were however of the unsaturated type, or partly saturated with heavier atoms such as chlorine. Little work had been done on the saturated compounds, and none on those saturated with the lighter atomic groups, such as hydrogen and the hydroxyl group, such as the hydroxy substitution products of cyclohexane. It seemed, then, that this might be an excellent field for x-ray investigation.

The writer here wishes to state that the burden of these considerations lay almost entirely on Dr. Patterson, and that in this respect he owes a particular debt, for at that time, due to the fact that his attention had previously been devoted largely to development of the laboratory, his knowledge of contemporary research was decidedly limited. All through his research the writer has benefitted from this wider knowledge of the field possessed by Dr. Patterson, and he feels that what success has been attained in the work described in this thesis has been largely dependent on what he has learned through this association.

In obtaining the substances used in this research, in the determination of some of their properties, and in their purification, much assistance has been given by chemists. A particular debt is due to Professor Whitby and Dr. Greenberg of the Department of Chemistry of this University. They supplied two of the substances and prepared a third, which would otherwise have been especially difficult to obtain. It is a particular pleasure to acknowledge the kindness of Dr. C. Anderson, of the Australian National Museum, in sending the specimens and a copy of the data of a crystallographic examination which he performed more than ten years ago.

The writer would also thank Professor Graham of the Department of Mineralogy for preliminary instruction in the use of the double circle goniometer.

An interest in the work of the x-ray laboratory led Mr. E. H. Johnson to give assistance in the taking of some of the photographs of the quercitol series, and this aid is gratefully acknowledged.

The high standard set by the research, in the Macdonald Physics Laboratory, of Dr. J. S. Foster on the Stark Effect, has been a very considerable source of inspiration to the writer during his three years of research here.

Finally, the writer wishes to record his most sincere thanks to Dr. A. S. Eve, the Director of the Macdonald Physics Laboratory, for the interest he has taken both in the provision of adequate apparatus and in the general progress of the research.

TABLE OF CONTENTS.

Page

Foreword and Acknowledgements 1

Table of Contents v

Summary vi

Section I. Introduction 2

Section II. Isomerism and the Hydroxy Substitution Products of Cyclohexane 13

Section III. Theory of Structure Determination

§1. Determination of the Unit Cell and Possible Space Groups 28

§2. Determination of Intensity of Reflection 37

§3. Methods of Determining the Crystal Structure 44

Section IV. Experimental 47

§1. The X-Ray Apparatus §2. The Spectrograph §3. Description of Automatic Control §4. Photographs of Apparatus §5. Operation §6. Choice of Crystal Settings §7. Analysis of Rotating Crystal Photographs

Section V. Results and Conclusions

Inactive Inositol 67

Laevo Inositol 75

Quebrachitol 85

Quercitol 90

Summary of Cell Data 101

General Remarks 102

References 104

Appendix:-

SUMMARY OF THE RESEARCH DESCRIBED IN THIS THESIS.

1. Object

It having first been recognized that the series of hydroxy substitution products of cyclohexane is of importance in the study of the structure of organic matter in the solid state, it was decided:

(i) To investigate the isomerism of the series with the purpose of arriving at a tentative opinion as to its promise as a series for x-ray examination.

(ii) To make a preliminary x-ray investigation of a few of the available members which seemed to be most closely related in order to see whether the opinion as to the promise of the series was well founded.

(iii) To push the investigation rather farther in one or two cases, both on account of the interest of the problem itself, and in order to arrive at a decision as to whether more detailed structure investigations of complicated substances of this type are at present to be regarded as problems capable of solution.

2. Results

A fairly thorough investigation of the literature has enabled the writer to present a list of most of the known members of the series, and considerable knowledge has been gathered as to the sources, chief properties and special interest of the individual members.
It was decided after a consideration of the isomerism and chief properties of a certain group of members that the series was a promising one for x-ray investigation. In addition, on the

assumption of either of the two configurations for the benzene ring which experiment had already indicated as possible, a sound basis has been established for the discussion of molecular models for the isomers.

(ii) The preliminary x-ray investigation of three of the hydroxy substitution products of cyclohexane (inactive inositol, laevo inositol and quercitol), and a methyl derivative (quebrachitol) of one of them, has been successfully carried through, so that the crystal class, dimensions of unit cell, number of molecules per unit cell, space group, and symmetry properties of the molecule are now known for all four. Three of these have been shown to possess the same space group and molecular asymmetry, while the fourth (inactive inositol) possesses a different space group. The differences of the fourth are however no greater than was to be expected from the consideration of isomerism and chief properties, and the x-ray evidence has so far tended to a confirmation of the tentative opinion. The preliminary investigation has also brought out several points of particular interest in individual cases (e.g. molecular association in inactive inositol).

(iii) The x-ray investigation has been carried somewhat farther in one case (quercitol), with the result that an indication has been obtained as to the molecular orientation. The success of the method of arriving at this result gives ground for the hope that the enhancement principle, which has recently been brought forth, may usefully be applied in a more detailed investigation of the structure of at least this particular group of hydroxy substitution products of cyclohexane.

- - - - - - - - - - -

In addition several improvements have been made in the apparatus and technique of this laboratory.

I. INTRODUCTION.

§ 1. One of the interesting features of organic chemistry is the small number of elements which are required to form the vast number of compounds which come within its range. There are simple compounds like methane CH_4, and complicated ones, of which phloroglucinol-trimethyl ether $C_9H_{12}O_3$ is a moderate example. In a great many of them carbon, hydrogen and oxygen are the only elements. It is clear that in such a science a knowledge of the relations of the elements is of primary importance, and indeed progress in this science has depended and still depends on the study of the reactions of each new compound in order to determine which atom is linked to which in its molecule. The very formulae which are used are so constructed as to lay emphasis on this linkage relation. For instance the reactions of methane are most easily interpreted by supposing that each of the four hydrogen atoms is linked directly to the carbon atom, and has little or no attraction for the other three hydrogen atoms. This information, and the corresponding information for the much more

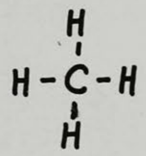


Fig. 1.
Methane
CH_4

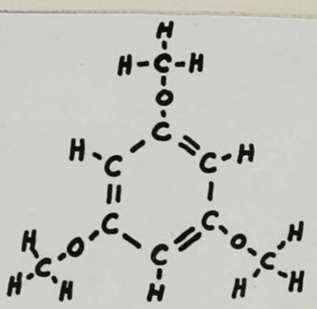


Fig. 2.
Phloroglucinol-trimethy
Ether
$C_6H_3(OCH_3)_3$

complicated phloroglucinol-trimethyl ether, is graphically shown by the formulae in Figs. 1 and 2. It must be emphasized, however, that these formulae tell us nothing as to the arrangement of the atoms in space, and indeed it may be said here that in no case has it been possible by chemical means to do more than assign an approximate space configuration to a molecule.

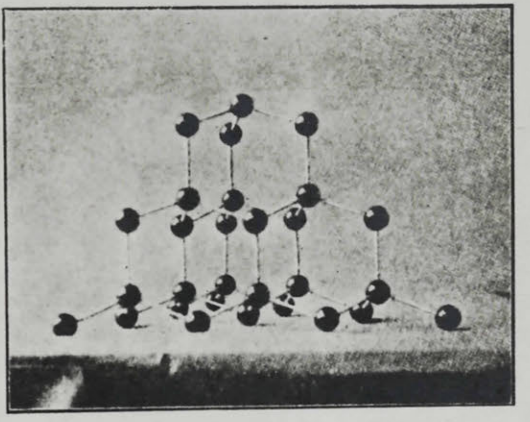
§ 2. The importance of the spatial arrangement of atoms in organic substances was first emphasized by Berzelius,1) who introduced the ideas of isomerism, polymerism and metamerism. The fundamental hypothesis of organic stereo-chemistry was made almost simultaneously by Van't Hoff 2) and Le Bel 3) in 1874. Van't Hoff's version (which agrees most closely with modern ideas) is as follows:- The carbon atom is supposed to possess four valency forces, directed toward the vertices of a regular tetrahedron at the centre of which it is placed. Any four monovalent radicals which are attached to the carbon atom will therefore be held in a tetrahedral arrangement, and if all four are the same, the group will possess tetrahedral symmetry.

This hypothesis has been of great use in the study of optical activity and isomerism. It was found that many optically active organic compounds possess an assymmetric carbon atom - i.e. one attached to four different radicals - and the tetrahedral arrangement provided an excellent model for the discussion of mirror image configurations. Likewise it provided a satisfactory basis for the discussion of geometrical isomerism. But not until the advent of x-rays in the field of chemistry was there any direct confirmation of these ideas or hope of an exact determination of configuration.

§ 3. When we come to consider just what is the structure of a molecule, i.e. the spatial arrangement of the atoms in the molecule, we realize that this is an indefinite question. Our knowledge of the meaning of heat alone prevents us from viewing a molecule as a static arrangement. The methane molecule under ordinary conditions (gaseous state) is pictured as an agitated group of four light atoms about a heavier fifth atom, the whole group moving with high velocity and occasionally colliding with other similar groups. Even in the liquid state the picture is not very much different, and the opportunity for getting definite information as to the configuration is decidedly limited.

In crystals, however, the molecules have linked themselves together in orderly array, and while both atoms and molecules are still in thermal agitation, their motion is strictly limited to regions comparable with their own dimensions. By the study of crystals, therefore, we may hope to get some information both as to the actual arrangement of the atoms in a molecule and as to the magnitude and direction of the binding forces involved.

The discovery and early history of the use of x-rays in the determination of crystal structure has already received such thorough and competent treatment 4) that its inclusion here would be superfluous. The first structure determination of interest in organic chemistry was that of diamond 5) and in this connection three things are particularly to be noted:-



MODEL OF DIAMOND.
Horizontal planes perpendicular to the paper are (111) planes.

Fig. 3

(1) Each carbon atom is surrounded by four others, at the corners of a regular tetrahedron.

(2) It is possible to pick from the structure a "puckered ring" of six carbon atoms.

(3) The great rigidity and openness of the structure would seem to indicate that the direction of the binding forces of a carbon atom are particularly well satisfied by the diamond arrangement, i.e. that the carbon atom tends strongly to hold attached atoms in a tetrahedral arrangement.

Evidence for a tetrahedral, or approximately tetrahedral arrangement has been obtained with methane, tetra-iodo-methane,6) tetra-bromo-methane,7) tetra-phenyl-methane,8) tetra-methyl-methane,9) tetra-nitro-methane,10) penta-erythritol tetra-nitrate,11) penta-erythritol tetra-acetate.12) 13) None of the compounds of the type CR_4 which have so far been investigated have yielded any strong evidence for a wide departure from tetrahedral symmetry.

The only other known crystalline form of pure carbon is graphite. Its structure was for some time in doubt, but it was finally settled by Hassel and Mark[14], and by Bernal[15] independently.

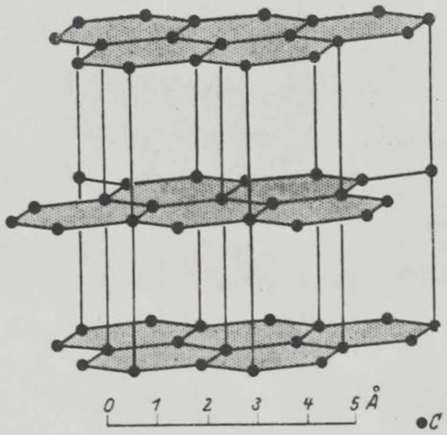


Abb. 141. Graphit nach HASSEL und MARK.

Fig. 4.

It is to be noted that

(1) Each carbon atom is surrounded by three coplanar, equidistant atoms, while away from this plane, and at a considerably greater distance, is a fourth.

(2) The atoms lie in nets characterized by a hexagonal ring structure.

(3) The remarkable flakiness and cleavage properties indicate that the atoms are strongly bound in the hexagonal nets.

(4) The carbon atoms can be considered as of two types - (a) those which have neighbors in neighboring planes, and in a direction perpendicular to the plane, and (b) those which have no neighbors perpendicular to the plane.

The differences of these two structures, diamond and graphite, are sufficient to show that the linkage forces of the carbon atom are not to be regarded as fixed vectors, and indeed there is nothing in atomic theory to indicate that they should be.

Before discussing x-ray examinations of any other crystals, it will be necessary to consider the class of organic compounds which is of particular interest in connection with the subject of this thesis.

§ 4. Organic compounds are usually divided into two groups - the aliphatic compounds, or open chain structures, and the cyclic compounds, whose molecules possess some group of atoms in a ring-like arrangement. Probably the most important of these cyclic units is the benzene ring (Fig. 5), which is the structural basis of the aromatic compounds.

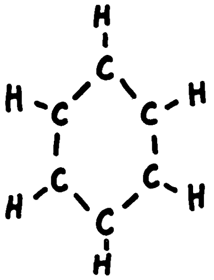


Fig. 5.
Benzene
C_6H_6

The arguments for the existence of such a structure were first clearly set forth by Kekule[16] in 1867. He also dealt with the problem of unsaturation and suggested possible directions for the residual valency forces. Since then the benzene derivatives have been studied with great success, and the chemical properties of a large number are now well known.

The number of theoretically possible isomeric substitution or addition products of benzene depends on the assumption which is made as to the configuration of the ring. The apparent existence of only one mono- and three di-substitution products, together with other evidence, led to the view that the benzene ring could be treated as though plane. Most of the discussion of both positional and geometrical isomerism has been based on this conception. As early as 1888, however, it was realised that this arrangement was inconsistent with the tetrahedral hypothesis of Van't Hoff and Le Bel, and various space formulae have since been proposed.17) These have been tested according to the properties which they would lead to, but in all cases it seems that the weight of evidence is in favour of the plane ring.18)

A closely allied problem is that of the configuration of the cyclohexane ring, C_6H_{12} (Fig. 6). In this case also the flat ring

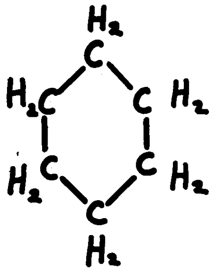
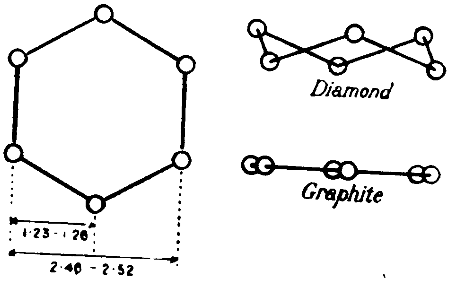


Fig. 6.
Cyclohexane
C_6H_{12}

seems to satisfy the requirements, but when two of these rings combine to form decahydronaphthalene, it would appear that a sufficient number of isomeric substitution products have been isolated to indicate that the cyclohexane rings can be joined in two different ways, so producing two distinct secondary units.[19)] This necessitates something in the nature of a puckered cyclohexane ring. The most satisfactory explanation of the failure to detect this in the case of the single ring compounds is that, under the ordinary conditions of chemical testing (liquid and gaseous state), there may be two interchangeable ring forms, in dynamic equilibrium, producing the same statistical result as a single plane ring.

§ 5. As has been pointed out in § 3, the structures of diamond and graphite, as determined by x-rays, show two different six-membered rings of carbon atoms, the one flat and the other puckered, as illustrated in Fig. 7. This is strong corroborative evidence in favor of the ring structure of benzene, if such still be needed. It does not however help much in deciding the shape of the ring.



~~Fig. 1.~~

Fig. 7.

As to the configuration, x-ray examinations have been made of naphthalene, anthracene,[20] benzene,[21] hexa-chlor- and hexa-brom-benzene,[22] naphthalene-tetra-chloride,[20] hexa-chlor-naphthalene[23] and hexa-methyl-benzene,[24] but in no cases except the last two has it yet been possible to tell whether the ring in the structure is flat or puckered. Except for the naphthalene chlorides, the molecules have been shown to possess centres of symmetry. In hexa-chlor-naphthalene the intensities of the higher order reflections indicate that the ring is nearly flat. The x-ray data from hexa-methyl-benzene can only be satisfied by a flat ring.

The problem of the symmetry of the carbon atom, and its relation to molecular symmetry has been studied by K. Lonsdale. She has been led to assign two distinct types of valency to the carbon atom in order to explain the symmetry which certain molecules exhibit.[25] She has shown that this assumption is consistent with the symmetry of hexa-methyl-benzene, and that it leads to results in agreement with those of de Laszlo on the absorption spectra of the ten di-chlor-naphthalenes.[26] Lonsdale has also very recently provided an excellent summary of the present state of knowledge of the structure of the benzene ring.[27]

From the sum total of the organic x-ray analyses that have so far been performed, the general conclusion may be drawn that the carbon atom probably behaves differently in different types of compounds. The laws of its behavior are as yet very uncertain and it would seem that in order to establish them on a sound basis, it will be necessary to analyse a considerable number of organic crystals and correlate the information so obtained. The results of the work on the long chain compounds and on the naphthalene group indicate that the best chances of success lie in the study of groups of closely related substances, and it is such a group that has been chosen as the subject of this thesis.

§ 6. Since the next section will be devoted exclusively to this subject, only brief mention will here be made of the hydroxy substitution products of cyclohexane. Cyclohexane itself is formed by the saturation of the benzene ring with hydrogen atoms. It resembles benzene in its physical properties, and presents the same difficulties for x-ray analysis. The various members of the hydroxy substitution family are given by the general formula

$$C_6H_{12-n}(OH)_n \qquad n = 1, 2, 3, 4, 5, 6.$$

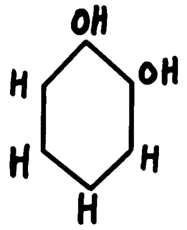


Fig. 8.
ortho-Cyclohexandiol
$C_6H_{10}(OH)_2$

Fig. 8 is an example for n = 2. (From here on the conventional hexagonal symbol will be used for the benzene ring C_6H_6.)

The formula gives no indication of the complexity of the series, for there are known to be several isomeric forms for every value of n (except $n = 1$). Thus there may be expected a fairly close inter-relationship in the crystal structures, which, if it exists, will not only aid in the analysis, but will also simplify the correlation of whatever information may be obtained.

Besides possessing an important position in the general scheme of organic chemistry, this group has an added interest in that a number of the higher members and their methoxy derivatives appear to play an important part in plant and animal metabolism. To give a single instance, one form of inactive inositol, $C_6H_6(OH)_6$ ($n = 6$), has recently been identified with Biose I, one of the two components essential to the normal growth of yeast.28) Examples might be multiplied indefinitely from the lists of sources given in Beilstein's Handbuch.

II. ISOMERISM AND THE HYDROXY SUBSTITUTION PRODUCTS OF CYCLOHEXANE.

§ 1. As has been stated in the previous section, there are many isomeric forms of the hydroxy substitution products of cyclohexane known. It is doubtful if all the stable forms have as yet been isolated, and the question arises - how many forms are theoretically possible? No one has as yet thoroughly discussed this problem for the whole series, and in the isolated cases the discussion has always been based on the assumption of a plane cyclohexane ring.

In order to provide a basis for the discussion of isomerism and molecular symmetry the writer has worked out by a specially developed form of analysis, and with the aid of models, all the possible isomeric forms of the hydroxy substitution products of cyclohexane, as obtained on the assumption (1) of a plane, (2) of a puckered cyclohexane ring. This work is presented in detail in an appendix to this thesis. Table 1 is a summary of the results, giving the number of isomers for each value of n in the formula:

$$C_6H_{12-n}(OH)_n$$

The isomers have been classified according to possible optical activity. Those listed as inactive possess planes or centres of symmetry; the others do not. It is well known that no structure possessing a plane or centre of symmetry can produce a rotation of the plane of polarization of a light wave; the converse proposition is however not necessarily true.

TABLE I

Puckered							Plane			
Total		Laevo	Dextro	Inactive	n	Subst.	Inactive	Dextro	Laevo		Total
2	2	0	0	2	1	1	1	0	0	1	1
13	6	3	3	0	2	1·2	1	1	1	3	8
	4	1	1	2		1·3	1	1	1	3	
	3	0	0	3		1·4	2	0	0	2	
28	8	2	2	4	3	1·2·3	2	1	1	4	14
	16	8	8	0		[1·2·5 1·2·4]	0	4	4	8	
	4	0	0	4		1·3·5	2	0	0	2	
46	20	10	10	0	4	2·3·4·5	2	4	4	10	25
	16	4	4	8		2·4·5·6	4	2	2	8	
	10	3	3	4		1·3·4·6	3	2	2	7	
32	32	12	12	8	5	1·2·3·4·5	4	6	6	16	16
16	16	3	3	10	6	1·2·3·4·5·6	7	1	1	9	9
137	Total									Total	73

It is seen that the number of forms is far greater in the case of the puckered ring, as is to be expected.

The number of plane ring isomers for n = 6 appears to have been common knowledge for some time, and the number for n = 5 has also previously been stated.29) There has recently been published30) a mathematical treatment of the general problem of isomerism and configuration, but its application to the present problem is not clear.

§ 2. Below is a table of the hydroxy substitution products of cyclohexane which have been isolated. The isomers are classified as they have been labelled in the literature. The remarks are, in most cases, merely the sources and chief properties of the substances. Most of the data have been obtained from the Beilstein-Prager-Jacobson "Handbuch der Organische Chemie," (ed. iv). Search of subsequent literature has not been fruitful in yielding any new isomers, though the knowledge of the properties of some of the substances has since considerably increased.

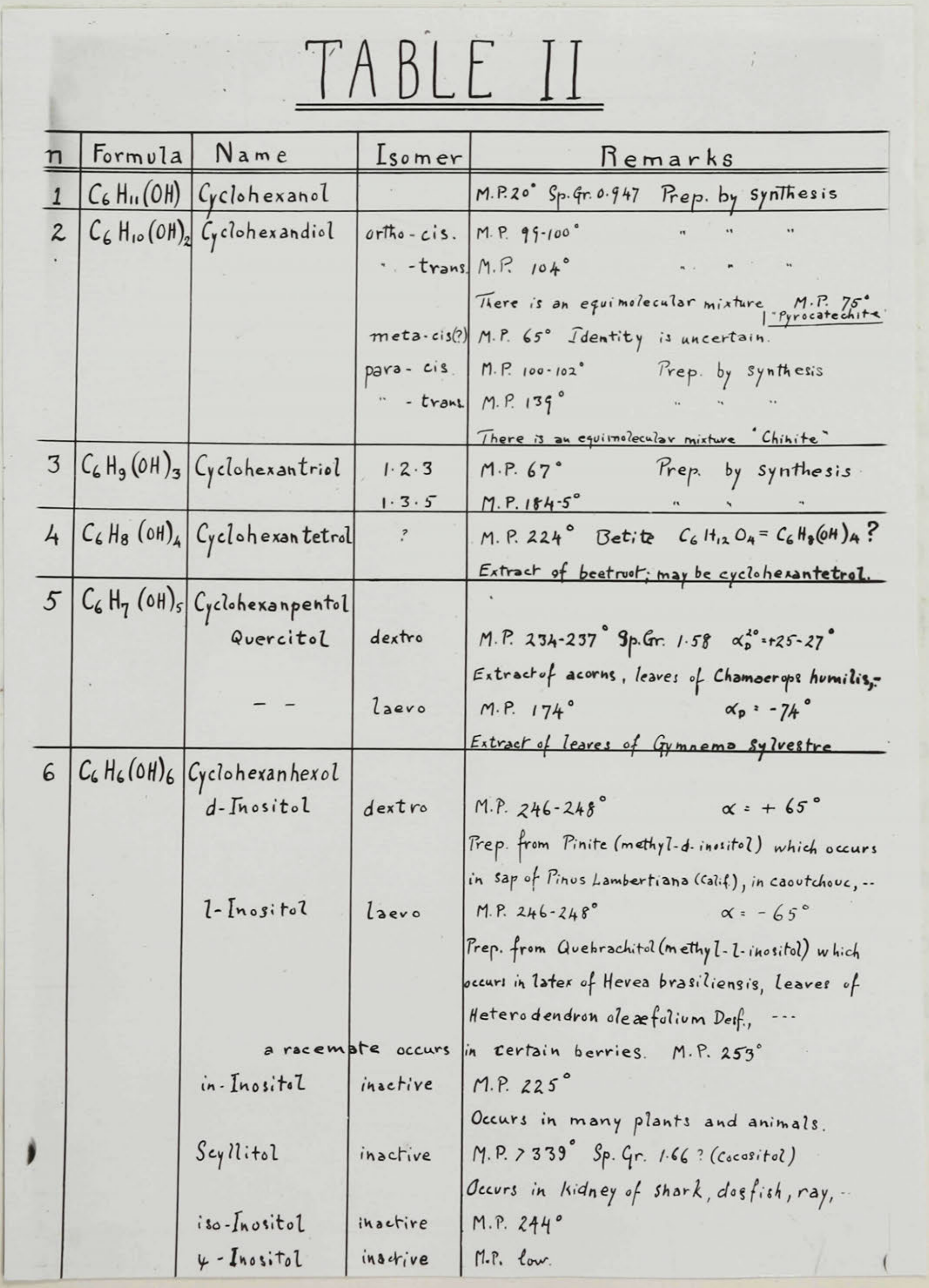


TABLE II

n	Formula	Name	Isomer	Remarks
1	$C_6H_{11}(OH)$	Cyclohexanol		M.P. 20° Sp. Gr. 0.947 Prep. by synthesis
2	$C_6H_{10}(OH)_2$	Cyclohexandiol	ortho-cis.	M.P. 99-100° " " "
			" -trans.	M.P. 104° " " "
				There is an equimolecular mixture M.P. 75° 'Pyrocatechite'
			meta-cis(?)	M.P. 65° Identity is uncertain.
			para-cis	M.P. 100-102° Prep. by synthesis
			" -trans	M.P. 139° " " "
				There is an equimolecular mixture 'Chinite'
3	$C_6H_9(OH)_3$	Cyclohexantriol	1·2·3	M.P. 67° Prep. by synthesis
			1·3·5	M.P. 184-5° " " "
4	$C_6H_8(OH)_4$	Cyclohexantetrol	?	M.P. 224° Betite $C_6H_{12}O_4 = C_6H_8(OH)_4$? Extract of beetroot; may be cyclohexantetrol.
5	$C_6H_7(OH)_5$	Cyclohexanpentol Quercitol	dextro	M.P. 234-237° Sp. Gr. 1.58 $\alpha_D^{20°} = +25-27°$ Extract of acorns, leaves of Chamoerops humilis,-
		– –	laevo	M.P. 174° $\alpha_D = -74°$ Extract of leaves of Gymnema Sylvestre
6	$C_6H_6(OH)_6$	Cyclohexanhexol d-Inositol	dextro	M.P. 246-248° $\alpha = +65°$ Prep. from Pinite (methyl-d-inositol) which occurs in sap of Pinus Lambertiana (Calif.), in caoutchouc, --
		l-Inositol	laevo	M.P. 246-248° $\alpha = -65°$ Prep. from Quebrachitol (methyl-l-inositol) which occurs in latex of Hevea brasiliensis, leaves of Heterodendron oleæfolium Desf., ---
		a racemate occurs		in certain berries. M.P. 253°
		in-Inositol	inactive	M.P. 225° Occurs in many plants and animals.
		Scyllitol	inactive	M.P. > 339° Sp. Gr. 1.66 ? (Cocositol) Occurs in kidney of shark, dogfish, ray, -
		iso-Inositol	inactive	M.P. 244°
		ψ-Inositol	inactive	M.P. low.

The Beilstein cis- and trans-classification of the two ortho-cyclohexandiols has been interchanged to bring agreement with recent[31] work.

It is interesting to note that the two penta derivatives cannot be mirror images of one another, due to the marked difference in melting point and optical rotation. The same can be said of pinite and quebrachitol (properties not listed here) though they are both methyl derivatives of optical antipodes (d- and l-inositol).

The configuration of the substances listed above is a problem of some difficulty. An attack on the cyclohexane series has recently been made by chemical means,[32] but most of the work has not been directly on the members of the group under consideration. A recent attempt to determine the relative positions of certain hydroxyl groups on quercitol has yielded contradictory results.[32]

The configuration of such groups as $C_6H_6Cl_6$ has a definite relation to the problem. Friedel[33a] discussed the possible arrangements in an early paper. At present there are known to be four crystalline modifications of the hexahalogen compounds. The β (cubic) type has been analysed[22] but the α type, which is monoclinic, will probably be of greater interest in connection with the structure of the inostols.

In conclusion it might be remarked that a comparison of Table I and Table II shows that the number of isolated substances falls far short of the number of theoretically possible substances, whichever of the two assumptions be adopted. It is difficult to see how the assumption of plane ring form could be further simplified to yield a smaller theoretical number, and any increase in the complexity of the ring will only add to the theoretical number. Two considerations then arise:

(1) It may be that there is still a considerable number of substances which may be isolated.

(2) It may be that a large number of the theoretically possible configurations are so unstable that they can never be isolated.

Both factors probably contribute to the discrepancy in number.

Another problem which arises is the relation of the isomerism of the substances in the solid state to isomerism of the same substances in the liquid state, but this cannot be profitably discussed until much more definite information has been obtained concerning the structures.

§ 3. The complete x-ray analysis, even of only those members of the cyclohexane series which have so far been isolated, presents, under the best circumstances, a task of some years duration. In the presence of so many isomers it is necessary to proceed with great caution, and to identify each substance with care. The data in the literature are incomplete, and in some cases unreliable, so that much preliminary investigation is required before the x-ray analysis can begin.

It has only been possible to bring into this thesis the results obtained with four substances. Three of these, inactive inositol, laevo-inositol and quercitol, are hydroxy substitution products of cyclohexane. The fourth is a closely related compound, quebrachitol, the methyl ester of 1 - inositol.

In order to relieve the later sections of this thesis of a considerable amount of miscellaneous argument, it was decided to include, at this stage, the discussion of the source, identification, crystallo-

:graphic data and important properties of each of the four substances mentioned above. A few references are also given to papers of interest which are not included in Beilstein's "Handbuch der Organische Chemie" or Groth's "Chemische Kristallographie." (The references are grouped with each discussion and are indicated by roman numerals to distinguish them from the general reference system.)

Inactive Inositol

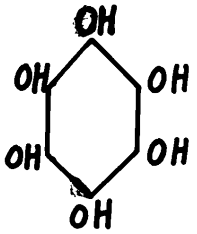


Fig. 9.
Inositol
$C_6H_6(OH)_6$

Source. A gram sample of "Inositol" obtained from Schuchardts many years ago. Recently purified by recrystallization and supplied to the writer by Dr. G. S. Whitby, Department of Chemistry, McGill University.

Preparation of Crystals. The crystals used in the x-ray analysis were prepared by crystallization from a dilute solution of acetic acid.

Identification.

Observed M. P. 220° (approx.) cf. 225.7° - Fick.[III]
Observed Sp. Gr. 1.58 cf. 1.752 - Tanret.[IV]

There is no recorded crystallographic data on the inactive inositol, though the dihydrate has been measured by four observers.[II] The most satisfactory method of identification would seem to be by obtaining and measuring the dihydrate. Several attempts were made to do this, under the conditions stated in the literature, but each time the crystallization yielded the original form. It is perhaps interesting to note in this connection that Petrie had the same experience with his 1- inositol (1- inositol, ref. [III]). In connection with the discrepancy in densities, the following comparison is suggestive:-

		Sp. Gr.		Sp. Gr.
x-rayed	in-inositol	1.58	cocositol - Muller[V]	1.66
"	1- inositol	1.60	(scyllitol) in-inositol of Tanret	1.752
"	quebrachitol	1.57 (from x-ray data)		
"	quercitol	1.58		

There is, of course, the possibility of a mistake in the Tanret value. It seems rather high.

Several isomers of inositol have been examined by Muller.[VI] He has proved that quercine and cocositol are identical with scyllitol,[V] but has discovered two new isomers, which he names iso-inositol and ψ- inositol. The writer's inositol is probably not scyllitol (M.P. 339°, Sp. Gr. 1.66). It might be iso-inositol (M.P. 244°) but not ψ- inositol, which Muller describes as being amorphous and gummy. Whether all the researches listed in Beilstein under "inactive-inositol" have dealt with a common variety of inactive-inositol is a question which would be difficult to answer. Projects are now under way to obtain the different isomers, so that a careful comparison and x-ray examination can be made, and it seemed best to leave the question of the identity of this particular specimen open for the present.

Crystallographic Data. A goniometric examination of the crystal was made, but the specimens were found to be so poor that the results could not be satisfactorily co-ordinated. This perhaps accounts for the absence of data in the literature.

Several attempts were made to obtain better specimens, but none were successful. The crystals are very thin, and of a fair width; all are very long proportionately, and in some cases needles 2 or 3 cm. long and about 0.5 mm. in diameter were grown.

Good terminal faces were occasionally observed, but the faces of the needle zone were uniformly poor and gave series of reflections over a large angular range. Sufficient data was obtained to get an approximate value of $\beta = 107^\circ$. The habit was such as to indicate that the crystals belonged to the monoclinic prismatic class, though this cannot be regarded as conclusive.

References.

I. Beilstein, Handbuch, 6, 1195.

II. Groth, Chemische Kristallographie, 3, 609.

III. Fick, Pharmazeutische Z. f. Russland, 26, 131.

IV. Tanret and Villiers, Ann. de Chimie, 5, 23, 392.

V. H. Muller, Trans. Chem. Soc., 91, 1768 (1907).

VI. H. Muller, Trans. Chem. Soc., 101, 2383 (1912).

VII. Beilstein, 1197, 1198.

VIII. J. Needham, Ergebnisse der Physiologie, 25, 1 (1926).

Laevo-Inositol, $C_6H_6(OH)_6$ (same chemical formula as in-Inositol).

Source. The sample was prepared by the action of hydriodic acid on the quebrachitol of this thesis

$$HI + C_6H_6(OH)_5\,OCH_3 = C_6H_6(OH)_6 + CH_3I \qquad I)$$

Preparation of Crystals. The crystals were obtained by precipitating the l-inositol from aqueous solution by the gradual addition of the ethyl alcohol.

Identification.

Observed M.P. 240° (approx.)	cf.	237°	Ref.	VIII
		238°	"	III
		238°	"	IV
		248°	"	VI
		248°	"	IX
Observed α_D = - 65.8°	cf.	- 64.8	Ref.	III
		65	"	IV
		65	"	VI
		65	"	IX

As there was some doubt as to the identity of the sample at one stage of the analysis, a combustion test was also made. The results were:-

	Observed	Theoretical
Carbon	39.72%	40 %
Hydrogen	6.35%	6⅔%
Ash	trace	-

It is considered that the above data establish the identity of the specimen beyond doubt.

Physical and Crystallographic Data.

M. P. 240° (approx.)

Sp. Gr. 1.60

Opt. rotation $\alpha_D = 65^\circ$

There are no crystallographic data recorded for l-inositol. A goniometric examination was therefore made, with the following results:-

Crystal class: Monoclinic sphenoidal.

$a : b : c = 0{\cdot}678 : 1 : 0{\cdot}750$ (From x-ray data)

$\beta = 106^\circ 36'$

Forms observed: a $\{100\}$, b' $\{0\bar{1}0\}$, p $\{011\}$, p' $\{0\bar{1}1\}$,
q $\{110\}$, q' $\{1\bar{1}0\}$, r $\{10\bar{1}\}$.

The crystals exhibited a fair number of good reflections, but the forms were somewhat distorted, so that high accuracy was not possible. In fact it was at first thought that the crystals were trichnic with a close approach to monoclinic symmetry. The x-ray data however proved conclusively that they were monoclinic, as will appear later. No crystal dimension was particularly pronounced.

References.

I. Beilstein, Handbuch, 6, 1193.

II. Groth, Chemische Kristallographie, 3, 608.

III. J. M. Petrie, Proc. Linn. Soc. N. S. Wales, 43, 850 (1918).

IV. Tanret, Comptes Rendus, 109, 909 (1889).

V. De Jong, Rec. trav. chim. P.-B. 25, 49.

VI. Maquenne and Tanret, Comptes Rendus, 110, 86.
VII. Berthelot, Comptes Rendus, 110, 1245.
VIII. Pickles and Whitfield, Proc. Chem. Soc. Lond., 54 (1911).
IX. Bourquelot et Fichtenholz, J. pharm. et de chim., 6, 346 (1912)

Quebrachitol

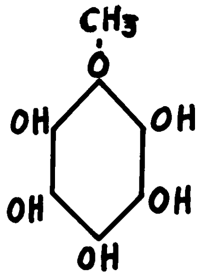


Fig. 10.
Quebrachitol
$C_6H_6(OH)_5OCH_3$

Source. The samples were extracted from the latex of Hevea brasiliensis according to the method described in the literature.1)

Preparation of Crystals. The specimens were obtained by crystallization from dilute alcoholic solution. Crystallization from water gave specimens of similar form.

Identification. As the samples were supplied from the Department of Chemistry of this University by Professor G. S. Whitby, who is an authority on the chemistry of ruber, the writer did not consider that any further identification was necessary. The separation of quebrachitol is one of the preparatory operations in some of Professor Whitby's researches, and a plentiful supply was available.

Physical and Crystallographic Data.

M. P.	190°	chosen from:	190°C.	Ref.	IV	(1-inositol)
			191^{-2} °C.	"	VIII	"
			190° C.	"	VII	"
			190° C.	"	III	"
Sp. Gr.	1.54			Ref.	IV	(1-inositol)
α_D	= - 80°	chosen from:	- 80° C.	Ref.	IV	(1 inositol)
			80° C.	"	VIII	"
			80.3°C.	"	VI	"
			80.2°C.	"	III	"

Goniometric examinations have been made by two observers, Anderson II) and Graham III). They both classified their specimens as orthorhombic. The x-ray examination, however, proved that they were monoclinic, and the data here recorded has been changed to refer to monoclinic axes (interchange of b and c).

Monoclinic sphenoidal

$a : b : c = 0.9251 : 1 : 1.1216$ Anderson.

$0.9258 : 1 : 1.1219$ Graham.

$\beta = 90^\circ$

Forms: a {100}, c {001}, m {101}, q {011}, and occasionally acet of r{110} occur.

The forms observed by Graham are consistent with monoclinic symmetry.

Anderson, on the other hand, records the orthorhombic form m {101}. His methyl- l-inositol was extracted from the leaves of Heteradendron oleæfolium, and it was considered possible that, in spite of the close agreement of axial ratios, it might be an isomeric substance different from quebrachitol. Dr. Anderson kindly sent the specimens he had used in making his measurements; and a close examination of them verified his observations. The question of identity will be further discussed in connection with the x-ray data on quebrachitol.

References.

I. Beilstein, Handbuch, 6, 1193.

II. Petrie, loc. cit. (l- inositol), p. 859.

III. Whitby, Dolid and Yorston, J. Chem. Soc., p. 1452 (1926).

Quercitol

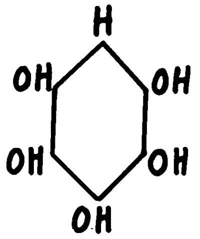


Fig. 11.
Quercitol
$C_6H_7(OH)_5$

Source. A 1-gm. sample supplied by Eimer and Amend, New York.

Preparation. The specimens used were obtained by crystallization from aqueous solution.

Identification. The following data were supplied by Eimer and Amend:-

M. P. 234°C.		Sp. Gr. 1.5806 at 15°C.	
cf. 222-223°	Ref. III.	cf. 1.5845 at 13°C.	Ref. III
232	" IV.		
234	" V.		
235	" VI.		
235-237	" VII.		

Crystallographic examinations have been made by four observers,II) The writer made measurements on two crystals and from the mean values plotted the sterographic projection. This, when superimposed upon the corresponding projection plotted from Groth's data, showed such excellent agreement that it was considered that the identity of the Eimer and Amend sample had been established beyond doubt.

Physical and Crystallographic Data.

M. P. 234° C.

Sp. Gr. 1.5806 at 15° C.

α_D =	25.3°	mean of	24.3°	Ref. III.
			25.6°	" VIII.
			27	" IV.

The optical rotatory power of the crystal has also been examined.IX) The optic axes lie in the plane of the a and c axes, and exhibit different amounts of rotation. For plates 1 mm. thick the respective rotations are - 3.5° and - 4.6°.

From Groth:

$a : b : c = 0.8058 : 1 : 0.7655 \qquad \beta = 110^\circ 57'$

Observed forms: a $\{100\}$, b' $\{0\bar{1}0\}$, c $\{001\}$, q $\{011\}$, p $\{110\}$, r $\{10\bar{1}\}$, q' $\{0\bar{1}1\}$.

The forms observed on the writer's specimens were:

b $\{010\}$, c $\{001\}$, r $\{10\bar{1}\}$, p $\{110\}$, p' $\{1\bar{1}0\}$, q $\{011\}$, q' $\{0\bar{1}1\}$.

References.

I. Beilstein, Handbuch, 6, 1186.

II. Groth, Chemische Kristallographie, 3, 607.

III. Prunier, Ann. de Chim., (5), 15, 24.

IV. v. Lippmann, Ber. 40, 4936.

V. Böttinger, Ber. 14, 1598.

VI. Dessaignes, Compt. Rend., 33, 308.
Liebig's Ann., 81, 104.

VII. Johansen, Arch. der Pharmazie, 209, 243.

VIII. Siegfried, Howwjanz, Z. f. Physiologische Chemie, 59, 387.

IX. Karandèev, Bull. Acad. Sci. Petrograd, 9, 1285 (1915).

A.E.H. Lutton, Crystallography and Practical Crystal Measurements, 1922 ed., Vol. 2, p. 111.

III. THEORY OF STRUCTURE DETERMINATION.

§ 1. Determination of Unit Cell and Possible Space Groups.

In the analyses to be described Bernal's method[34)] of interpreting x-ray single crystal rotation photographs was used. A brief description, illustrated by diagrams from his paper follows:-

If every net in the space lattice of a crystal be represented by a vector of magnitude

$$\rho = \frac{\lambda}{d} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

and direction normal to the net, then it can be shown that the points at the ends of these vectors will form another space lattice, which is called the reciprocal lattice of the crystal.

The axes of the "reciprocal lattice" so obtained are given by

$$a^{*} = \frac{\lambda bc}{\Delta} \sin\alpha \quad (a^{*} \text{ is normal to the bc plane})$$

$$b^{*} = \frac{\lambda ca}{\Delta} \sin\beta \qquad \text{etc.}$$

$$c^{*} = \frac{\lambda ab}{\Delta} \sin\gamma \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where a, b, c, α, β, γ define the axial system of the crystal and Δ is the volume of the unit cell.

The plane with indices (h k l) in the space lattice will be represented by the point

$$(ha^{*}, \ kb^{*}, \ lc^{*})$$

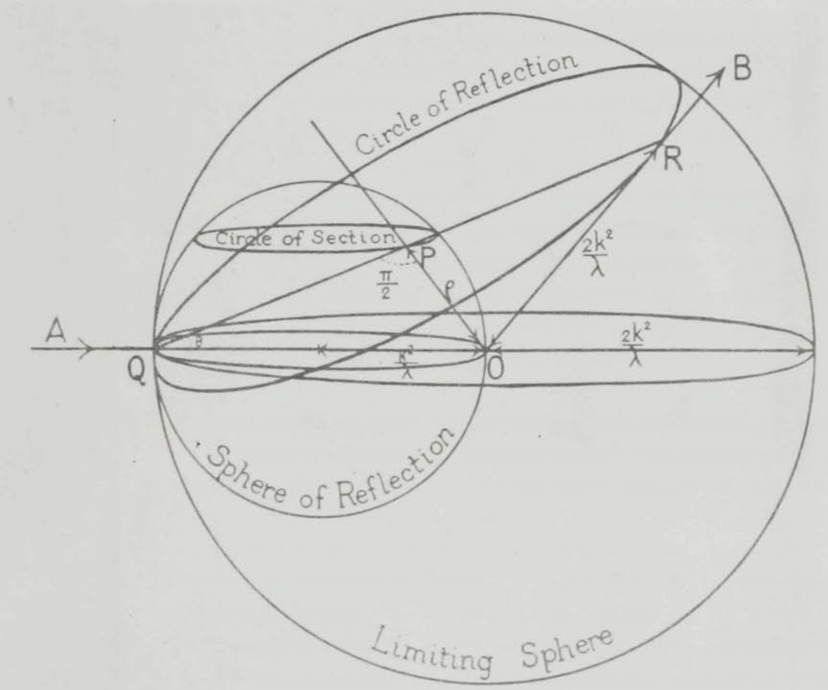
in the reciprocal lattice.

The interpretation of the Bragg Law for x-ray reflection

$$n\lambda = 2\,d\,\sin\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where λ = wave length of x-rays
d = spacing of the reflecting planes
θ = glancing angle of reflection
n = order of reflection

into terms appropriate to the reciprocal lattice is as follows:-



~~Fig. 2~~

Fig. 12 a (note $k^2 = \lambda$)

Combining equations (1) and (3), we get

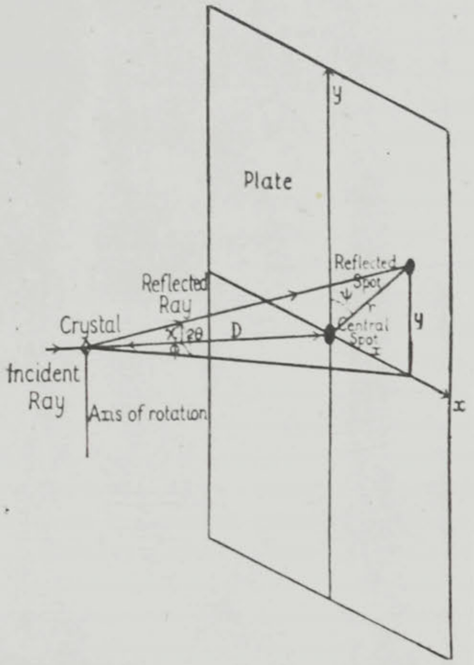
$$\rho = 2 \sin\theta \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

Hence, if a plane is to reflect, the point in the reciprocal lattice must lie on the surface of a sphere, whose diameter, of magnitude 2, extends away from the origin in the direction of the oncoming x-ray beam, as shown in Fig. 12 a. Under this condition the beam will make the required angle θ with the reflecting plane. This sphere is called the <u>sphere of reflection</u>.

If instead of considering the crystal as rotating, we regard the sphere of reflection as swinging around the crystal axis, we see that its surface will pass through a certain group of points in the reciprocal lattice (regarded as fixed in position), and the passage of the surface through these points will correspond to the fulfilment of the Bragg Law by the successive planes during the rotation of the crystal.

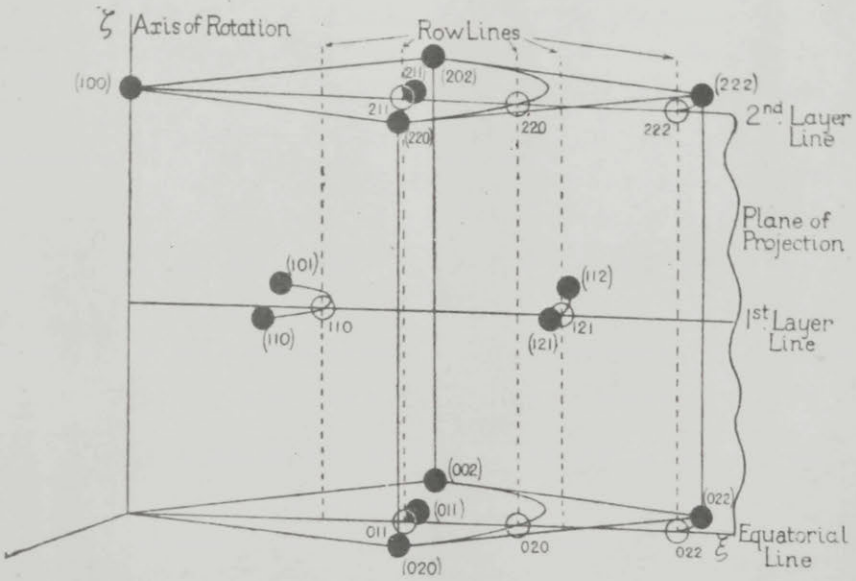
From the relations between the reciprocal and the space lattice, it will be seen that rotation of a crystal around one of its axes corresponds to rotation of the reciprocal lattice around the normal to a set of planes, or nets, in the reciprocal lattice, and vice versa. If a plane is passed through the axis of rotation, and the points of the reciprocal lattice are allowed to record on it as they pass through it, a pattern, called a rotation diagram, is obtained which is not dissimilar to the x-ray diffraction pattern obtained with a rotating crystal in the arrangement shown diagrammatically in Fig. 12 b. This "cylindrical projection" of the reciprocal lattice is illustrated in Fig. 12 c, for the case of rotation about a crystal axis. Fig. 12 d shows the relation of the rotation diagram and the rotation photograph.

By applying Bernal charts to the appropriate enlargement of a crystal rotation photograph, the co-ordinates (ξ, ζ) of the "rotation diagram" may be read off directly, and the rotation diagram plotted. The relation between the cylindrical co-ordinate system (ω, ξ, ζ) in the reciprocal lattice and the planes of the space lattice is shown in Fig. 12 e. When the reciprocal lattice is projected (cylindrically) to form the rotation diagram, the co-ordinate ω is lost; this of course corresponds to the lack of knowledge of the position during rotation, at which any plane reflects the x-rays to give a spot on the photographic plate.



~~Fig. 7.~~

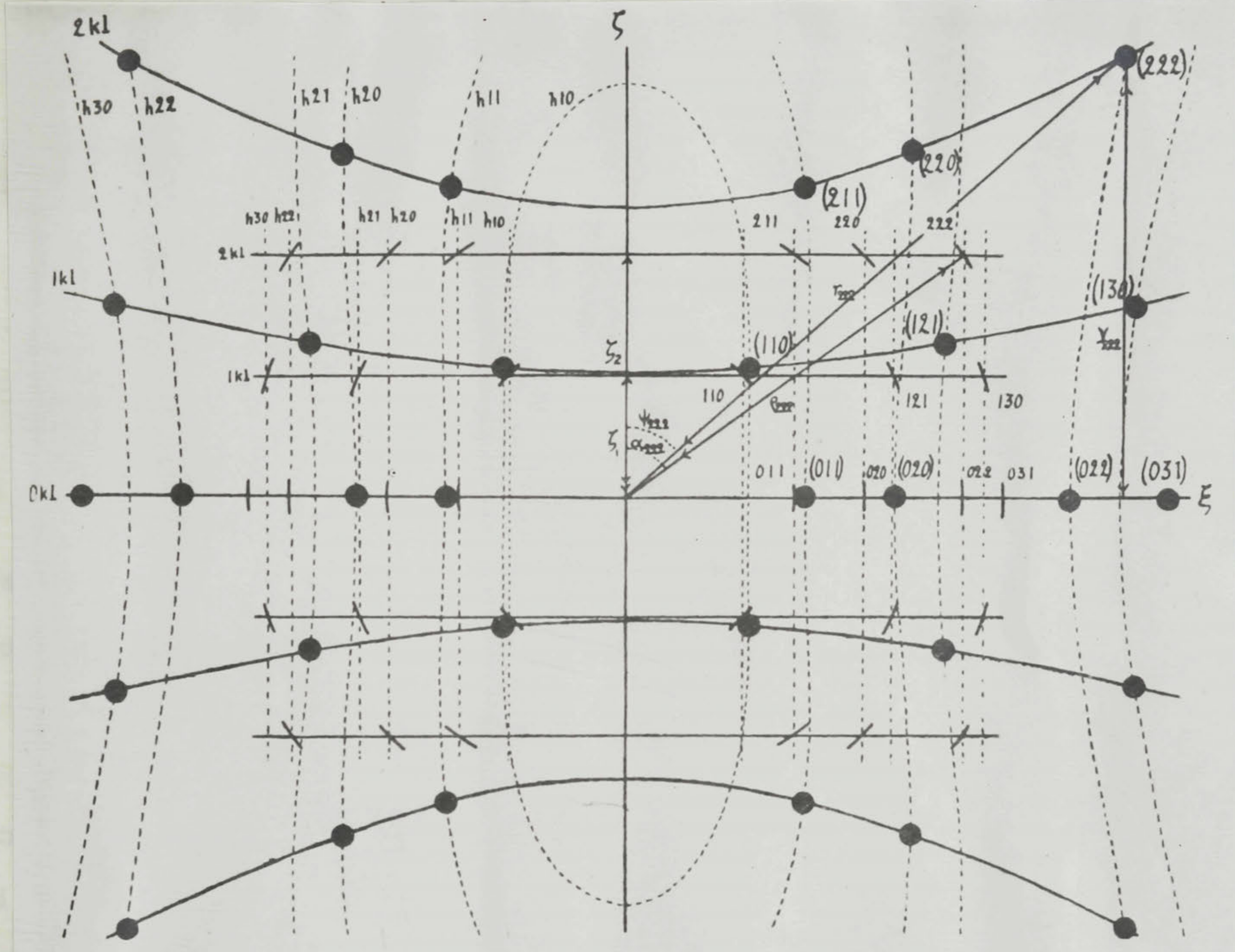
Fig. 12 b.



~~8.~~—Formation of Rotation Diagram from a face-central cubic reciprocal latt
corresponding to a body-centred crystal.

● (222) Point of reciprocal lattice. ○ 222 Point of rotation diagram.

Fig. 12 c.



—Rotation Diagram of Body-Centred Cubic Crystal rotated about its (*a*) axis : shown with Projection of Photograph on the same scale. (See fig. 8.)

● (222) Spot of Photograph Protection. ⊹ Point on Rotation Diagram,

Fig. 12 d.

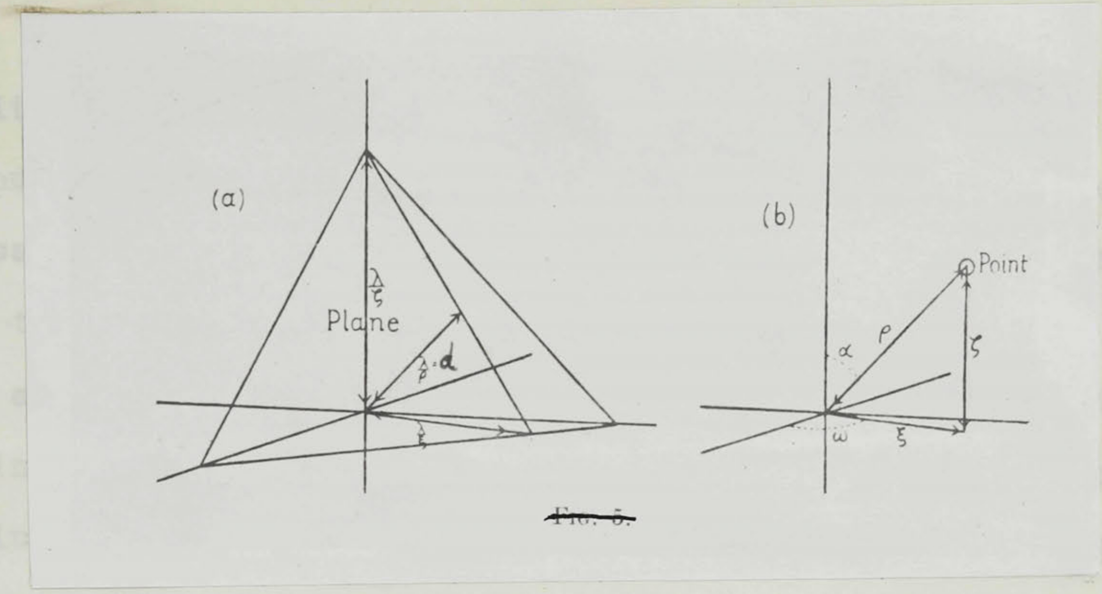


Fig. 12 e.

If the crystal is rotated about one of its axes, the reciprocal lattice nets, to which the axis is perpendicular, will project (cylindrically) into lines of points on the rotation diagram for which

$$\zeta = \pm n \zeta_a \qquad n = 0, 1, 2, \quad \ldots\ldots \; (5)$$

and the crystal lattice spacing (translation) along the rotation axis will be

$$a = \frac{\lambda}{\zeta_a} \qquad \ldots\ldots\ldots \; (6)$$

(supposing rotation about the a - axis, for example)

Thus, by charting the enlargements of three axial rotation photographs, and calculating mean values of ζ_a, ζ_b, ζ_c, from the rotation diagrams so obtained, we can get the axial translations of the space lattice of any crystal. If the inter-axial angles are also known, an axial system is fixed, with respect to which the reflecting planes of the crystal can be indexed.

The method of doing this is very simple, and it is in this simplicity that the power of the Bernal analysis lies.

From the axial system determined as outlined above, the reciprocal axial system is calculated (equations (2)). The principal nets of the reciprocal lattice are drawn, and the points at which the crystal axes pass through the nets is calculated. The distances from this point to the points of the net will then give the "calculated" ξ values for each ζ constant line on the rotation diagram. The "observed" rotation diagram will already have been plotted, and to this may now be added the "calculated" rotation diagram. But the reciprocal lattice co-ordinates

$$ha^*, \quad kb^*, \quad lc^*$$

of each point of the "calculated" rotation diagram are known. It is thus possible to assign the indices (h k l) of the reflecting plane to each point on the "observed" rotation diagram. The degree of coincidence of the "observed" and "calculated" diagrams provides an excellent check on the accuracy of the analysis.

A list of reflecting planes may then be drawn up, and from a consideration of the experimental plate limits, and the path of the sphere of reflection through the reciprocal lattice, an additional list of planes whose reflections could have been recorded, but were not. The lists, when compiled from all three axial rotation diagrams, will, in general, account for all points of the reciprocal lattice with a definite assignable range:

$$0 < \rho < \rho_{max.}$$

Ambiguity may occur, due to lack of resolution on the diffraction pattern, but this can be removed by changing the wave length, or by taking photographs with the crystal oscillating between defined limits: $\omega_1 < \omega < \omega_2$

The sphere of reflection will then pass through a known set of reciprocal lattice points, i.e. only a certain set of planes can reflect. The analysis of such diagrams is carried out by an obvious modification of the method for the rotation diagrams. It will not be described here.

When the lists of reflecting and absentee planes have been drawn up, it will, in general, be possible to determine whether or not the cell is face or body centred, and hence the type of lattice.

The presence of planes (h k l) where:

(h + k + l) is odd, precludes a body centred cell
(k + l) " " " centring of the (100) face
(l + h) " " " " " " (010) " .... (7)
(h + l) " " " " " " (001) "

This can also be done by determining, from the appropriate axial rotation photographs, the lattice spacing along the [011], [101], [110], and [111] axes.

From the cell dimensions and crystal density, the number of chemical molecules associated with each lattice point can then be calculated:

$$n = \frac{\sigma \Delta}{\cancel{p}\, M\, m_H} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where n = no. of chemical molecules to the lattice point
Δ = volume of unit cell
σ = density of crystal
M = molecular weight of chemical molecule
m_H = mass of hydrogen atom

If, then, the crystal class be known, reference to Astbury and Yardley's tables[35)] will give the possible space groups consistent with the type of lattice and the properties of these space groups, together with formulae for the types of planes which are "halved", i.e. which cannot reflect x-rays on account of special phase relations arising from the symmetry properties of the structure.

An examination of the list of reflecting planes will result in the elimination of certain space groups. In fortunate cases it will be possible to eliminate all but one. When there are several possibilities, an idea can be gained as to which are the most probable by reference to the list of absentee planes. No rigorous conclusions can be drawn from the absence of a record of reflection, however, for this may merely mean that the reflected beam was too weak to produce a visible photographic effect.

The space group data give also the number of asymmetric molecules per cell. Usually the number of chemical molecules will be equal to or less than the number of asymmetric molecules. If the number is less, then the chemical molecule must possess symmetry. In a few cases it has been found that the number of chemical molecules is greater, and we must then conclude that there is some form of molecular association present.

§ 2. The Determination of Intensity of Reflection.

The determination of the unit cell and possible space groups of a crystal is now a routine performance; an outline of one standard procedure has just been given. There are cases, notably among the simple inorganic compounds, where the structure is completely determined by the symmetry requirements of the space group. In organic compounds, however, this is seldom the case, and further progress toward a complete analysis depends largely on a knowledge of the intensity of the reflections from a considerable number of planes. The problem of the measurement of intensities, and the reduction of observations has been fully discussed by a number of authorities, and a general treatment will not be attempted here.36) For the determination of absolute intensities, the method employing the ionization chamber is the only one which has so far yielded accurate results. Useful values of relative intensities can, however, be obtained from photographic diffraction patterns. This problem has been studied by Astbury, who has developed an integrating photometer which promises to be of much use.37) In the past visual estimations of intensity have been used, and though they are necessarily inaccurate, they have proven of sufficient value for the determination of the chief characteristics of structures. The discussion of the details in any analysis must of course always depend on more accurate measurements. The following treatment of the problem of determination of intensity of reflection is intended to cover only such considerations

---

In the case of a "powdered" substance, i.e. when the crystals are too small and imperfect to use single crystal technique, even the determination of the unit cell may be a matter of great difficulty, involving methods of trial and error.

as will be involved in the work described in this thesis.

Since visual estimations are here used, there are certain corrections which are usually applied in absolute intensity determinations, but which are in this case within the limits of experimental error, and will therefore be neglected. The general formula for the integrated intensity of reflection from a rotating single crystal is 36)

$$\frac{E\omega}{I_0} = Q\,\delta V \quad .... \quad (9)$$

where E = total energy reflected
ω = angular velocity of the reflecting plane through the position of reflection
I_0 = intensity per unit area at the crystal of the incident beam
δV = volume of the crystal, which is supposed completely bathed in the x-ray beam

$$Q = \left(\frac{Fe^2N}{mc^2}\right)^2 \lambda^3 \cdot \frac{1+\cos^2 2\theta}{2\sin 2\theta} \quad ...... \quad (10)$$

F = structure factor of the reflecting plane
e = charge on an electron
m = mass of an electron
c = velocity of light
N = number of scattering units per unit volume
= $1/v$ where v = volume of unit crystallographic cell
λ = wave length of the incident and reflected beams
θ = the glancing angle of the beam on the plane of reflection.

The following points are to be noted:-

(1) The formula (9) takes no account of absorption of the x-rays in the body of the crystal. In the case of organic crystals of the type here considered, the absorption is not sufficient to show up in the character of the spots on the diffraction patterns even when fairly large crystals are used (nearly 1 mm. in linear dimensions).

In the discussion of <u>relative</u> intensities this factor would only be important in comparing reflections of greatly differing θ .

(2) The temperature factor e^{-M} has been omitted from the equation. With such complicated crystals there is no possibility of making such a correction.

(3) In general the value of ω will be different for different planes. It may be shown* that

$$\omega = \omega_0 \frac{4\sin^2\alpha - \rho^2}{4 - \rho^2} \quad \ldots\ldots\ldots\ldots\ (6)$$

where ω_0 = angular velocity of rotation of the crystal
α = angle between the rotation axis and the normal to the reflecting plane
ρ = 2 sin Θ
= radius vector of the plane in the reciprocal lattice

(4) It has been proven by Bouwers 39) that, under proper conditions, the law of blackening of photographic emulsion by x-rays is correctly given by Busé's 40) formula

$$D = C \log_{10} \left(\frac{x}{a} + 1\right) \quad \ldots\ldots\ldots\ (7)$$

D = photographic density
x = total x-ray intensity (It)
C,a are constants

E cannot therefore be estimated as proportional to the blackness of the spots, and a scale of intensities must be set up. Probably the most reliable method is by utilizing the known ratio of the intensity of the K_α and K_β spots 45) due to the same plane.

---

* This expression, suitable for use in connection with the Bernal analysis, was worked out by Dr. A. L. Patterson and the writer (vide infra). Charts of the ω correction appropriate for direct application to an x-ray plate have been prepared by S. B. Hendricks. 38)

For Cu this ratio has been determined to an accuracy of better than 2%.[41)] Another method is by the comparison of photographs obtained with accurate axial settings of the crystal with ones obtained with known mis-settings. With certain types of lattice it is possible to get doubling of equivalent spots in certain places, and quadrupling in other places on the diffraction pattern.

(5) Although the shape of the spot on the photograph does not affect the value of the integrated intensity, it does introduce serious difficulties into the problem of visual estimation. The form of the spot depends on the geometry of the apparatus and the crystal. A certain amount of variation from one part of the diagram to another is unavoidable, but the worst trouble comes when the crystal is a needle or thin flake. The optimum shape is a sphere, and the nearer to this form the crystal can be chosen, the greater the reliance that can be placed on the visual observations.

(6) In work of this nature the variation of intensity due to absorption of the reflected beam in different lengths of air path to the plate or film may well be neglected. The divergence of the beam, resulting in greater diffuseness of the spot for longer paths is probably a consideration of greater importance.

- - - - - - - - - - - - - - -

Now the integrated intensity of reflection is affected by two other factors which are not directly dependent on the structure of the particular crystal used. These are the "polarization factor," $\frac{1 + \cos^2 2\theta}{2}$, and the "Lorentz factor", $\frac{1}{\sin 2\theta}$. If we write

$$\left(\frac{F e^2 N}{mc^2}\right)^2 \lambda^3 = \frac{2 \sin \theta}{1 + \cos^2 2\theta} \; \frac{E\omega}{I} \qquad \ldots\ldots\ldots\ldots (8)$$

we are carried one step further toward the determination of the structure factor F, which is the most important quantity in the determination of the precise structure of the crystal. Since the observed quantity in the case of visual estimates of relative intensity is merely:

$$\frac{E}{E_0}$$

where E_0 refers to the standard spot on a photograph, it is of no use to calculate the factor $\left(\frac{e^2 N}{m c^2}\right)^2 \lambda^3$

Note. It has been shown 42) that if the beam incident on the crystal be itself polarized, then the ordinary polarization factor should be replaced by

$$\frac{\sin^2\alpha + P \cos^2\alpha + (P \sin^2\alpha + \cos^2\alpha) \cos^2 2\theta}{1 + P}$$

where P is the primary polarization ratio, and α defines the orientation of the primary beam with respect to the plane of reflection.

This function is practically the same as the other for small values of θ , and does not differ seriously in the larger range. The difference is usually well within the limits of visual error, and will not be considered in this work.

Summary. From the above it is seen that, for purposes of visual intensity estimation, we may write

$$\frac{F}{F_0} = \sqrt{\frac{W}{W_0} \; \frac{E}{E_0}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

where $W = \dfrac{\sin 2\theta}{1 + \cos^2 2\theta} \; \dfrac{4\sin^2\alpha - \rho^2}{4 - \rho^2}$ .... (10)

$\dfrac{E}{E_0}$ is the estimated intensity ratio.

The zero subscript refers to the plane or spot on the photograph adopted as an arbitrary standard of reference.

Charts consisting of the curves

$$W(\alpha, \rho) = \text{const.}$$

have been prepared by Dr. A. L. Patterson and the writer in such a form as to be directly applicable to the Bernal rotation diagrams (see Fig. 13). It is fortunate that these curves approximate closely to vertical straight lines over a considerable part of the useful region of the plate. The proximity of the loci close to the circle of reflection shows in a striking way the unreliability of this region for intensity determinations. The dotted line shows roughly the limits of a photographic quarter plate ($3\frac{1}{4}$" x $4\frac{1}{4}$") at 5 cm. from the crystal. By using the known ratio of the intensity of the K_α to the K_β components of the x-rays, a rough scale of intensities may be set up as a calibration for any photograph, and the relative intensities so determined, after correction by the W factor, will provide a set of ratios:

$$\frac{F}{F_0}.$$

which is what is required.

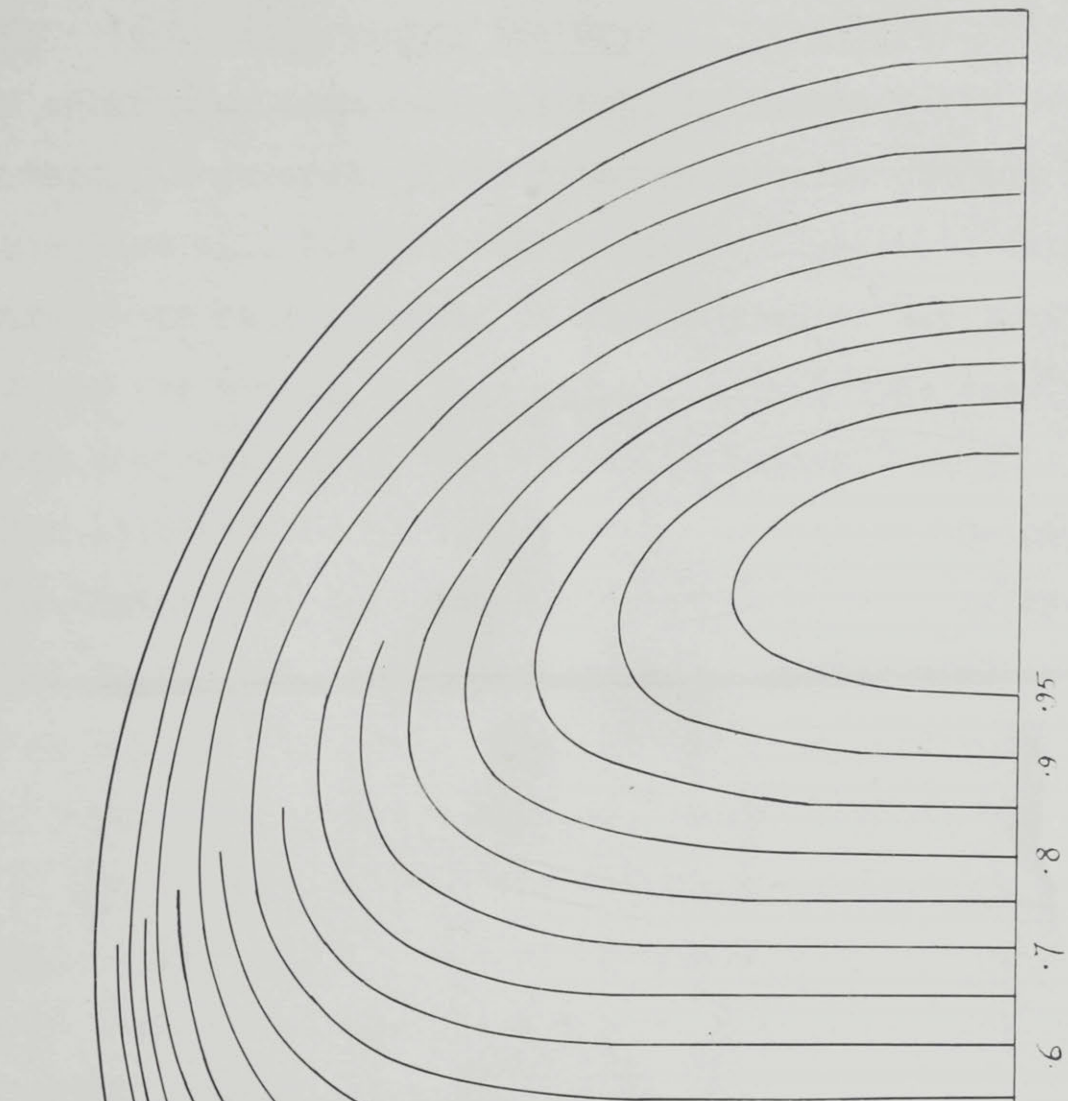


Fig. 13.

§ 3. Methods of Determining the Crystal Structure.

In commencing such a discussion, it should first be plainly stated that, in general, there is at present no cut and dried procedure that will lead directly even to a possible crystal structure. In fact it would be almost true to say that every crystal has its method. This is particularly the case with organic crystals, and complicated structures in general.

When absolute intensity measurements can be obtained with crystals containing atoms whose atomic F curves are known, the rules are fairly well laid down to the last stages of the analysis, but if this is not the case a variety of considerations have to be brought to the aid of the analysis. Some of these are listed below:

(1) Considerations of Shape and Dimensions of the Molecule and Unit Cell. The significance of progressive change of axial ratio through a series of isomorphous crystals has long been recognized in morphological crystallography.43)

In x-ray analysis knowledge of the angles and dimensions of the unit cell enables such considerations to be used with much greater advantage. If some knowledge is possessed of the size and shape of the molecule, and of added groups of atoms, it is often quite a simple matter to find the approximate orientation of the molecule. Good examples in x-ray analysis are provided by the well known cases of naphthalene and anthracene,44) and the naphthalene chlorides.45)

(2) The Enhancement Principle. In structures possessing certain peculiarities, certain groups of spots on the diffraction diagram show up in a special way. Three cases are noted by W. H. Bragg in a very illuminating article on this phenomenon:-46)

(a) The case of cyanite.

This structure may be regarded as two interpenetrating lattices, one bearing the oxygen atoms, and the other the aluminium and silicon atoms. The diffraction pattern has the appearance of two superimposed patterns, the spots of one being much more intense than those of the other.

(b) The long chain compounds.

These contain chains of CH_2 groups, introducing a subsidiary periodicity in the molecule, which is detected by the isolated appearance on the diffraction pattern of a small group of high index planes.

(c) Naphthalene and anthracene.

These molecules also have a subsidiary periodicity inherent in their ring structure.47) As the molecules lie parallel to the c - axis, the c - rotation photograph shows certain hyperbolae with a much weaker group of spots than the neighbouring hyperbolae.

(3) Pseudo-Symmetry. This consideration has already been used in a variety of ways.48) A close geometrical approach of one axial system to the symmetry of a higher system does not necessarily indicate anything of special interest with regard to the structure. If, however, in addition to geometrical pseudo-symmetry, it can be shown that certain groups of reflections which would be equivalent in one of the pseudo-symmetrically related space groups, are actually similar in intensity, there is much more ground for the use of such considerations as a guide to the structure.[*] It would then be expected

---

[*] This point of view, which is, in a sense, a generalization of the Enhancement Principle, has been developed by A. L. Patterson in a paper not yet published.

that the halvings of the pseudo space group would appear as a statistical weakness of the corresponding reflections in the true space group. Indeed it seems at the present time that some such statistical consideration of intensities of reflection from special groups of planes, promises great hope of advance in the complex organic field.

(4) Physical Properties (Growth Habit, Cleavage, etc.) At the present time there is not enough known of the mechanism of interatomic and intermolecular forces to make it generally possible to use these phenomena in the determination of structure. They are, however, valuable in connection with other data, especially as a check on the reasonableness of any structure which is proposed.

- - - - - - - - - - - -

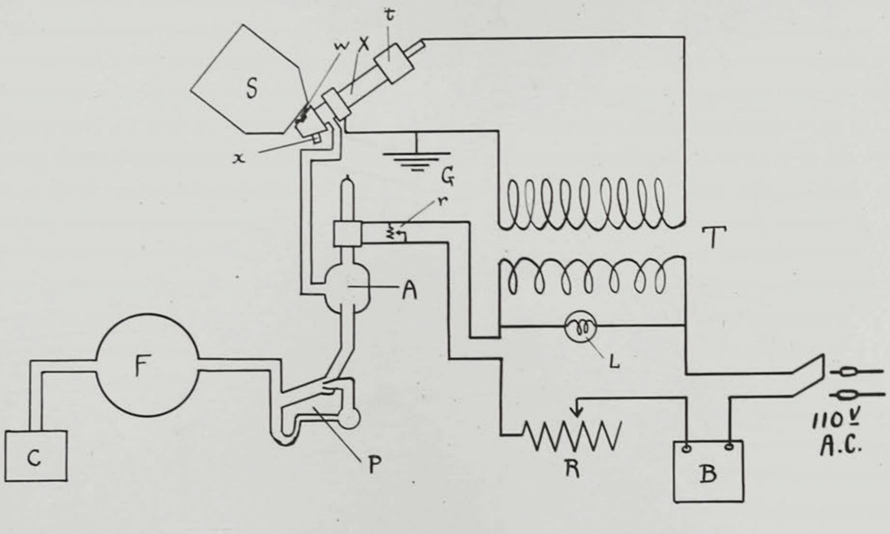
Whatever considerations may lead to a proposed structure, the strict test is whether or not it is consistent with the observed intensities of reflection. If the atoms are so disposed that the distribution of scattering matter across each plane gives F values for successive orders in reasonable agreement with the observed values for the plane, we may be sure that we have at least obtained a possible structure of the crystal.

IV. EXPERIMENTAL

§1. The X-Ray Apparatus

A Shearer X-ray tube was used, with its copper target. The chief features of this tube are: (1) it rectifies its own current, (2) it has interchangeable targets, (3) the spectrograph can be brought very close to the target. The tube was pumped continuously by a mercury vapor pump backed by

CONNECTIONS of APPARATUS



LEGEND

S - X-ray Spectrograph.
X - X-ray Tube.
x - Replaceable Target.
w - Aluminum Window.
t - Cooling Tank.
T - Transformer.
R - Rheostat.
L - Lamp.
B - Circuit Breaker.
G - Ground.
A - Automatic Vacuum Control.
P - Mercury Pump.
F - Fore Vacuum Chamber.
C - Cenco Pump.
r - Adjustment for A

Fig. 14.

a forevacuum reservoir and Cenco Hyvac pump, and during the latter part of the experimentation, the control was maintained by an automatic valve devised by the writer. The power was supplied by a Watson transformer, run at 40 - 50 kilovolts, controlled by a rheostat in the primary circuit. Fig. 14 is a diagrammatic sketch of the apparatus.

§ 2. The Spectrograph

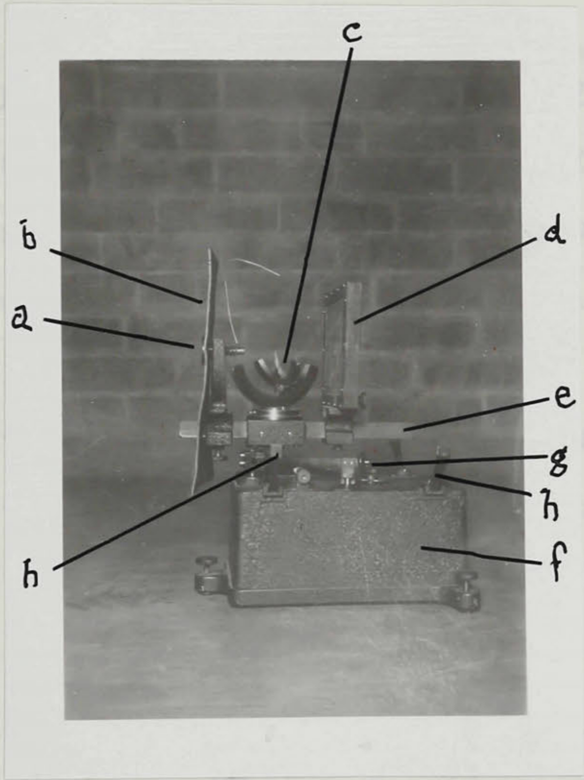


Photo. 1.

a. Pinhole
b. Lead Shield
c. Goniometer
d. Camera for Plate
e. Carriage Bar
f. Box containing Clockwork
g. Rotating and Oscillating Gear
h. Supports for Side Shields

Above is a photograph of the Muller X-ray Spectrograph, Type E60, which was used to obtain the diffraction patterns. It is shown set up for the rotating crystal method. These fittings can be replaced on the carriage bar by others, such as a cylindrical camera, slits and mounting for a crystal with a large face (early Bragg method), camera and mounting for powder photographs, etc. The instrument is manufactured by Adam Hilger, London, and is fully described in their Instructions E60.

Ilford X-ray Quarter Plates 3-1/4" x 4-1/4", Eastman Duplitized X-ray Films, and Eastman X-ray Developer were used.

§3. Description of Automatic Vacuum Control.

The satisfactory running of any gas-type X-ray tube depends on a good control of the vacuum. The method recommended for use with the Shearer tube, is control by a pinchcock on a piece of rubber tube running from the fore vacuum to the X-ray tube, by-passing the mercury pump. Two years' experience with this device convinced the writer that it was

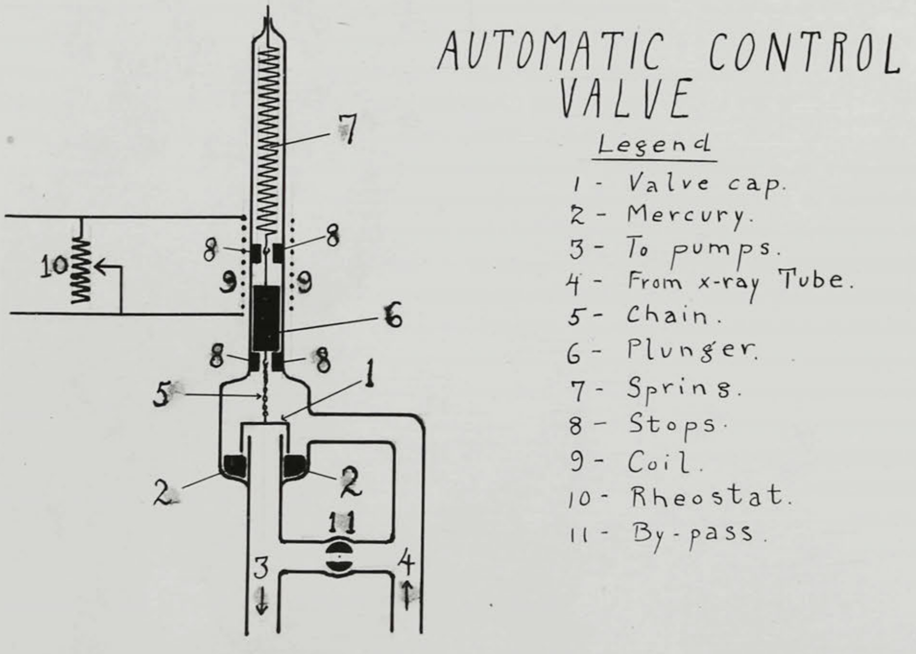


Fig. 15.

not to be relied upon and that it would be worth while to go to some trouble to obtain a more satisfactory arrangement. The automatic valve which is illustrated in Fig. 15 has been found to work very satisfactorily. At the worst, the variations of current do not exceed 10 - 15%, and when in proper condition, the fluctuations are much less. The plunger is actuated by the primary current of the transformer. When the pressure increases in the X-ray tube, the current increases, and if it exceeds a certain value, the valve cap is lifted, allowing the pump to remove the superfluous gas. When the correct pressure is attained the cap again seats on the mercury and the pump is shut off. The motion of the plunger is scarcely observable and there is no "hunting".

Fig. 15 is an earlier model. Gradual contamination of the mercury surface eventually spoiled the seal and prevented the pump from being effectually shut off. This difficulty was overcome by the addition of a slit aluminium foil skirt to the cap, which was then rigidly attached to the plunger. The passage of gas is thus allowed only when the apex of the slits come above the surface of the mercury.

§ 4. Photographs of Apparatus

a. Spectrograph (shielded)
b. " (unshielded)
c. X-ray Tube

d. X-ray Tube Cooling Tank

e. " " Water Jakkets and Supply Tubes.

f. " " Window.

g. Transformer built into table

h. " High Tension Terminal

i. Primary Current Ammeter

j. Lead Shields

k. Automatic Control Valve

l. Shunt Rheostat

m. Mercury Pump

n. Fore Vacuum Reservoir

o. Circuit Breaker

p. Main Rheostats

q. Discharge Tube and Induction Coil.

The Cenco Hyvac Pump is mounted on a shelf under the table.

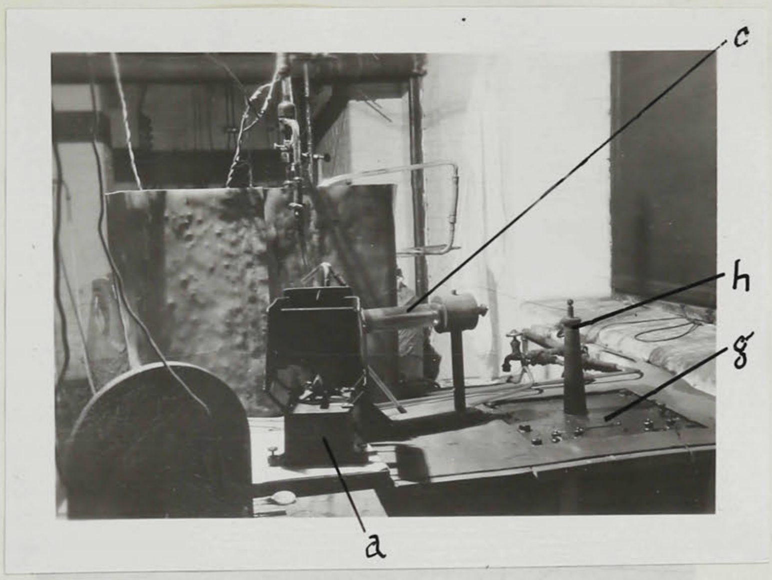


Photo. 2

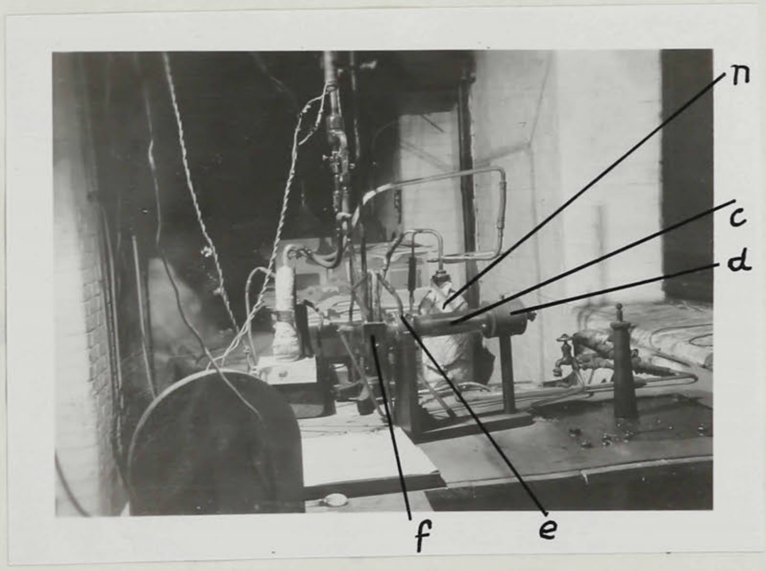


Photo. 3.

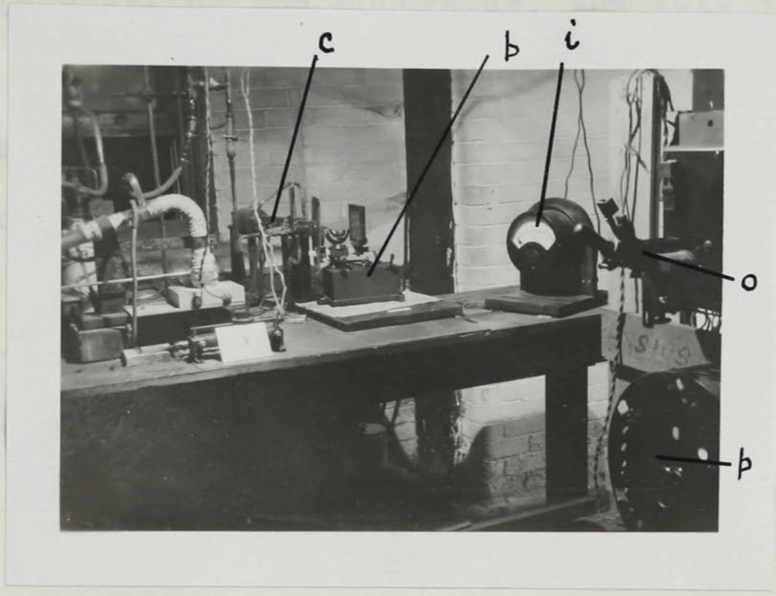


Photo. 4.

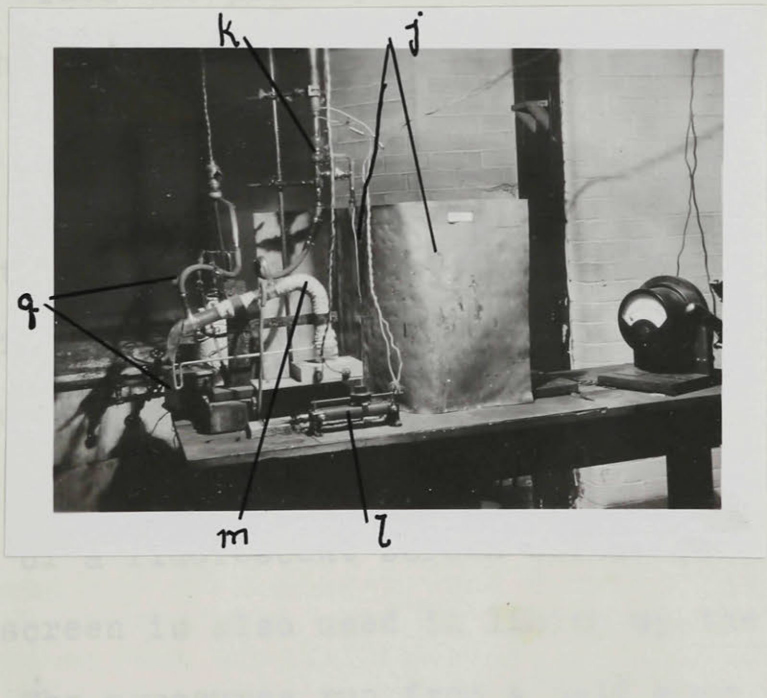


Photo. 5.

§ 5. Operation

In starting the apparatus, the fore vacuum is first pumped down to a suitable value by means of the Cenco pump. This can be tested either by means of a small discharge tube and induction coil or by a cautious trial of the behaviour of the X-ray tube itself.

Then the mercury pumps are brought into play, and when it is found that the X-ray tube is "hard", the by-pass of the automatic control is closed, so bringing the valve into operation.

The full load is brought on the X-ray tube by gradually cutting out the resistance in the main rheostat. The desired vacuum is attained by adjustment of a shunt (10, Fig. 15) across the coil of the automatic valve; the setting of this shunt fixes the primary current at which the valve will commence to function.

Besides the problem of maintaining the correct vacuum there are other factors such as cathode adjustment, focussing of cathode stream on target, heating, etc., requiring attention in the Shearer X-ray tube but these have been well discussed elsewhere49), and will be omitted here.

The intensity of the X-ray beam is roughly tested by means of a fluorescent screen before commencing an exposure; this screen is also used in lining up the spectrograph.

The exposures run from a half hour to four hours according to the nature of the crystal and the type of photograph.

The shielding of the tube is attained by means of lead screens about 1/4" thick (see photos). A month's test with films placed a couple of yards from the tube in various directions, and partly covered with lead, proved that there was enough stray radiation to produce an appreciable blackening, and that shielding was highly desirable.

§ 6. Choice of Crystal Settings

As has been pointed out in Sect. III, § 2, the reliability of the visual estimations of intensity is greatly increased by the choice of a crystal of suitable shape, i.e. approximating as closely as possible to a sphere. In order to prevent overlapping of spots on the plate, and to obtain the most accurate rotation diagrams, it is also desirable to use as small a crystal as is consistent with accurate settings and reasonable exposure time. It is of course absolutely necessary that the crystal should be as well formed as possible, and quite free from twinning.

In practice, a small group of crystals is picked out from a pile using a low power magnifying glass. These are then examined both in ordinary, and in polarized light, under the microscope, and those showing serious imperfections and signs of twinning are rejected. One or two of the best specimens are then chosen, and in most cases these are then measured on the crystallographic goniometer. In the case of substances for which there is crystallographic data available, the measurements are used to identify the faces and axes of the crystal. Where such information has not been obtained, this examination is used in connection with the X-ray data, to assign the crystal class and obtain the axial ratios and angles.

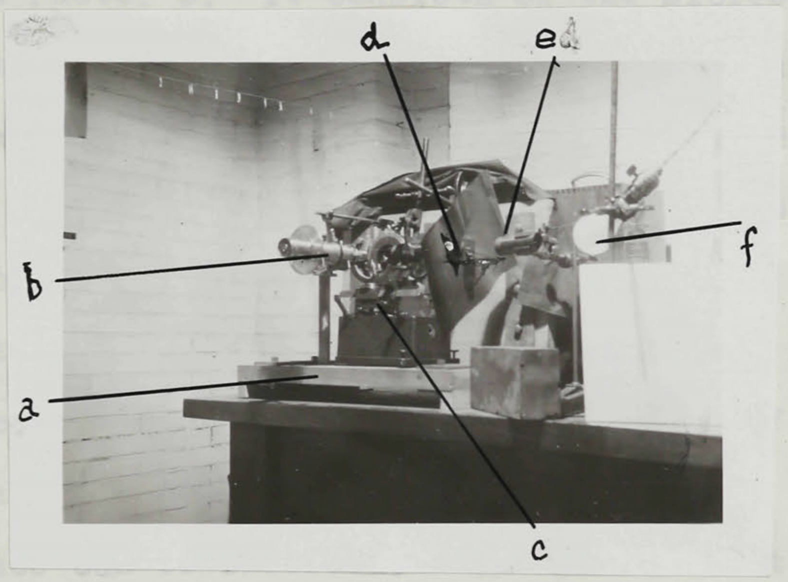


Photo. 6

a. Supporting Frame
b. Microscope
c. Spectrograph in Position
d. Collimator
e. Condensing Lens
f. Source of Light.

The obtaining of accurate settings is a problem which must be dealt with in ways depending on the peculiarities of the particular crystal specimen being used. If there are several faces of the specimen belonging to the zone which is to be the axis of rotation, the setting is most accurately made by using the optical reflections from these faces.

Although the best modern X-ray spectrographs (e.g. the Bernal Universal X-ray Photogoniometer) possess the proper accessories for making such settings, the Muller Spectrograph does not, and experience led the writer to the conviction that it would both conserve time and improve the photographs to construct an apparatus for this purpose. The apparatus is illustrated in Photo. 6. It consists of the microscope mounted firmly in a horizontal position, and a collimater tube, also horizontal, mounted at right angles to the microscope axis. When the microscope is used with a low power objective, there is sufficient room for the goniometer bearing the crystal to be rotated through 360°, thus allowing all faces of a zone to reflect. The microscope possesses a lens for converting it into a telescope so that either a face, or the light signal from a face can be observed. The mirror of the microscope is maintained in such a position that the crystal can be examined by either direct or transmitted light, and the polarizing and analyzing nicols can still be used. The apparatus possesses a number of other advantages which need not be mentioned here. The microscope is so clamped that it can be dismounted quickly for use in the ordinary way.

The most difficult problem in obtaining good photographs arises when there are no faces or edges (or none sufficiently good) to give accurate settings. The alternatives then are (1) the trial and error method, (2) the calculation of the unknown from known settings. The latter, if possible, is, of course, much to be preferred. Now just as the determination of the orientation of four non-coplanar faces suffices, in the ordinary crystallographic procedure, to fix a possible axial system from which all other planes can be determined and indexed, so the corresponding information with regard to four non-coplanar axes will do the same thing directly for the axes. Consequently, by determining the settings for four axes, we can calculate the setting for any other which we may not be able to determine directly. If the crystallographic data is available, two settings will, in general, suffice. The writer is indebted to Dr. Patterson for pointing out the usefulness of the following application of the gnomonic projection in this connection.

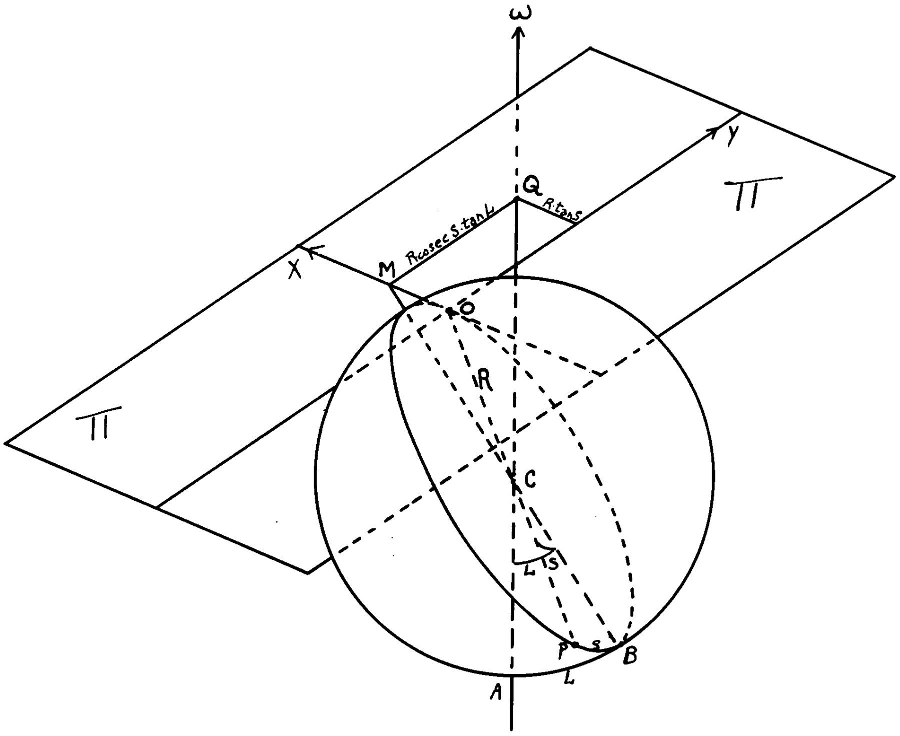


Fig 16

Let π be the plane of the gnomonic projection, fixed with respect to, and at a distance R from, the crystal, which is set on the goniometer head at C.

AB and BP are the large and small circles of the goniometer, in the general positions given by the readings L and S. The vertical AC is the axis of rotation.

π is tangent at O to the sphere, centre C, radius R.

Now when $L = S = 0$, π is horizontal, and the axial system OX, OY, on the plane of projection, is determined by the intersections of the small and large circles respectively with π

Suppose the crystal axis given by the setting L, S, passes through π at Q. Then, as we swing this crystal axis into the axis of rotation C , by moving the goniometer head to the setting L, S, the plane π will swing into the position shown in Fig. 16, and the coordinates X, Y, of Q, are given by:

$$X = OC \tan OCM = R \tan S$$

$$Y = CM \tan MCQ = R \operatorname{cosec} S \tan L.$$

Thus four known axial settings define four points representing four axes on the gnomonic projection, and any other axes may be determined by the rules of the gnomonic projection. When the crystallographic data are known, two settings, plus various constructions which need not be detailed here, will simplify the determination of the correct setting for any required axis.

When, with a crystal whose faces are but little distorted, this graphical construction is carried out with care, very satisfactory settings are obtained. Frequently, however, imperfections in the crystal make the settings inaccurate, and then, and also when using the trial and error method, the final accurate setting can often be attained by calculations from one or two mis-settings.

In oscillating for special reflections, it is necessary to determine the orientation of the crystal with respect to the horizontal circle of the goniometer. This may be conveniently done by observing the position of reflection of some known face, using the horizontal microscope, or by a simple calculation from the gnomonic projection.

§ 7. Analysis of Rotating Crystal Photographs

The plates and films are developed according to the standard procedure. When satisfactory pictures have been obtained, they are "spotted" for enlargement. On account of the low intensity of a considerable number of the spots on an X-ray plate, they will not show in the image obtained with an ordinary projection camera. For this reason, ink spots are placed on the back of the plate in positions opposite the X-ray spots, and then the ink spot pattern is enlarged. Film patterns are transferred to a glass plate. If this process is carried out with due care, using a proper background, the results are very satisfactory. Most of the spots can be located, using an ordinary viewing screen, but the sky is the best background, and is used in a final search for the weakest reflections.

The following example will serve to illustrate the application of the Bernal method outlined in Section I, § 1.

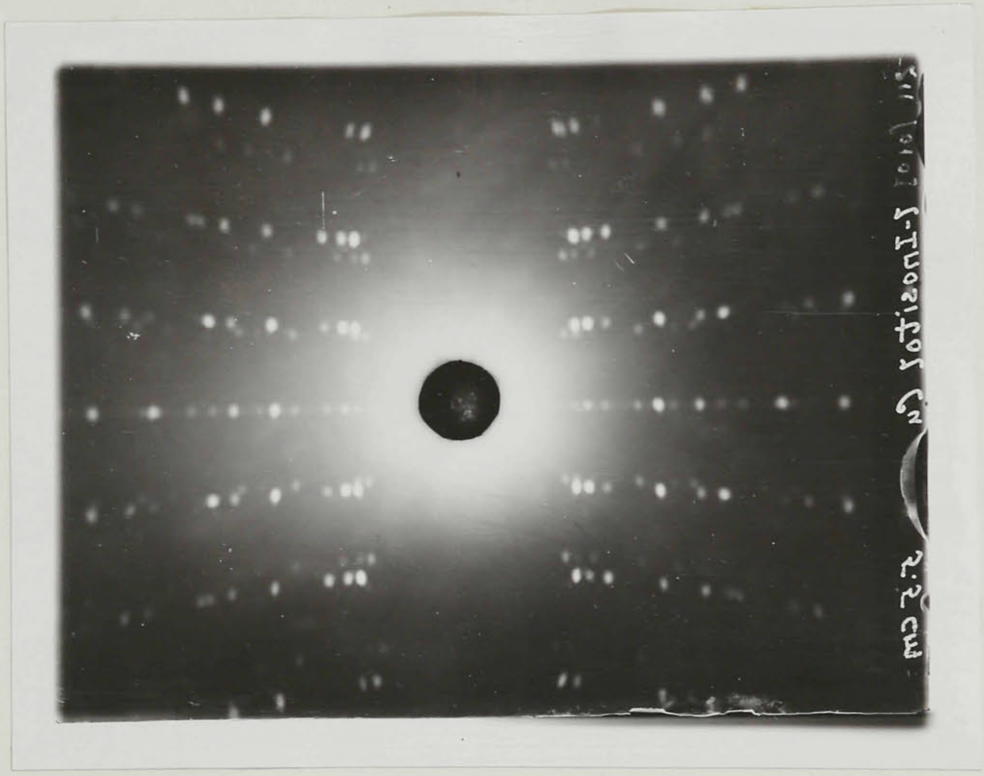


Fig. 17 (No. 211) b-axis.

Fig. 17 is a print obtained from the b-axis rotation photograph of l-inositol. Fig. 18 is its enlargement. A Bernal net (Fig. 19) was placed on the enlargement, and the co-ordinates ξ, ζ. read off. (Tables III, IV).

No. 211. b-axis.

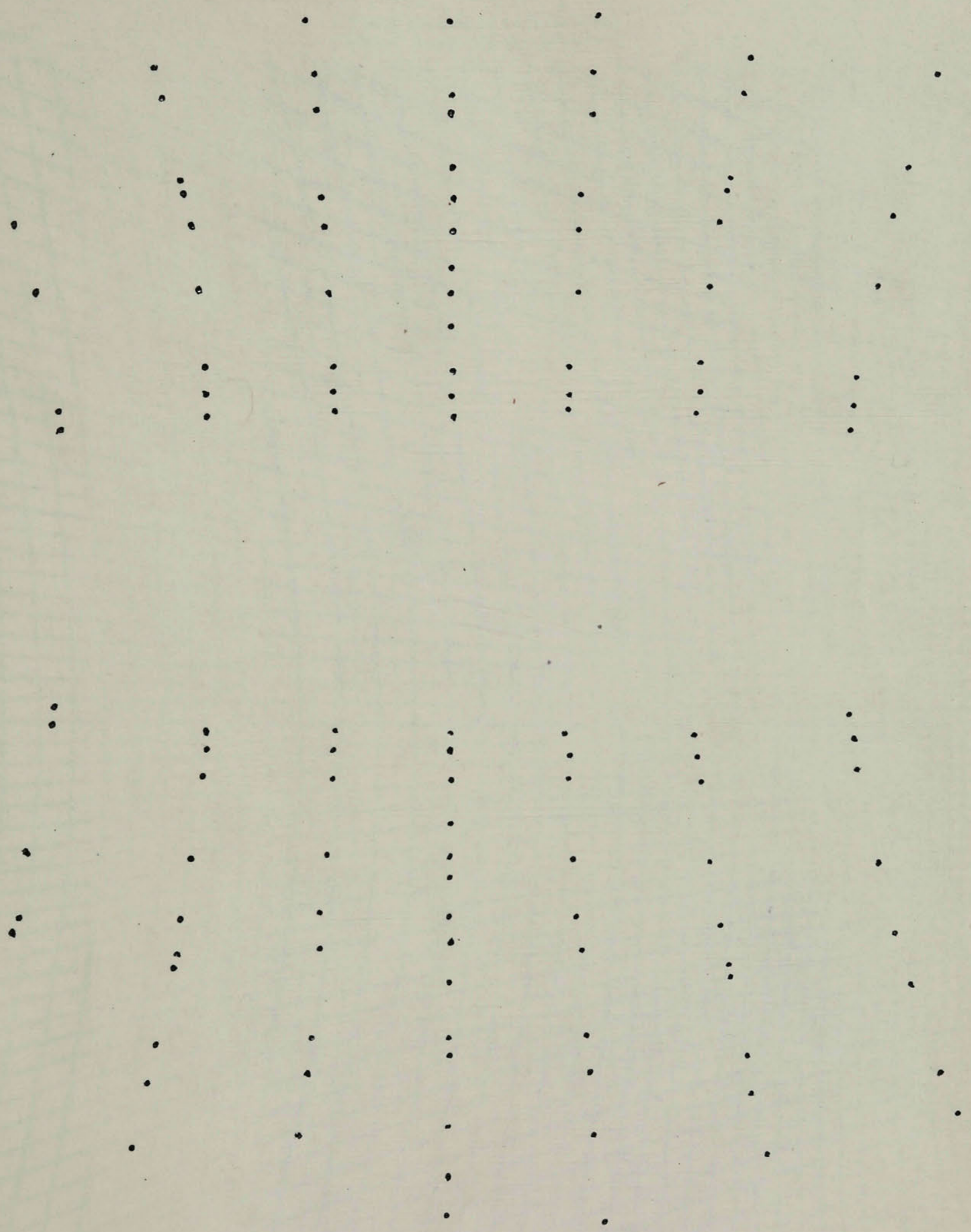


Fig. 18.

Fig. 19. Bernal Chart
for
Plane Plate

Bernal.

CHART I.

(Reprinted by permission from the Proceedings of the Royal Society.)

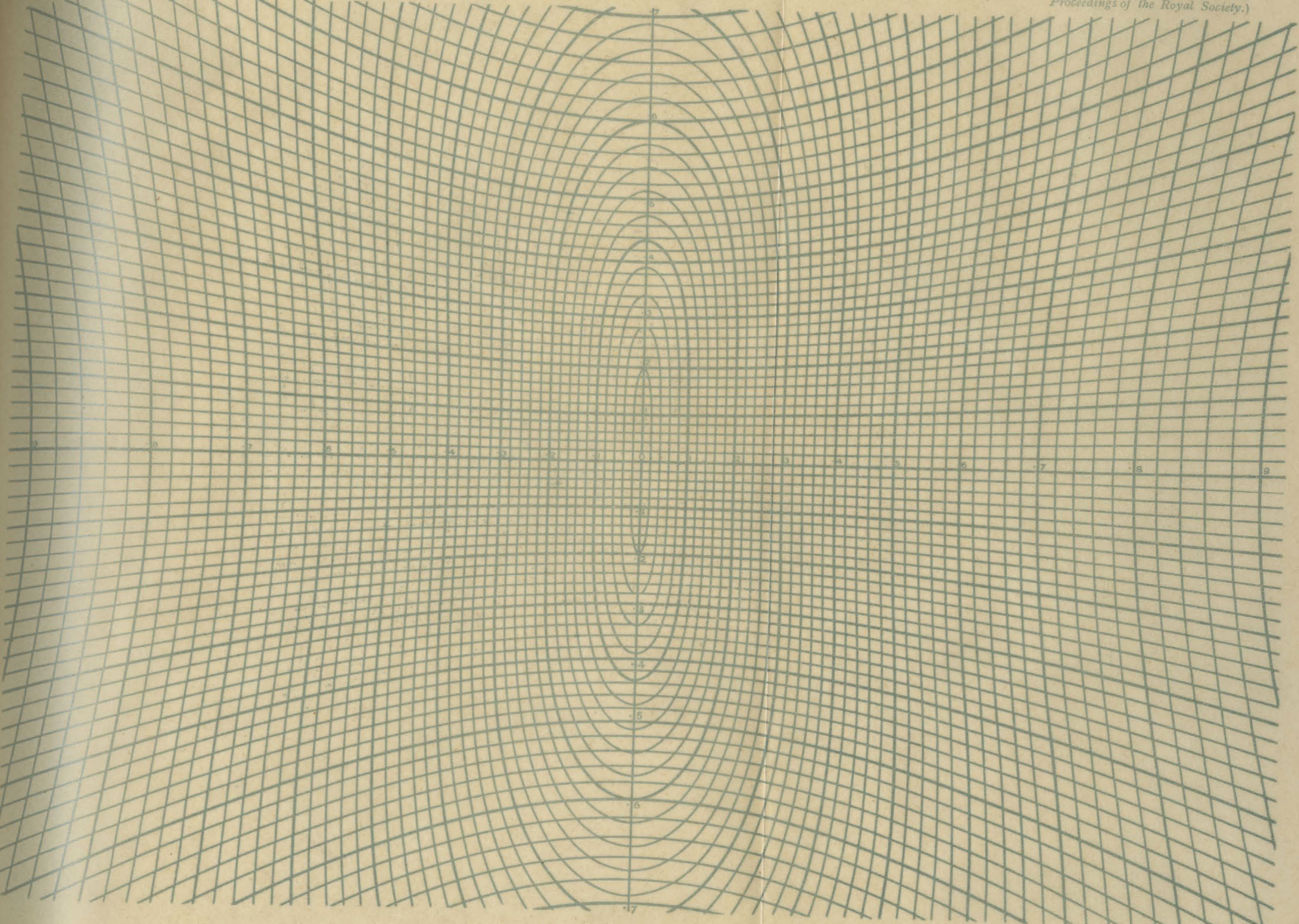


Table III

No. 211 b-axis l-inositol

ξ_b		$2\xi_b$		$3\xi_b$	
0.165	0.168	0.339	0.339	0.507	0.508
7	5	9	10	7	4
10	8	9	7	8	4
3	11	9	8	10	4
4	9	9	6	7	12
9	10	10	8	10	11
5	8	10	9	12	15
8	16	10	12	11	6
6	10	11	12	13	8)64∟8
5	9	11	11	10	0.508
7	7	12	13	12	
4	8	10	10	12	
7	13	11	10	11	
7	16	11	12	10	
11	11	10	9	13	
7	10	8	10	15)153∟102	
8	11	10	11	0.5102	
2	14	17)169∟99	11		
3	18)184∟102	0.3399	12		
19)118∟6.2	0.1702		19)190∟10		
0.1662			0.340		

mean 0.1682

mean 0.3400

÷ 2 = 0.1700

mean 0.5091

÷ 3 = 0.1697

Final Mean

$\xi_b = 0.1693$

$b = \frac{1.54}{0.169} = 9.11$ A.U.

Table IV

ξ values

Equator	1st Layer	2nd Layer	3rd Layer
0.238	0.239	0.238	0.238
262	263	262	262
300	300	299 Check here	300
360	399	400	400
400	472	471	476
428	508	508	526
474	599	523	604
505	632	600	631
544	680	632	
600	750	682	
618			
680			

The mean values of ζ_b were calculated for the different hyperbolae, and from them the axial translation of the b crystal axis was determined:

$$b = \frac{\lambda}{\zeta_b} = \frac{1.54}{1.69} = 9.11 \text{ A.U.}$$

From the a and c axis photographs the axial lengths were obtained in a similar manner. Using also the value of the β angle obtained from crystallographic measurements (l-inositol is a monoclinic crystal), the following data were obtained:

$a = 6.17$ A.U. $\qquad a^* = 0.261$

$b = 9.11$ $\qquad b^* = 0.169$

$c = 6.83$ $\qquad c^* = 0.236$

$\beta = 106°36'$ $\qquad \beta^* = 73°24'$

The volume of the unit cell

$$\begin{aligned} &= abc \sin \beta \\ &= 6.17 \times 9.11 \times 6.83 \times 0.958 \\ &= 368 \text{ A.U.}^3 \end{aligned}$$

The number of chemical molecules per unit cell is

$$\begin{aligned} n &= \frac{\sigma \Delta}{M m_H} \\ &= \frac{1.60 \times 368 \times 10^{-24}}{180 \times 1.66 \times 10^{-24}} \\ &= 1.97 \\ &\doteqdot 2 \end{aligned}$$

The density from the X-ray data is then

$$\sigma = \frac{n\,M\,m_H}{\Delta} = \frac{2 \times 180 \times 1.66}{368} = 1.62$$

which is in reasonable agreement with the observed value 1.60. (Note: This forms additional evidence that the formula $C_6H_{12}O_6$ is correct for the substance which is being analysed.)

The b - axis rotation diagram was then plotted:

(a) the "observed diagram" from the ξ, ζ, co-ordinates from the enlargement

(b) the "theoretical diagram" from the b*c* net of the reciprocal lattice. The completed diagram is shown in Fig. 20. For remainder of analysis see Results on l-inositol.

No. 211 [010] b-axis

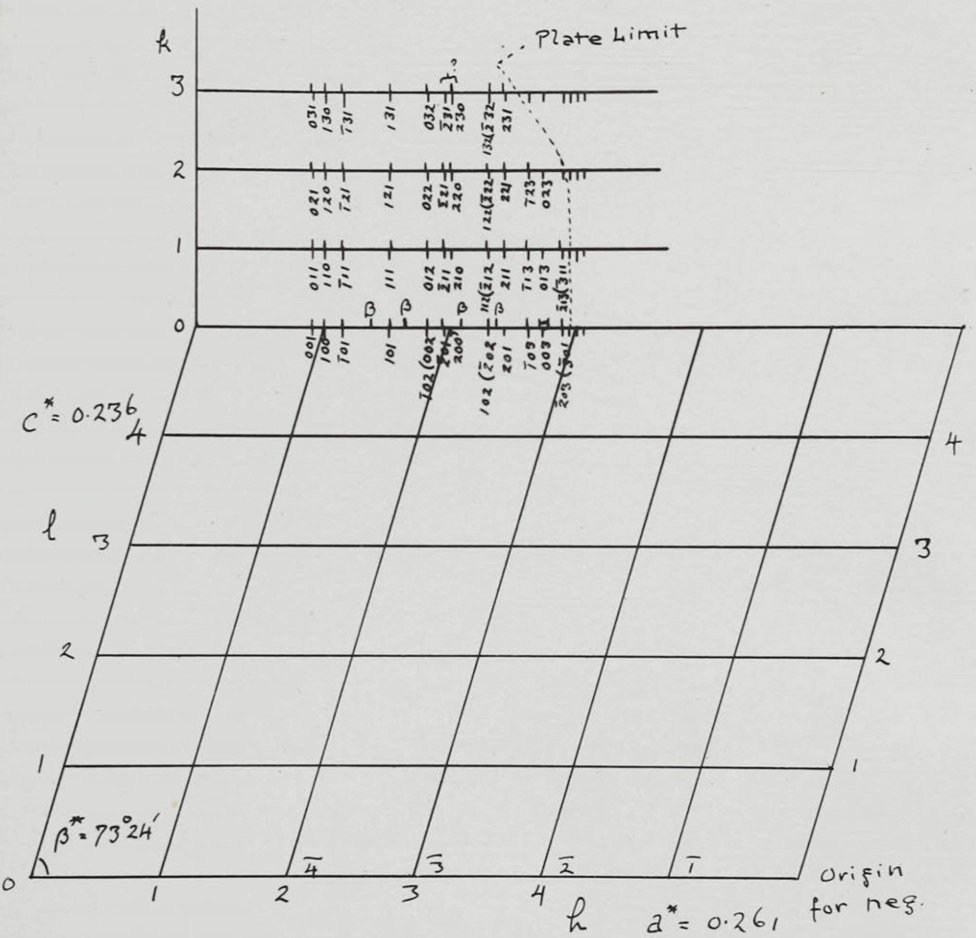


Fig. 20.

V. RESULTS AND CONCLUSIONS.

Inactive Inositol.

1. Choice of Axes, Axial Rotation Photographs.

On account of the growth habit of the crystals, the choice of two of the axes was a simple matter. The needle axis was taken as the a - axis, and the first photograph taken showed, as was to be expected, that it was an important axis. The normal to the tablet face proved to be a diagonal axis, in agreement with the goniometric observations. The choice of a c - axis was a matter of some difficulty, and it was only after a considerable number of photographs had been taken that it was possible to decide on the most suitable direction. Figs. 21, 22 and 23 are prints from the x-ray diagrams obtained by rotation about these three axes, and it is easily seen that of the three the a - axis shows most prominently and the c - axis least prominently the periodic properties of the structure.

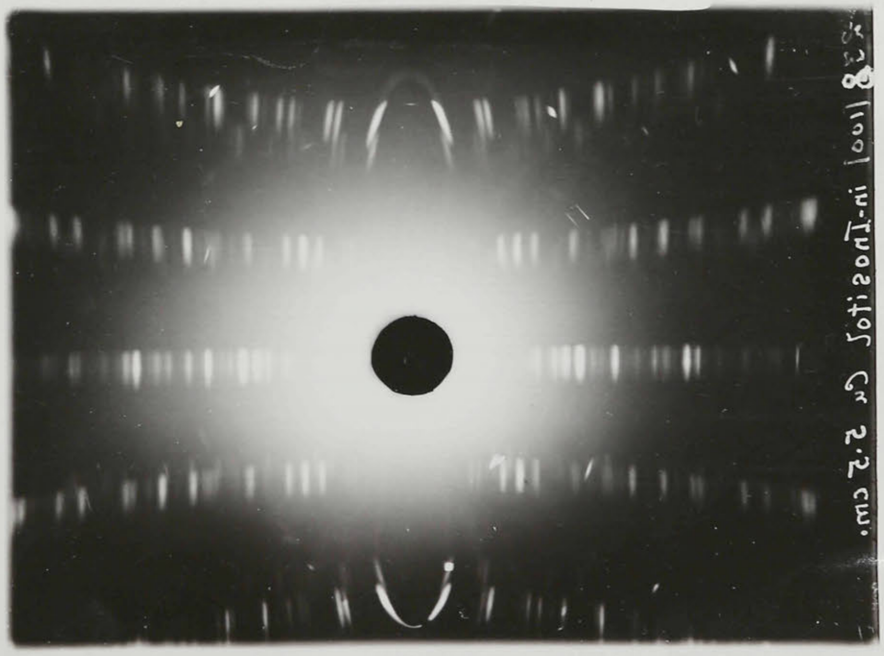


Fig. 21. (No. 238) a - axis

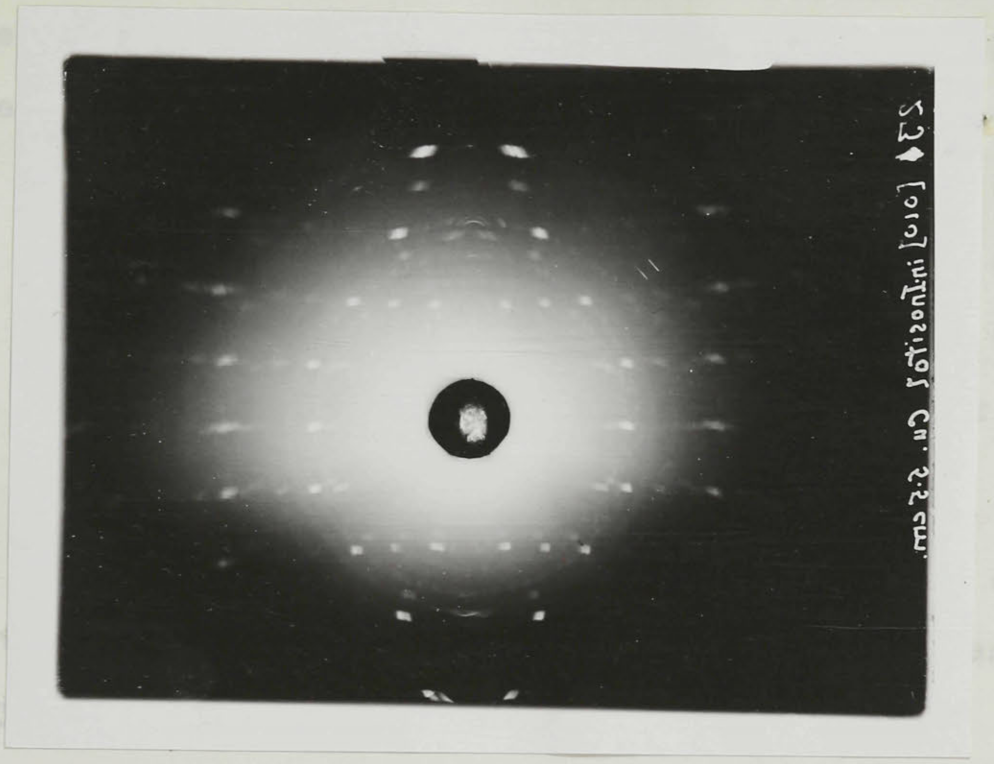


Fig. 22. (No. 231) b - axis.

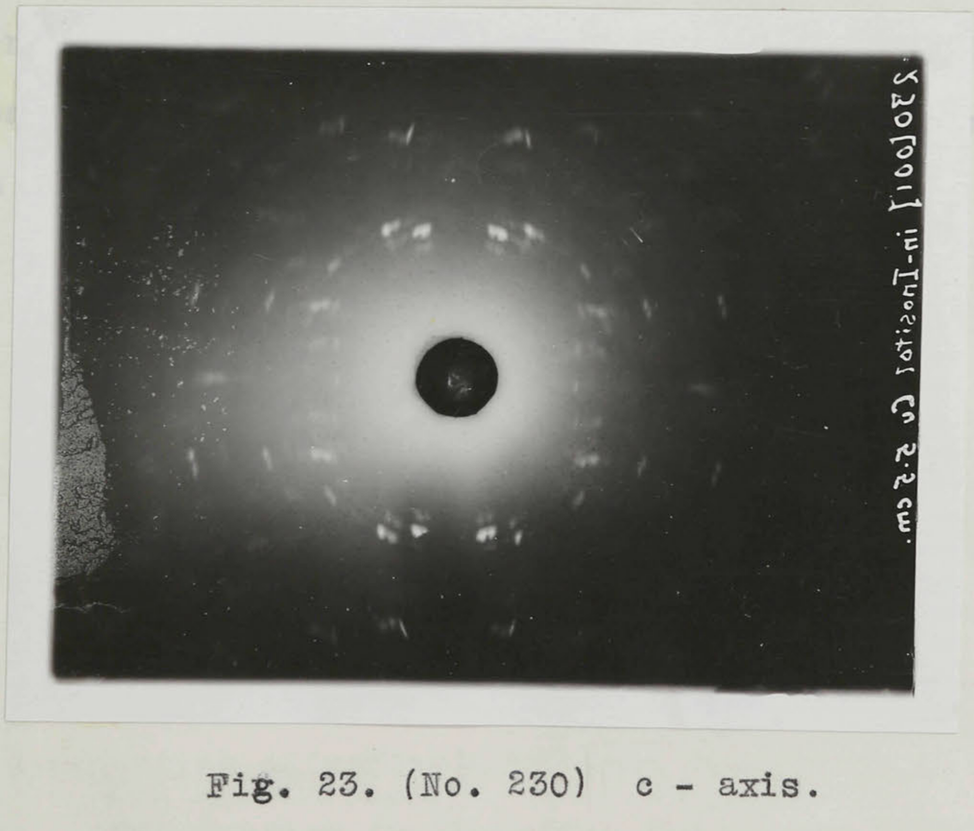


Fig. 23. (No. 230) c - axis.

2. Dimensions of Unit Cell. Calculation of Density.

The analysis of these three photographs yielded the following axial data:

$a = 6.64$ A.U. $\quad a^* = 0.243 \quad \zeta_a = 0.232$

$b = 12.0 \quad b^* = 0.128 \quad \zeta_b = 0.128$

$c = 19.7 \quad c^* = 0.0820 \quad \zeta_c = 0.0784$

$\beta = 107^\circ \quad \beta^* = 73^\circ \quad a : b : c = 0.552 : 1 : 1.64$

Volume of unit cell $= 1490$ A.U.^{3}

On the assumption of 8 molecules per cell, the density was calculated to be 1.61 gm. cc.$^{-1}$ in reasonable agreement with the directly measured value of 1.58 gm. cc^{-1}.

3. Observed and Absentee Reflections.

The data in Table V were obtained from the indexing of the axial rotation diagrams, and several oscillation diagrams about the a - axis in a search for planes of the type $\{10l\}$, $\{20l\}$, which were required for the space group determination.

Table V

Observed (0kl)	Observed (1kl)	Observed (2kl)
021 022 032 042 004 014 025 006 026	111 $11\bar{1}$ 110 $10\bar{2}$ $11\bar{2}$ $11\bar{3}$ 124 $12\bar{5}$ $13\bar{5}$ $13\bar{7}$ 102 112	220 231 232 242 $22\bar{4}$ $20\bar{6}$ $24\bar{5}$ $20\bar{4}$ 204 206 $20\bar{8}$ 224 226 217 236 218 237 219 $21\bar{1}$ $22\bar{3}$
011 031 002 012 010 003 005 030	$10\bar{1}$ 100 101 $12\bar{2}$ $13\bar{2}$ $12\bar{3}$ $13\bar{3}$ $11\bar{2}$ $10\bar{3}$ 104 114 105 103 113	202 203 204 $20\bar{5}$ 207 $23\bar{5}$ 205 232 $23\bar{3}$ $21\bar{5}$
Absent	Absent	Absent

4. Type of Lattice.

Rough estimations of axial lengths from photographs obtained by rotation about the [011], [101], [110], and [111] axes precluded the possibility of face or body centred lattices. This was corroborated by the observation of reflections from the groups of planes of Table VI. The lattice is therefore the simple monoclinic type Γ_m.

Table VI

$(k+l)$ odd $(0kl)$	$(h+l)$ odd $(h0l)$	$(h+k)$ odd $(hk0)$	$(h+k+l)$ odd (hkl)
021 032 014 025 ∴ (100) cell face not centred	$10\bar{2}$ 102 ∴ (010) face not centred		021 032 014 025 $10\bar{2}$ 102 111 $11\bar{3}$ 124 $13\bar{5}$ $13\bar{7}$ 232 $24\bar{5}$ 236 218 $22\bar{3}$ body not centred

5. Possible Space Groups.

Reference to Astbury and Yardley's Tables shows that the following monoclinic space groups are possible with the simple lattice:

C_s^1 C_s^2 C_2^1 C_2^2 C_{2h}^1 C_{2h}^2 C_{2h}^4 C_{2h}^5

6. Elimination of Space Groups by Observed Reflections.

It is not possible to eliminate any of the above groups on account of observed reflections.

7. Probable Space Groups.

Since the external form of the crystal is such as to indicate that it belongs to the holohedral class, the space groups

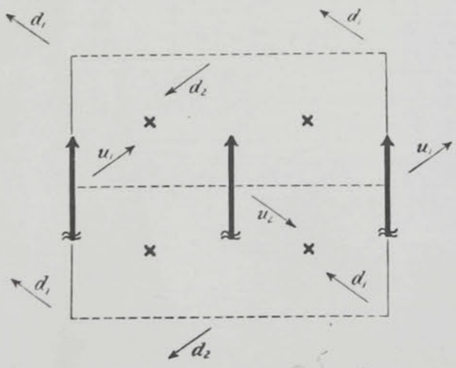
C_{2h}^1 C_{2h}^2 C_{2h}^4 C_{2h}^5

may be considered more probable. Also the failure to record reflections from the planes (010), (030), on special oscillation photographs would indicate that space groups

C_{2h}^2 C_{2h}^5 are more probable.

Due to crystalline imperfection, and the peculiar nature of the lattice ($a^* \gg b^*, c^*$), the indexing, even of the oscillation diagrams for $\{10\ell\}$ and $\{20\ell\}$ could not be done without ambiguity in many cases. Examination of Table VI will show that the absentee list contains all the planes of type $\{h\,o\,\ell\}$ ℓ odd. This would indicate that of the two remaining space groups, C_{2h}^5 is the more probable. It may be argued that there is also a fair number of planes $\{h\,o\,\ell\}$ ℓ even, in the absentee list. But on the other hand, all planes $\{h\,o\,\ell\}$ which are present, are of type ℓ even.

The question of the direction of the glide plane translation then arises. The group of absentee reflections just mentioned lends support to the choice of the c - axis as the direction of translation, but here we have rigorous proof, for the presence of reflections (102), (10$\bar{2}$), and (106) preclude the choice of the a - axis, or [101] directions, which are the other possibilities.



14 C_{2h}^5, Γ_m

Fig. 24.

Fig. 24 is Astbury and Yardley's diagrammatic representation of space group C_{2h}^{5}.

Since the glide plane translation is along the c - axis, Fig. 24 is to be regarded as a projection of the structural elements on the (100) face of the unit cell. The b - axis is in the direction of the heavy arrow, which represents a dyad screw axis. The molecules are represented by arrows, u or d for slanting up or down, from the cell face. Molecules whose symbols bear the suffix 2 are enantiomorphous to molecules with symbols bearing the suffix 1. The dotted line represents the glide plane of translation $\frac{c}{2}$ which relates the molecules d_1 and d_2, u_1 and u_2. The dyad screw axis of translation $\frac{b}{2}$ relates the molecules d_1 and u, d_2 and u_2.

8. The Molecule.

Assuming for the moment that C_{2h}^{5} is the correct space group, reference to Astbury and Yardley's tables shows that there are 4 asymmetric molecules per cell, or two molecules possessing centres of symmetry. We must then choose between association of the 8 chemical molecules (1) in pairs, to give 4 asymmetric molecules, (2) in fours, to give 2 molecules with the required symmetry. Indeed, since the largest number of asymmetric molecules allowed by the Γ_m lattice is 4, it is clear that there must be some form of molecular association, no matter what the correct space group may be. If it be assumed that association in pairs is more probable than association in fours, and that the chemical molecules are optically inactive in the structure, as they are in solution, reference to Plate XXVII of the appendix shows that there are 7 plane ring, and 10 puckered ring models to choose between in forming the asymmetric pairs. To treat the various possibilities thoroughly would require the development of a theory of pairing of point symmetry groups since this has not, to the writer's knowledge, yet been done. A theory of generalized pairing would probably be rather complicated, but it may perhaps be seen intuitively that (i) there will be an infinity of pairings which will be completely asymmetric, (ii) in certain special configurations, one or more of the sub-groups of the symmetry of the members may be preserved, (iii) in other special configurations the pair may possess higher symmetry than that of the members, and (iv) in still other special configurations, some of the symmetry operations of the members will be lost, but the pair will possess new symmetry operations. A knowledge of the relative orientation of the paired groups would therefore lead to a very considerable simplification of the problem. A thorough discussion of molecular models must also take account of the remaining hexa substitution models, since the absence of planes and centres of symmetry does not necessitate optical activity.

At present it seems wise to postpone these considerations till a much more detailed knowledge of the structure has been obtained.

9. Conclusions.

It would appear that, due to the large number of molecules in the unit cell, the complete structural analysis of this substance will be a problem of considerable difficulty. This difficulty is increased by the extreme thinness and marked imperfection of the crystals, which give photographs on which intensity estimations are treacherous. It was only after crystallizing out several lots that it was possible to obtain crystals which were sufficiently satisfactory for the above analysis.

On the other hand it is worthy of note that the peculiar form of the crystal may bear a significant relation to its internal structure, and it is quite possible that there may be an advantage in this respect which will counterbalance the experimental difficulties introduced by the habit. The analysis was pushed no farther because the information which was obtained indicated that there was little relation between the inactive inositol and the other crystals, l - inositol, quebrachitol and quercitol, the first two of which had already been partly analysed, and appeared to have a simpler structure. At present it would seem that the most hopeful procedure with regard to inactive inositol would be to obtain and conduct an x-ray examination of the other inactive isomers, and as has been stated in Section II, § 3 (Identification of inactive inositol), this project is now under way.

Laevo Inositol

1. Choice of Axes. Axial Rotation Photographs.

Laevo Inositol forms nearly ideal crystals for rotation photographs. They are of nearly uniform dimensions and exhibit good reflecting faces in the principal zones. The faces of the [001] zone are particularly prominent. Rough photographs were first taken with a large crystal which had been used for the goniometric observations, in order to identify the rotation photographs later obtained with a small crystal, which gave much more accurate patterns, but whose faces could not at first be recognized. During the first rough analysis, it was discovered that the crystal was truly monoclinic, and not triclinic with an approach to monoclinic symmetry, as the goniometric analysis had indicated (Section II, § 3, 1 - inositol). Examination of the characteristic crystal forms in the light of this information made it possible at once to assign the crystal to the sphenoidal class of monoclinic symmetry. A sufficient number of rough photographs was taken to enable the most important axes (shortest translations) to be chosen as a and c axes.

Consideration of the geometry of monoclinic reciprocal axes will make it clear that:-

(i) By rotation about any axis $[h\,o\,\ell]$, a photograph will be obtained on which:

(a) On the equator, 2 spots for every plane for which $k = o$ will be superimposed, and 4 spots for every plane for which $k \neq o$ will be superimposed.

(b) On the other layer lines, there will be single spots for every plane for which $k = o$, and 2 superimposed spots for every plane for which $k \neq o$.

(ii) By rotation about the axis [010] a photograph will be

Furthermore, if the crystal structure possesses monoclinic symmetry (as distinct from a merely geometrically monoclinic lattice), each spot of a doublet or quadruplet will be of the same intensity, which again is easily observed on a missetting photograph. This forms a particularly powerful method of assigning the true symmetry of a crystal, if a careful examination be made, since small structural variations always produce relatively much larger intensity variations in the reflections from certain planes, and a very high degree of pseudo symmetry would have to be possessed by the crystal in order that it should escape notice.

L - Inositol may be given as an example of the application of this method. Fig 25 was obtained with the [010] axis misset. The numbers of any pair can always be picked out if the missetting is not too great, because of the fact that they must always be equi-distant from the centre of the photograph. For l - inositol this conclusion was corroborated by a comparison of photographs about the [011] and [$0\bar{1}1$] axes, which proved to be identical, as should be the case. (Fig. 25.)

The b - axis photograph has been used as an example of the Bernal method in Section IV, § 7. Figs. 26 and 27 are the a- and c - axis rotation photographs.

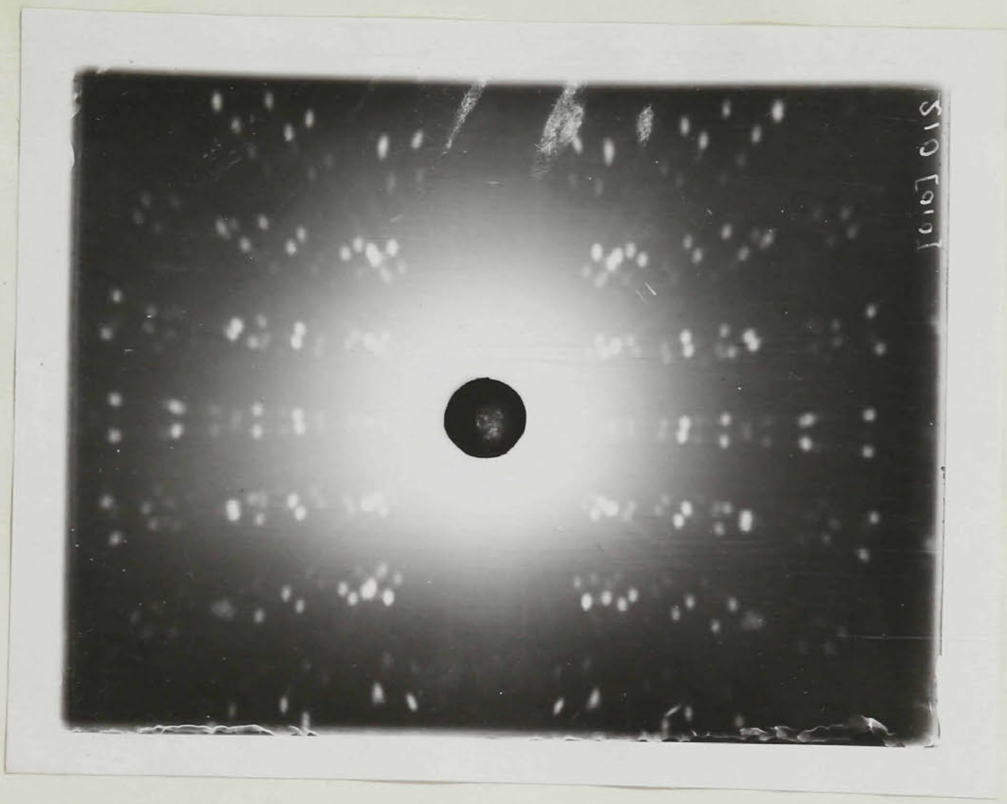


Fig. 25. (No. 210) [010] misset.

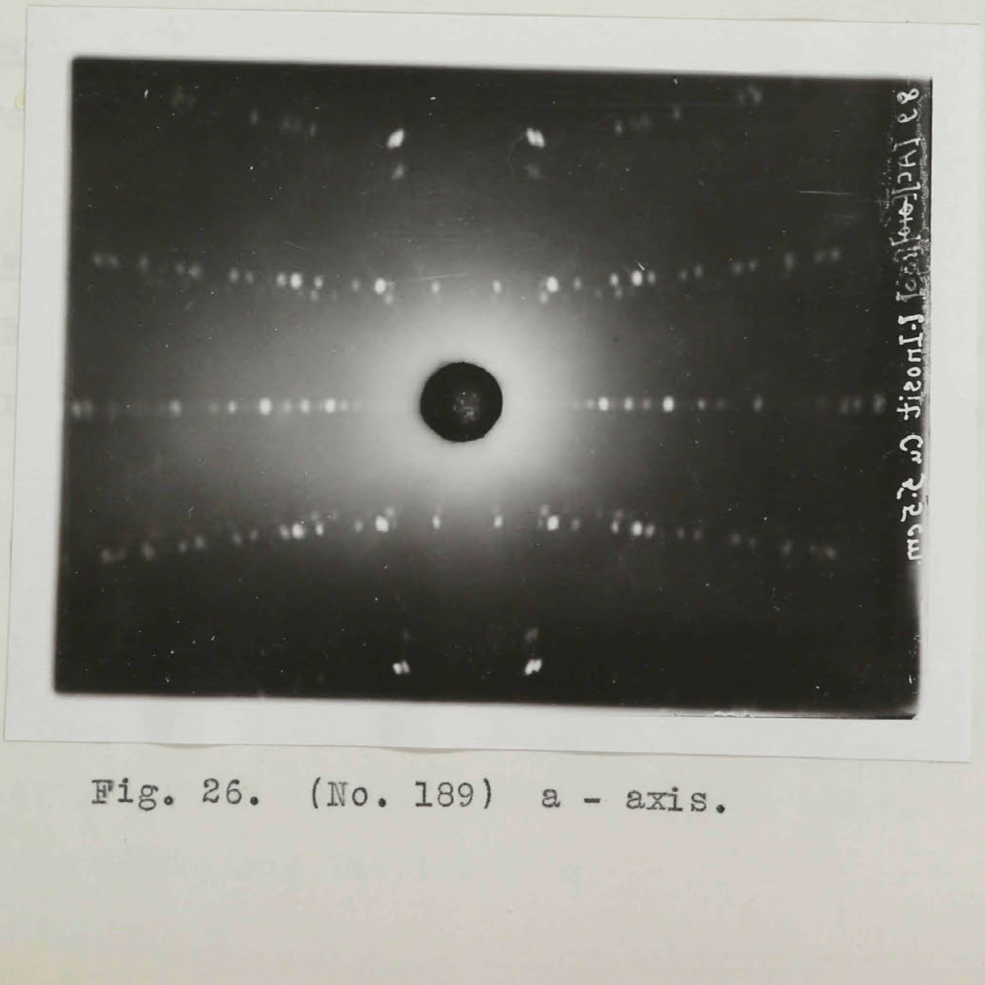


Fig. 26. (No. 189) a - axis.

Fig. 27. (No. 190) c - axis.

2. Dimensions of Unit Cell. Calculation of Density.

For data, see page 64.

3. Observed and Absentee Reflections.

The data in Table VIII were obtained from the indexing of the axial rotation diagrams, and from oscillation diagrams used in a search for reflections from (010), (030), (050).

Table VII

Observed (h0l)	Observed (h1l)	Observed (h2l)	Observed (h3l)	Observed (h4l)
100	110	020	130	040
001	$11\bar{1}$	120	031	$04\bar{1}$
101	111	021	$\bar{1}31$	$04\bar{2}$
$20\bar{1}$	$21\bar{1}$	$12\bar{1}$	131	$14\bar{1}$
$10\bar{2}$	011	121	032	$14\bar{2}$
$\bar{1}01$	012	022	230	$24\bar{2}$
$\bar{1}03$	211	$\bar{2}21$	231	$24\bar{3}$
	$\bar{1}13$	220	$23\bar{2}$	
		221	$33\bar{3}$	
		$\bar{1}23$	$33\bar{4}$	
		$32\bar{3}$	$03\bar{3}$	
200 201	010 210 013		030	050
Absent	Absent	Absent	Absent	Absent

4. Type of Lattice.

Rough estimations of axial lengths from photographs obtained by rotation about the [011], [10$\bar{1}$], [110], [11$\bar{1}$] axes precluded the possibility of face or body centring. This conclusion was found to be supported by the data of Table VIII ~~IX~~. The crystal therefore possesses the simple monoclinic lattice Γ m.

Table VIII

(k+l)odd (0kl)	(h+l)odd (h0l)	(h+k)odd (hk0)	(h+k+l)odd (hkl)	
001	100	100	100	$14\bar{2}$
012	001	120	001	$24\bar{3}$
021	$20\bar{1}$	230	$20\bar{1}$	
$04\bar{1}$	$10\bar{2}$		$10\bar{2}$	
			$11\bar{1}$	∴
			111	cell not
			~~101~~	body centred
∴	∴	∴	012	
(100) face not centred	(010) face not centred.	(001) face not centred.	$\bar{1}13$	
			120	
			021	
			$\bar{2}21$	
			221	
			$\bar{1}31$	
			131	
			032	
			230	
			$23\bar{2}$	
			$33\bar{3}$	
			$04\bar{1}$	

5. Possible Space Groups.

In view of the fact that the habit of the crystal is very definitely sphenoidal, and that the substance is optically active in solution, it was concluded that the possible space groups are:

$$C_2^1 \quad C_2^2$$

6. Elimination of Space Groups by Observed Reflections.

If reflections can be observed from the planes (o k o) when k is odd, the space group C_2^2 can be eliminated. Reference to Table VIII shows that the special search for reflections of this type was not successful. Both space groups therefore remain possible.

7. Probable Space Groups.

In view of the failure to record reflections from (010), (030), (050) under conditions such that all would have recorded unless extremely weak, it may be concluded that the space group C_2^2 is much more probable than C_2'.

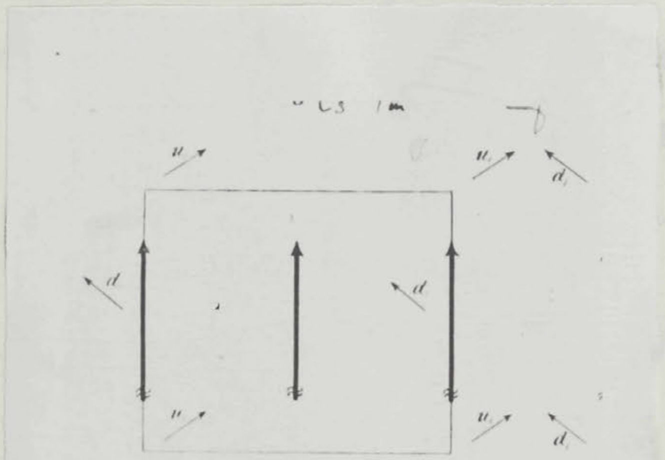
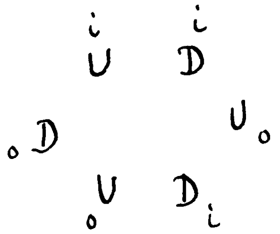


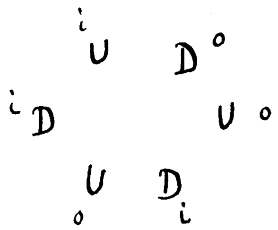
Fig. 28.

The diagrammatic representation of the space group C_2^2 is given in Fig. 28. It may conveniently be regarded as the projection of the structure on either the (100) or (001) face of the unit cell. The [010] axis is vertical. There are 2 asymmetric molecules to the cell, and they are related by a dyad screw axis. The significance of the symbols is the same as is given in the description accompanying Fig. 24.

The Molecule.

The number, 2, of $C_6H_6(OH)_6$ groups calculated for the unit cell agrees with the 2 asymmetric molecules required by the space group C_2^2, which we may tentatively assume to be correct. The chemical molecule is therefore the structural unit, and it is asymmetric. Reference to Plate XXVII of the appendix shows at once that, if we limit ourselves to plane and puckered ring models, there is only one model which is asymmetric, and that it is a puckered ring model. Reference to Plate XIV then gives this model. In the notation of the appendix (see §1) it is represented by one of:





the choice depending on which of these is the laevo model. The test of this model will have to be made in a much more complete analysis of the structure than has been attempted here.

Conclusions.

The writer considers that the space group has been determined with a considerable degree of certainty. The question which then arises is: What is the orientation of the molecules in the unit cell? This problem divides itself into two parts, (i) what is the azimuthul orientation about the dyad screw axis? - and (ii) what is the inclination of the molecule to the same axis? It is seen that the first part of the problem may be simplified if we consider the projection of all scattering matter in the unit cell on its base. We then have a two dimensional problem, and the advantage of the presence of centres of symmetry. This structure is responsible for the reflections from planes of the type $\{h\ o\ \ell\}$. It is shown in the case of quercitol that the estimation of relative intensities of reflections from a considerable number of planes of this type gives data which may without great difficulty be used to find indications of what the orientation in question may be.

Quebrachitol

1. A preliminary X-ray examination of quebrachitol had already been made by Dr. A. L. Patterson[50)] with whom the writer has been collaborating. He had found:

$a = 6.60$ A.U.
$b = 7.15$
$c = 8.65$

Volume of unit cell : 408 A.U.^{3}
Number of molecules in unit cell : 2

(Note: Throughout the following discussion all planes have been referred to the true monoclinic axes.)

As the crystal had been assigned orthorhombic symmetry by the morphological observers (Section II, § 3, Quebrachitol), the data from the axial rotation diagrams had led Dr. Patterson to the choice of Q^{1}, Q^{2}, as the most probable space groups. The presence of only 2 chemical molecules in the unit cell then necessitated that the molecule should possess a digonal symmetry axis. As he has pointed out, this is only possible if the unique CH_3 group lies on the digonal axis, which, since it passes between diammetrically opposite pairs of carbon atoms of the six membered ring, places the CH_3 group in a position altogether at variance with the generally accepted ideas of stereochemistry. (Note: The digonal axes of the puckered ring models always pass between carbon atoms. Reference to Plate XXVI of the appendix shows that this is also the case in the only possibly optically active plane ring model for hexa substitution products.) Noticing then the significance of the different forms recorded in the crystallographic data, Dr. Patterson took a series of oscillation photographs about the (true monoclinic) b-axis, with the purpose of making a more detailed examination. He was not however able to continue at the time, and the writer toom up the problem and analyzed his photographs. A comparison of the intensities of the most prominent reflections, with the intensities of those reflections which should, in the case of orthorhombic symmetry, be equivalent, gave strong evidence for the truth of what had been suspected, i.e. that the symmetry of the structure was really monoclinic, and not orthorhombic.

Conspicuous examples, from the data of Table IX are:

Plane	Intensity Number
101	1
$10\bar{1}$	75
221	80
$22\bar{1}$	3

Choosing, then, a new crystal, a series of oscillation photographs about the (monoclinic) c-axis, using the cylindrical camera in order to record reflections from the higher orders. This series was then analyzed, and the intensities estimated for all planes within the range Table IX gives the results. The method of estimating in-

Table IX

h0l	Intensity Number
100	57
102	90
$\bar{1}01$	75
$\bar{2}00$	75
202	15
201	17
101	1
$\bar{3}00$	25
$\bar{3}01$	25
$\bar{2}02$	25
$\bar{1}02$	25
302	12
203	11
303	6
401	6
$\bar{4}01$	3
402	1
$\bar{2}03$	25
103	10
304	6
$\bar{4}02$	2
$\bar{2}04$	3
$\bar{3}04$	3
$\bar{4}04$	3

h1l	
$11\bar{3}$	110
$21\bar{1}$	17
$21\bar{2}$	17
$\bar{3}1\bar{1}$	17
$\bar{2}1\bar{3}$	12
$\bar{3}1\bar{2}$	4
310	6
$31\bar{1}$	5
$\bar{2}1\bar{1}$	35
$\bar{2}1\bar{2}$	35
210	21
$21\bar{4}$	12
$\bar{3}1\bar{3}$	6
$\bar{1}1\bar{3}$	6
$\bar{1}1\bar{2}$	80
$11\bar{2}$	80
$11\bar{1}$	80
110	45
$11\bar{4}$	60
$31\bar{4}$	6
$\bar{2}1\bar{4}$	6
$\bar{1}1\bar{4}$	8
$\bar{3}1\bar{4}$	6
$\bar{4}1\bar{3}$	6
$41\bar{2}$	6
$\bar{4}1\bar{1}$	6
$41\bar{3}$	3
$41\bar{1}$	1
$\bar{4}1\bar{2}$	1
211	40

h1l (cont'd)	Intens. No.
$01\bar{3}$	25
$\bar{1}10$	55
$\bar{2}10$	25
311	14
$\bar{2}11$	25
312	6
$\bar{3}10$	6
$\bar{4}1\bar{4}$	2
$\bar{1}11$	80
212	35
$\bar{2}12$	35
111	17
213	14
313	10
413	10
$\bar{4}12$	10
$\bar{4}13$	3
$\bar{4}11$	3
$\bar{4}10$	3
112	90
$\bar{1}12$	90
314	10
012	6
$11\bar{4}$	4
$\bar{1}13$	120
$01\bar{1}$	120
$11\bar{4}$	30
113	6

h2l	
320	37
$\bar{3}2\bar{2}$	17
$32\bar{1}$	17
$22\bar{4}$	12
$\bar{4}20$	5
$\bar{4}2\bar{1}$	5
$32\bar{2}$	3
$32\bar{3}$	4
$\bar{3}2\bar{3}$	1
$12\bar{4}$	35
$\bar{2}2\bar{3}$	17
$22\bar{2}$	12
$22\bar{3}$	13
$\bar{1}2\bar{4}$	11
$42\bar{3}$	6
$\bar{4}2\bar{3}$	6
$\bar{3}2\bar{1}$	6

h2l (cont'd)	Intensity Number
$\bar{3}2\bar{4}$	3
$\bar{2}2\bar{1}$	80
$12\bar{3}$	12
$\bar{2}2\bar{2}$	12
$\bar{1}2\bar{3}$	11
$22\bar{4}$	3
220	2
$12\bar{2}$	40
$02\bar{4}$	14
$12\bar{1}$	14
$\bar{3}20$	35
$\bar{1}21$	35
120	14
$\bar{1}20$	14
$02\bar{3}$	17
321	4
221	90
$02\bar{2}$	105
222	35
322	35
321	10
$\bar{3}23$	4
323	4
$\bar{3}22$	4
020	120
$02\bar{1}$	120
223	30
121	12
$\bar{2}23$	12
$\bar{2}22$	12
$\bar{1}21$	12
$\bar{3}24$	3

h3l	
$33\bar{3}$	12
$\bar{4}30$	5
$23\bar{4}$	3
$\bar{3}3\bar{3}$	4
$\bar{3}3\bar{4}$	1
$33\bar{4}$	1
$\bar{3}3\bar{1}$	17
$23\bar{3}$	9
$33\bar{2}$	6
$\bar{2}3\bar{4}$	4
$\bar{3}30$	4
$\bar{3}3\bar{2}$	3
$\bar{2}3\bar{2}$	25
230	12
$13\bar{4}$	11
$\bar{1}3\bar{4}$	6
$\bar{2}3\bar{3}$	6
$\bar{2}3\bar{1}$	4

h3l (cont'd)	Intensity Number
$23\bar{2}$	3
$23\bar{1}$	3
$13\bar{2}$	55
$\bar{2}30$	13
$03\bar{4}$	10
130	17
$\bar{1}30$	17
$\bar{1}3\bar{1}$	17
$\bar{1}3\bar{2}$	14
$03\bar{3}$	14
$\bar{1}3\bar{1}$	10
$03\bar{2}$	35
330	4
232	12
$13\bar{3}$	12
$\bar{1}3\bar{3}$	12
$03\bar{1}$	6
231	6
331	6
$\bar{2}31$	6
$\bar{3}31$	6
$\bar{3}32$	6
332	3

h4l	
$\bar{3}4\bar{4}$	3
$\bar{2}4\bar{4}$	12
$24\bar{4}$	1
$\bar{1}4\bar{4}$	10
$\bar{2}4\bar{3}$	6
$\bar{2}4\bar{2}$	6
$14\bar{4}$	3
$24\bar{2}$	1
$\bar{1}4\bar{3}$	6
$14\bar{2}$	2
$04\bar{4}$	2
$\bar{1}4\bar{1}$	8
$04\bar{3}$	10
140	7
$\bar{1}40$	8
$14\bar{1}$	3
$04\bar{1}$	6
040	6
$04\bar{2}$	6
$24\bar{3}$	3

tensities was rather different from that mentioned in Section III 2. One of the photographs was chosen as a standard of comparison and the intensities of certain spots ranging from the highest to the lowest, were assigned arbitrary values. The intensity of any other spot was then assigned a value according to where, by visual comparison , it seemed to come in the scale. The values recorded might then better be termed intensity numbers. This process was carried through twice, and the correlation of the results showed that it was a fairly satisfactory method. In any series such as this, comparison of photographs is unreliable, unless the tube is running steadily. In this series the tube, though not controlled automatically, happened to be running in a stable condition, and the reliability of the comparison was checked by a comparison of spots common to successive photographs due to overlapping of the range of oscillation.

2. Possible Space Groups.

An examination of Table IX will show that it contains record of reflections from about:

92 planes of type $(h\ k\ \ell)$ when $(h + k + \ell)$ is odd
100 " " " " " $(k + \ell)$ " "
92 " " " " " $(h + k)$ " "
92 " " " " " $(h + \ell)$ " "

This precludes all monoclinic space groups based on the lattice Γ_m except:

C_s^1 C_2^1 C_2^2 C_{2h}^1 C_{2h}^2

3. Probable Space Groups

Examination of a number of crystals showed that the forms occurring indicated that quebrachitol belongs to the sphenoidal class C_2. This eliminates all except C_2^1 and C_2^2, and of these C_2^2 may be chosen as the most probable on account of the absence of (010) and (030) from the oscillation photographs. This space group has been described under ℓ-inositol. The remarks with regard to molecular symmetry also apply, and will not be repeated here.

4. Identity of Methyl-ℓ-inositol from Different Sources

Quebrachitol is the name given to the methyl-ℓ-inositol which is extracted from the latex of Hevea brasiliensis. The methyl-ℓ-inositol which he obtained from the leaves of Heterodendron oleoefolium was identified by Petrie with Quebrachitol. The possibility of a difference has been mentioned in Section II, § 3, Quebrachitol, and this has been tested, using specimens kindly sent by Dr. Anderson. A small crystal, of suitable size for X-ray examination, was found, and several photographs taken. They showed immediately that the lattice is the same as that of quebrachitol, as is perhaps to be expected from the agreement of the Anderson and Graham axial ratios. Furthermore a visual comparison of intensities showed that, as far as could be judged they were also the same as those of quebrachitol. It was therefore concluded that if there be any difference, it must be exceedingly small.

6. Conclusions.

The correct symmetry having been determined, and the space group having been determined with a high degree of probability, it appears that in these respects it is the same as *l*-inositol. The remarks with regard to a further investigation of the structure of *l*-inositol will therefore apply equally well to quebrachitol.

Petrie's identification of methyl-*l*-inositol from Heterodendron obeoefolium with quebrachitol has been corroborated with x-ray evidence.

Quercitol.

(1) Choice of Axes. Rotation Photographs.

Since there is complete crystallographic data on quercitol (Section II, 3, Quercitol), there was no necessity for making a choice of axes. Figs. 29, 30, and 31 are the axial rotation photographs. Fig. 32, which was obtained with the ($0\bar{1}1$) face misset about 4^{o}, and the (0 1 1) face correctly set, illustrates the monoclinic symmetry (see Section V, ℓ-Inositol)

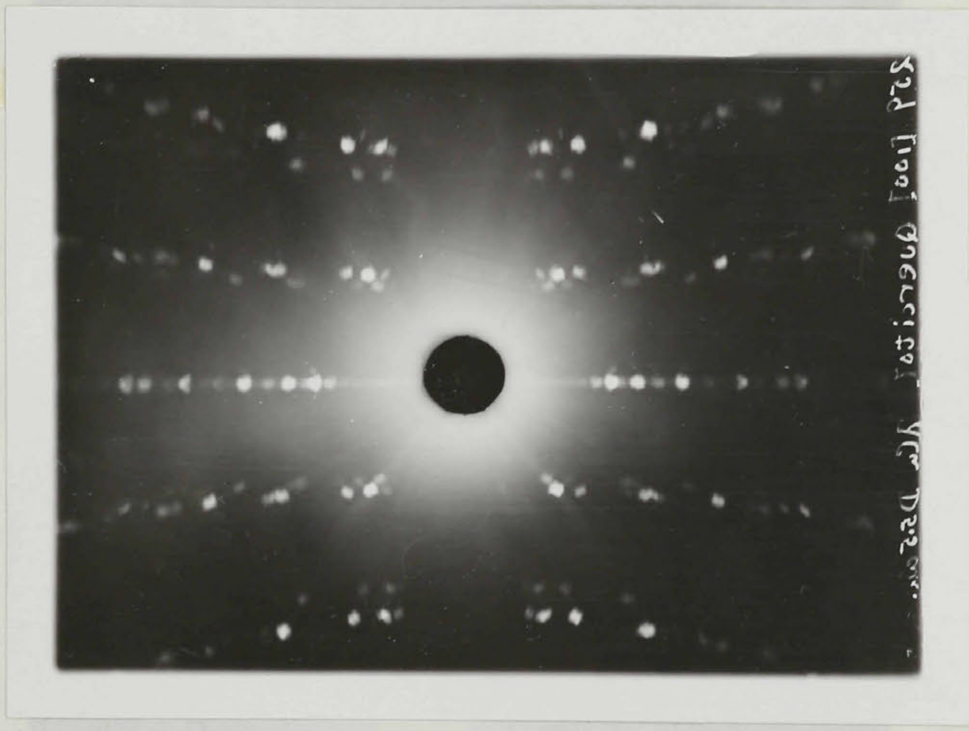


Fig. 29. (No. 259) a-axis.

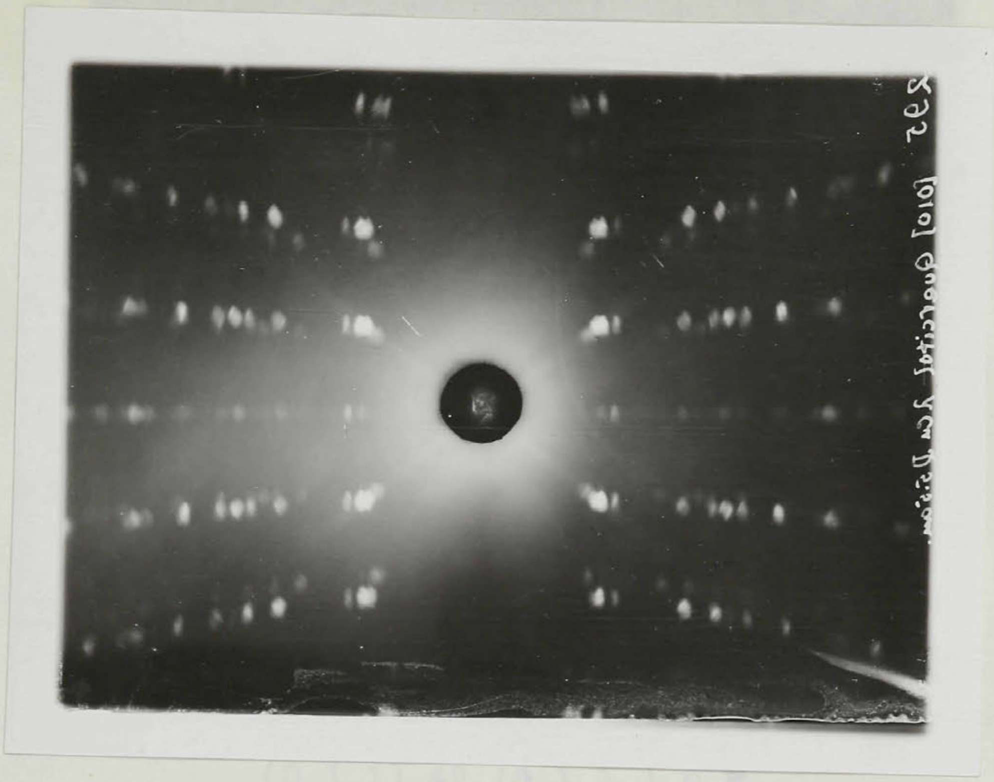


Fig. 30. (no. 295) b-axis.

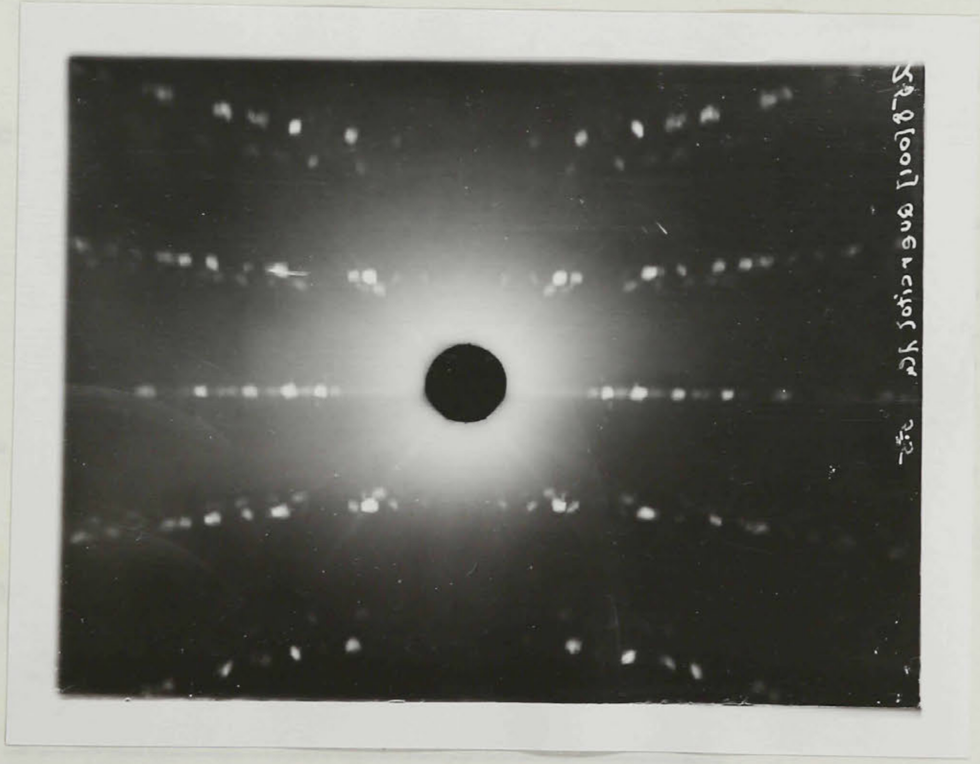


Fig. 31 (No. 258) c-axis.

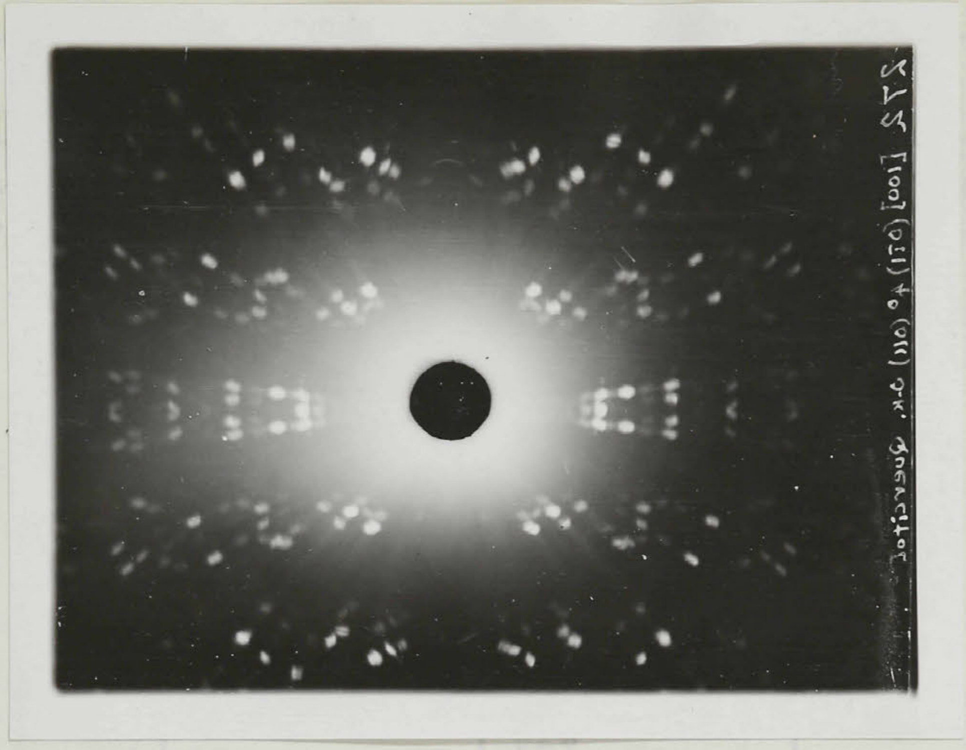


Fig. 32 (no. 272) a-axis

(0 $\bar{1}$ 1) 4° (0 1 1) O.K.

(2.) Dimensions of Unit Cell. Calculation of Density.

From analysis of the axial rotation photographs the following data was obtained:

a = 6.83 A.U.	a^* = 0.242	ζ_a = 0.225
b = 8.53	b^* = 0.181	ζ_b = 0.181
c = 6.45	c^* = 0.256	ζ_c = 0.239

β = 110° 57' (Groth) β^* = 69° 3' a:b:c: = 0.802:1:0.756

cf. Groth " = 0.8058.1:0.7655

Volume of Unit Cell = 351 A.U.^{3}

(3.) Observed and Absentee Reflections.

Table X contains the data obtained from the indexing of the axial rotation diagrams, and of oscillation diagrams taken in a search for the reflections from (0 1 0) and (0 3 0).

Table X

Observed (h0l)	Observed (h1l)	Observed (h2l)	Observed (h3l)
$\bar{1}01$	110	120	$\bar{1}31$
101	011	021	131
002	$\bar{1}11$	$\bar{1}21$	$03\bar{1}$
201	111	121	$\bar{2}32$
102	$\bar{2}11$	$\bar{2}21$	
200	012	022	
001	$\bar{2}12$	$\bar{2}22$	
$20\bar{2}$	211	221	
	112	122	
	210	$\bar{3}21$	
	$\bar{2}13$	020	
		220	
100 $\bar{2}01$ $\bar{1}02$	010 $\bar{1}12$	$12\bar{2}$	030
Absent	Absent	Absent	Absent

(4.) Space Lattice.

The observation of planes as recorded in Table XI precludes the possibility of face or body centering, and the lattice is therefore Γ_m .

Table XI

(k+l)odd (0kl)	(h+l)odd (h0l)	(h+k)odd (hk0)	(h+k+l)odd (hkl)
001 021	201 102 001	210 120	001 021 201 102 210 120 111 $\bar{2}12$ $\bar{2}21$ 221 122 $\bar{1}31$ 131 $\bar{2}32$
∴ (100) face not centred.	∴ (010) face not centred	∴ (001) face not centred	∴ cell not body centred

(5) Possible Space Groups.

Since the crystal is known to belong to the sphenoidal class, and has been shown above to possess the lattice Γ_m, the only possible space groups are C_2^1 and C_2^2. It is not possible to eliminate C_2^2 from the observed reflections.

(6) Probable Space Groups.

As in the case of *l*-inositol and quebrachitol, the absence of reflections from (0 1 0) and (0 3 0) on the oscillation photographs makes C_2^2 the more probable space group. The description of this space group, and the discussion of possible molecular symmetry for ℓ -Inositol again apply, and will not be repeated here. Reference to the appendix will show that there are a considerable number of asymmetric models for Quercitol.

(7) <u>Molecular Orientation.</u>

Reference to Fig. 28 shows that if the structure be projected on the (0 1 0) cell face, a diagram such as Fig. 33 will be obtained.

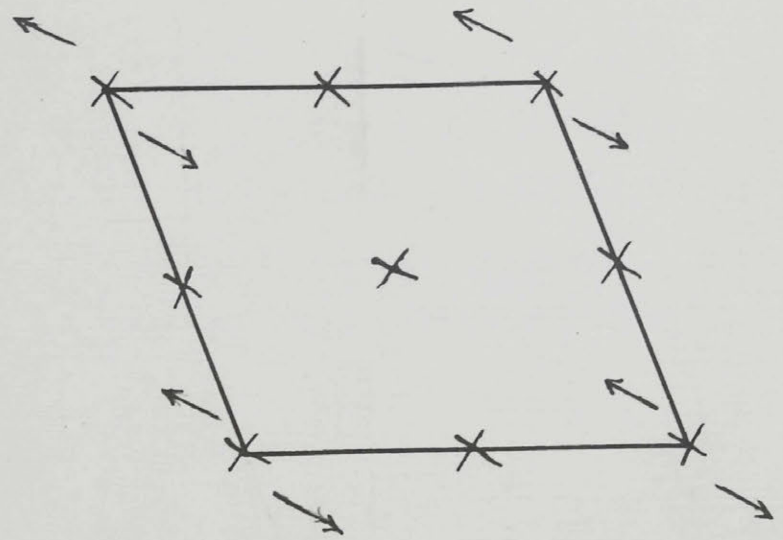


Fig. 33

Fig. 33

This is a two dimensional space group, which possesses centres of symmetry at the points indicated by crosses. It is seen that if the molecules related by the dyad screw axis in the quercitol crystal are each centered somewhat away from the axis, the projection of scattering matter on the (0 1 0) cell face may be represented somewhat as in the above diagram. There would then be expected a subsidiary periodicity along some axis (h 0 ℓ), which might be detected by the application of the enhancement principle analysis to the planes of type (h o ℓ). If therefore, such a periodicity can be detected in some such axis, it would indicate firstly, that there is a departure of the molecules from the axis, and secondly, the direction of the departure.

In order that this analysis might be carried out, a series of oscillation photographs about the b-axis was taken, and the results of the indexing and intensity estimations of the (h o ℓ) planes within the range $\rho < 1{\cdot}7$ are presented in Table XII. The K_α to K_β intensity ratio for copper was used in setting up the scale of intensities, and the reflection from (1 0 0) was taken as a standard of reference. Comparison of spots common to successive photographs showed that no serious error was introduced in assuming all exposures equivalent.

Table XII

(h o l)	Intensity	(h o l)	Intensity	(h o l)	Intensity	(h o l)	Intensity
100	1	$\bar{7}02$	0.5	403	0	$\bar{6}06$	0.5
200	5	$\bar{6}02$	0.8	503	2	$\bar{5}06$	4
300	1	$\bar{5}02$	1.5	$\bar{7}04$	0.5	$\bar{4}06$	0
400	5	$\bar{4}02$	1.2	$\bar{6}04$	0	$\bar{3}06$	0
500	0.5	$\bar{3}02$	6	$\bar{5}04$	0.1	$\bar{2}06$	2
600	2.5	$\bar{2}02$	3	$\bar{4}04$	1	$\bar{1}06$	2.5
700	2.5	$\bar{1}02$	1	$\bar{3}04$	2	006	0
~~8~~		002	2	$\bar{2}04$	0.5	106	0.5
$\bar{7}01$	0.5	102	15	$\bar{1}04$	1	206	0.7
$\bar{6}01$	0	202	0	004	1	$\bar{5}07$	0.5
$\bar{5}01$	0	302	0.2	104	0	$\bar{2}07$	3
$\bar{4}01$	0	402	0	204	0		
$\bar{3}01$	9	502	1	304	0		
$\bar{2}01$	1.1	602	0	404	0		
$\bar{1}01$	5	$\bar{6}03$	1	$\bar{7}05$	3		
001	3	$\bar{5}03$	10	$\bar{6}05$	0.4		
101	3	$\bar{4}03$	0.6	$\bar{5}05$	0.2		
201	6	$\bar{3}03$	12	$\bar{4}05$	3		
301	2	$\bar{2}03$	0.6	$\bar{3}05$	1		
401	1	$\bar{1}03$	8	$\bar{2}05$	0		
501	0.4	003	10	$\bar{1}05$	1		
601	2	103	11	005	0.5		
		203	7	105	0		
		303	0	205	0		
				305	0.5		

(100) taken as standard of reference

The enhancement analysis was then applied for the axes [1 0 0], [2 0 1], [1 0 1], [1 0 2], [0 0 1], $[\bar{1}\ 0\ 2]$, $[\bar{1}\ 0\ 1]$, $[\bar{2}\ 0\ 1]$. The results for the axes containing the index 2 were irregular, and by a judicious choice of minima, could be made to reveal several different periodicities. They have therefore been excluded from the evidence.

The axes [1 0 1] and $[\bar{1}\ 0\ 1]$ were taken as a pair, and the indices changed in accordance with the equations:

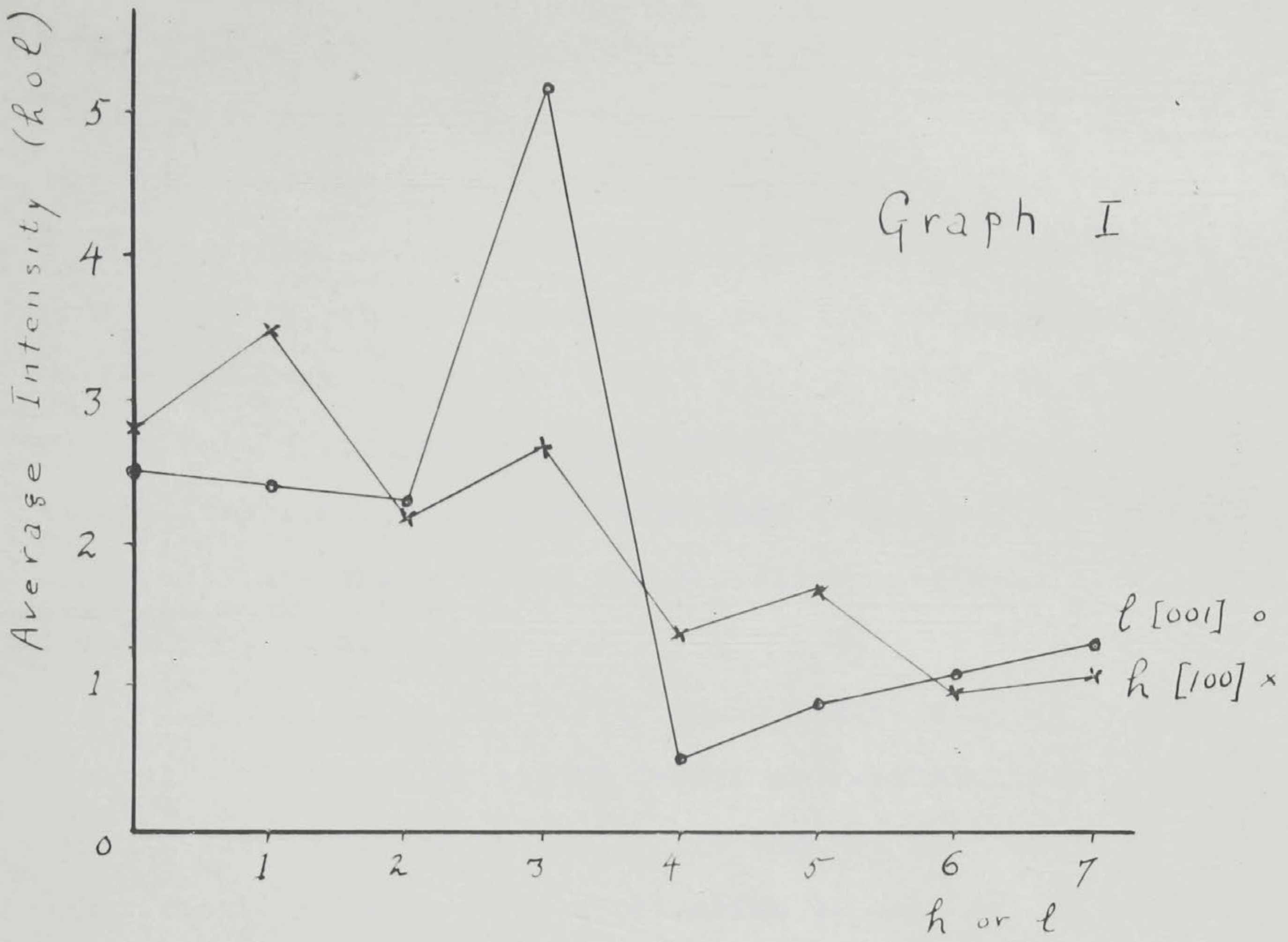
$[1\ 0\ 1]$, : $H = \frac{h+l}{2}$

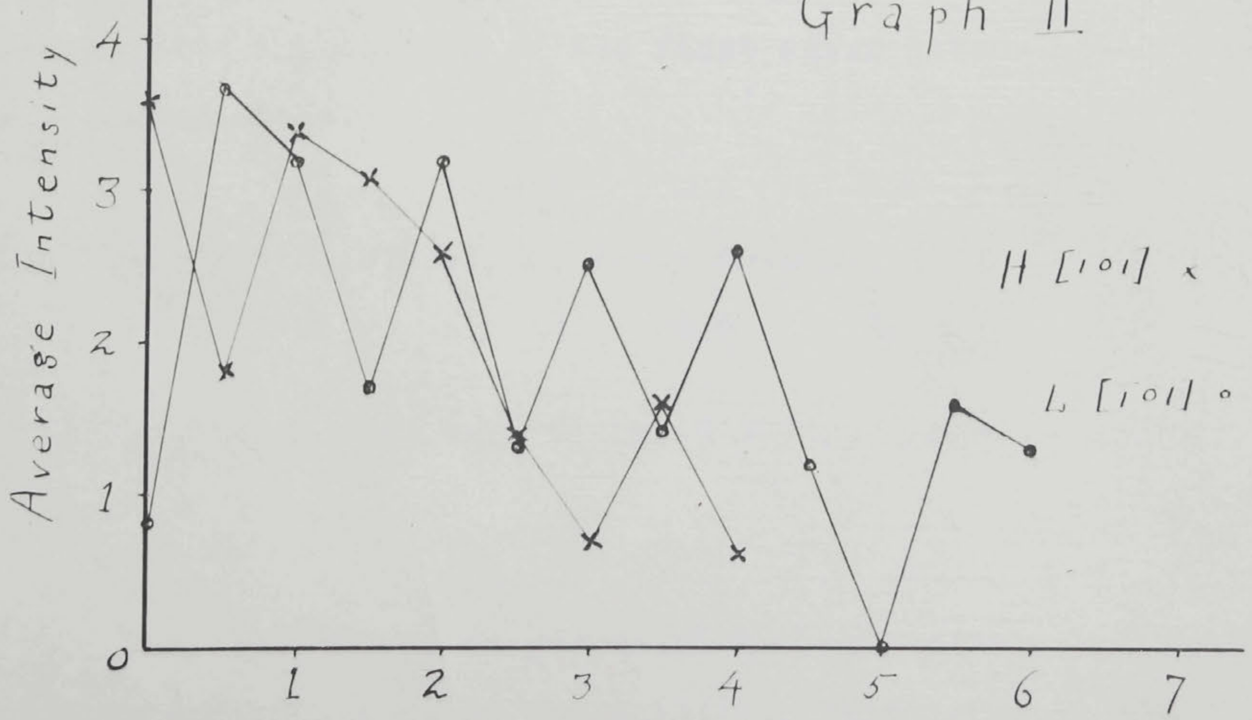
$[\bar{1}\ 0\ 1]$: $K = \frac{h-l}{2}$

The average values of the intensities were plotted for successive values of the axial index. The labor of calculation was much reduced by plotting the intensities at the intersection points of the same $a^* c^*$ net, which had been used in plotting the theoretical oscillation diagrams. For each axis there is a family of row lines, each bearing the points representing planes with the same axial index, so that it was only necessary to take the averages of series of values plotted along lines. The results for the $[1\ 0\ 0]$, $[1\ 0\ 1]$, $[0\ 0\ 1]$, and $[\bar{1}\ 0\ 1]$ axes are shown on Graphs I and II. An examination of these reveals a marked periodicity along both the $[1\ 0\ 0]$ and the $[\bar{1}\ 0\ 1]$ axes. The subsidiary periodicities along these axes were calculated to be:

$[1\ 0\ 0]$	3.4 A.U.
$[\bar{1}\ 0\ 1]$	4.4 A.U.

The acute angle between these axes is 35° (approx.), and it might well be expected that if the main body of the projection of the molecules lies between these axes, that a periodicity would appear on both. In such a case the difference of the estimated periodicities might be thought to be accounted for by a closer approach of the main length of the molecular projection to the $[\bar{1}\ 0\ 1]$ axis. Some further calculations which have not been presented here have however led the writer to regard this consideration as a speculation rather than a deduction, and opinion is for the present reserved


Graph I
Average Intensity (h o l)
0
1
2
3
4
5
1
2
3
4
5
6
7
h or l
l [001] o
h [100] ×


Graph II
Average Intensity (H o L)
0
1
2
3
4
1
2
3
4
5
6
7
H [101] ×
L [101] o

until a more detailed examination has been made. Such an examination might well be commenced by a Fourier analysis of the distribution of scattering matter between several of the (h o ℓ) planes, and in this connection it is interesting to note, firstly, that the absence of all the higher orders of reflection from the plane (1 0 1) would at once indicate an approximately sinusoidal distribution, and secondly, that the intensities 1,5,1,5, of the first four orders of (1 0 0) tend to corroborate the evidence for subsidiary periodicity along the [1 0 0] axis.

In conclusion the writer would record a doubt as to the value of the polarization factor correction of section III § 2 in such analyses as these. It has not been used in the enhancement analysis. Its application to some of the above intensity data appears to throw a weight upon the higher orders of reflection which seems hardly warranted in view of the fact that they refer only to the detail of the structure. For example, the intensities of the first seven orders of (1 0 0) were estimated as:

1 5 1 5 0.5 2.5 2.5

With the correction applied, these become:

1 15 4 30 4.5 25 20

A final decision will have to await further investigation.

(8). Conclusions.

The space group of quercitol has been determined as C_2^2 with a high degree of probability. This is again the same as for ℓ-inositol and quebrachitol.

Furthermore, the application of the enhancement principle analysis to the projection of the structure on the (0 1 0) plane has led to a definite indication that the molecules are centred away from the dyad screw axis, and that the direction of departure lies between the $(\bar{1}\ 0\ 0)$ and $(\bar{1}\ 0\ 1)$

Table XIII Summary of Cell Data

Substance	Formula	Symmetry	Density	Lattice	a-axis	b-axis	c-axis	β	Cell Volume	Space Group	Molecules per Cell	Remarks.
Inactive Inositol	$C_6H_6(OH)_6$	Monoclinic Bisphenoidal	gm cc^{-1} 1.61	Γ_m	A.U. 6.64	A.U. 12.0	A.U 19.7	107°	A.U.^{3} 1490	C_{2h}^5	8	Chem. Molecules: In pairs, asymmetric In fours, centro symmetric
Laevo Inositol	$C_6H_6(OH)_6$	Monoclinic Sphenoidal	1.62	Γ_m	6.17	9.11	6.83	106°36'	368	C_2^2	2	Molecule asymmetric
Quebrachitol	$C_6H_6(OH)_5OCH_3$	Monoclinic Sphenoidal	1.57	Γ_m	6.60	7.15	8.65	90°	408	C_2^2	2	Molecule asymmetric
Quercitol	$C_6H_7(OH)_5$	Monoclinic Sphenoidal	1.55	Γ_m	6.83	8.53	6.45	110°57'	351	C_2^2	2	Molecule asymmetric

GENERAL REMARKS.

The cell data resulting from the X-ray investigation of the four crystals is summarized in Table XIII in such a way as to facilitate comparison. It is at once seen that while *l*-inositol, quebrachitol, and quercitol show certain marked similarities, inactive inositol is in a number of important respedts considerably different. Perhaps the most striking difference is the presence in the inactive isomer of molecular association, for this is probably a more fundamental characteristic than the number of molecules in the unit cell, which might be expected to be larger if the molecule possessed properties tending to association. The four crystals possess a common property in their densities, which are quite close in value. This is very interesting, for it indicates that the mode of atomic packing in all the crystals is similar. If the recorded value for Tanret's inactive inositol be correct, then there are at least three inactive inositols, of densities 1.61, 1.66, 1.75, and considering the evidence of this data alone, it might be expected that the packing structure of the inactive inositol of this analysis approaches most closely that of the optically active substances.

With regard to the three latter substances, perhaps the most striking similarity is their possession of the same space group, also the dimensions of the unit cells are fairly close. It is to be noted in the latter connection that there is no regular variation in the axial lengths, and indeed none is to be expected with asymmetric molecules possessing a dyad screw axis relation. It has been found in the case of quercitol that the obtaining of more definite information with regard to the structure is not so difficult as might at first have been thought.

Hence, although the evidence for orientation has not been sufficiently corroborated to prove beyond question the success of the enhancement principle analysis in this case, it certainly has provided reason to hope that future investigations may yield valuable information with regard to the behaviour of the hydroxy substitution products of cyclohexane, in the solid state.

References

1) Jahresbericht 1829, 1831, 1832.

2) Voorstel tot Uitbreiding der Structuurformules in de Ruimte, Brochure, 1874.

3) Bull. Soc. Chim. 1874, 22, 337.

4) See, for example, W. H. and W. L. Bragg, "X-rays and Crystal Structure"

5) W. H. and W. L. Bragg, Proc. Roy. Soc. A89, 277, 1913

6) J. C. McLennan and W. G. Plummer, Nature, 122, 571 (1928)

7) H. Mark, Berichte, 57, 1820, (1924)

8) Ibid.

9) W. H. George, Proc. Roy. Soc., A113, 585 (1927)

10) H. Mark and W. Noethling, Zeit. f. Krist. 66, 435, (1927)

11) Ibid.

12) Gerstaecker, Moeller, and Reis, Zeit. f. Krist., 66, 355, (1927)

13) I. E. Knaggs, Nature, 121, 616, (1928)

14) O. Hassel and H. Mark, Z. f. Phys. 25, 317, (1924)

15) J. D. Bernal, Proc. Roy. Soc. A106, 749 (1924)

16) Kekule, "Chemie der Benzolderivate" 1867

17) See, for example, Graebe, Ber. 35, 526 (1902)
W. Barlow and W. Pope, Trans. Chem. Soc., 89, II, 1675 (1906)
Proc. Chem. Soc., 22, 264 (1906)
G. Jerusalem, Trans. Chem. Soc., 95, 1275 (1909)
H. E. Armstrong, R. T. Colgate, and E. H. Rodd, Proc. Roy. Soc. A90, 111, (1914)
R. Fraser, Trans. Chem. Soc. 121, 188, (1922)

18) Cohen, Organic Chemistry, ed. IV, Part II, p.440

19) Chem. Soc. Annual Reports XXI, p.92 (1924)

20) W. H. Bragg, Proc. Physical Soc. 34, 33 (1921)
Ibid. 35, 167 (1923)

21) E. G. Cox, Nature, 122, 401 (1928)
J. R. Katz, Z. f. Phys., 45, 97 (1927)
E. D. Eastman, J. Am. Chem. Soc., 46, 917 (1924)
B. Broome, Z. f. Krist., 62, 325, (1925)
B. Broome, Physik. Z., 24, 124, (1923)
P. Debye and P. Scherrer, Gött. Nachr., 16 (1916)

22) Hendricks and Bilicke, J. Am. Chem. Soc., 48, 3007 (1927)
Dickinson and Bilicke, Ibid., 50, 364 (1928)

23) J. M. Robertson, Proc. Roy. Soc. A118, 709 (1928)

24) K. Lonsdale, Proc. Roy. Soc. A123, 494 (1929)

25) K. Lonsdale, Phil. Mag., 6, 433, (1928)

26) K. Lonsdale, Proc. Leeds. Phil. Soc. Vol. I, Part III, p.346 (1929)
H. de Laszlo, J. Am. Chem. Soc., 50, 892 (1928)

27) K. Lonsdale, Trans. Faraday Soc. 25, 352 (1929)

28) E. V. Eastcott, J. Phy. Chem. XXXII, No.7, p.1094 (1928)

29) P. Karrer, Helv. Chim. Acta., 9, 116 (1926)

30) A. C. Lunn and J. K. Senior, J. Phys. Chem. XXXIII, No.7, p.1027 (1929)

31) P. Bedos, Comptes Rendus, 183, 750 (1926)

32) Godchot and P. Bedos, Bull. Soc. Chim, 37, 1451 (1925)
Ibid. 37, 1635 (1925)
Ibid. 39, 83 (1926)
Ibid. 39, 674 (1926)

33) J. Boeseken and A. Julius, Rec. trav. chim. P-B., 45, 489 (1926)

33A) Friedel, Bull. Soc. Chim. 3 5, 130 (1891)

34) J. D. Bernal, Proc. Roy. Soc., A113, 117 (1926)

35) W. T. Astbury and K. Yardley, Phil. Trans. Roy. Soc. A224, 221. 1924.

36) See, for example, W. L. Bragg and J. West, Z. f. Krist., 69 Bd., 1/2 Heft 119 (1928)

37) W. T. Astbury, Proc. Roy. Soc. A115, 640 (1927)
Ibid. A123, 575 (1929)
J. Sci. Instr. vi, 192 (1929)

38) S. B. Hendricks, Am. J. Sci., xiv, 273 (1927)

39) A. Bouwers, Z. f. Phys. Vol.14, 374 (1923)
Physica, Vol.3, 113 (1923)
" Vol.5, 8 (1925)
Dissertation Utrecht, (1924)

40) Buse, Physica, Vol. 2, 84 (1922)

41) W. T. Astbury, loc. cit. p.594 (1929)

42) Bishop, Phys. Rec., Vol. 28, 625 (1926)
Kirkpatrick, Ibid. Vol. 29, 632 (1927)

43) See, for example, A. E. H. Tutton, Proc. Roy. Soc. A118, 423 (1928)

44) W. H. and W. L. Bragg, "X-rays and Crystal Structure," 5th ed. p.233.

45) J. M. Robertson, Proc. Roy. Soc. A118, 709 (1928)

46) W. H. Bragg, Nature, 121, 327 (1928)

47) Bragg, Zeit. f. Krist. 66, 22, 1927

48) See, for example Lonsdale, Proc. Roy. Soc. A123, 496 (1929)

49) Muller, Proc. Roy. Soc. A117, 30 (1927)
Piper, J. Sci. Instr., 6, 105 (1929)
Clay, Proc. Phys. Soc. Lond. 40, 221 (1928)

50) A. L. Patterson, "Application of X-rays to the Study of Organic Substances", McGill University Theses

APPENDIX.

Determination of the Isomers of the Hydroxy Substitution Products of Cyclohexane, on the Assumption (1) of a Puckered, (2) of a Plane Cyclohexane Ring.

Contents.

§ 1. Models.

§ 2. Note on rigor of the analysis.

§ 3. Method of analysis.

§ 4. Notation, Definitions, Propositions.

Plates I, II, The Skeletons and their symmetry.

(1) Analysis of the Puckered Ring.

Plate III. Mono-Substitution Forms.

" IV.) Di-Substitution Forms (ortho 1.2
" V.) (meta 1.3
" VI.) (para 1.4

" VII.) Tri-Substitution Forms (1. 2. 3
" VIII.) ((1. 2. 4)
" IX.) ((1. 2. 5)
(1. 3. 5

" X.) Tetra-Substitution Forms (2. 3. 4. 5
" XI.) (2. 4. 5. 6
" XII.) (1. 3. 4. 6

" XIII. Penta-Substitution Forms.

" XIV. Hexa-Substitution Forms.

(2) Analysis of the Plane Ring.

Plate XV. Mono-Substitution Forms.

" XVI.) Di-Substitution Forms (ortho 1.2
" XVII.) (meta 1.3
" XVIII.) (para 1.4

" XIX.) Tri-Substitution Forms (1. 2. 3
" XX.) ((1. 2. 4)
" XXI.) ((1. 2. 5)
(1. 3. 5

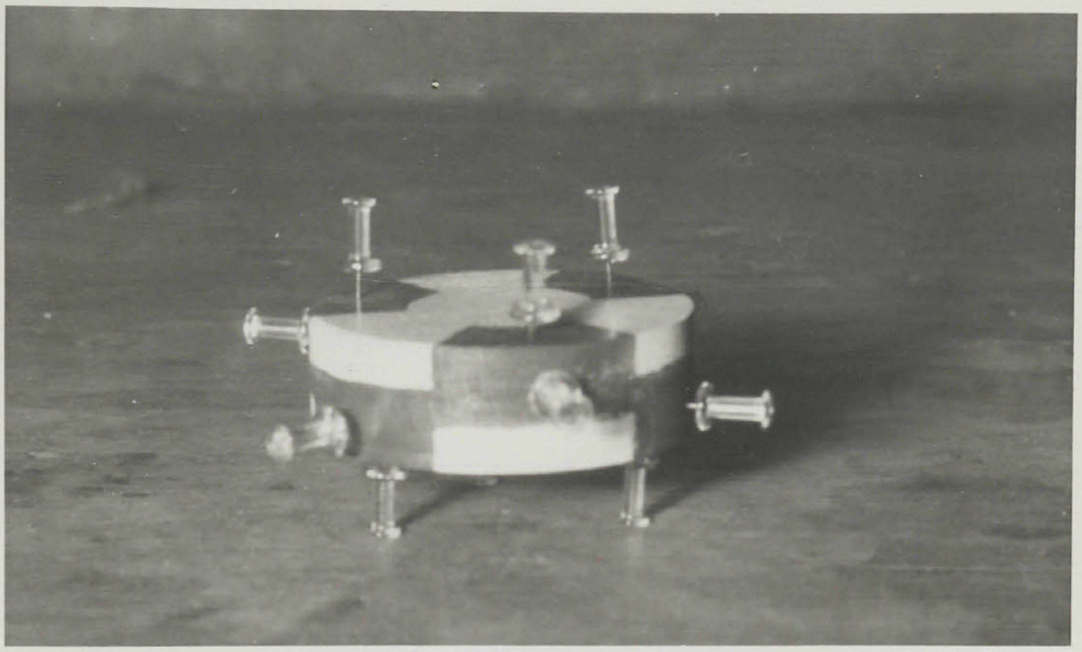
" XXII.) Tetra-Substitution Forms (2. 3. 4. 5
" XXIII.) (2. 4. 5. 6
" XXIV.) (1. 3. 4. 6

" XXV. Penta-Substitution Forms.

" XXVI. Hexa-Substitution Forms.

" XXVII. Joint Summary.

§ 1. Models.



The photograph shows the type of symbolic model used to aid in the visualization of the different isomers. The dark patches on the disc stand for carbon atoms in puckered array. The glass headed pins are the substituents. In the above arrangement all the external valencies of the carbon atoms are satisfied in a (symbolic) tetrahedral manner, and if the pins are considered as hydrogen atoms (instead of OH groups) it will represent the puckered cyclohexane ring.

In the formal analysis it was found convenient to represent the puckered ring as in Fig. 1, and the flat ring as in Fig. 2.

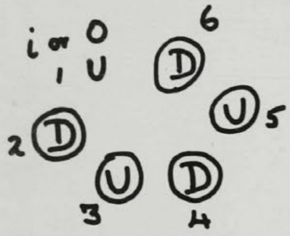


Fig. 1.

Puckered Ring.

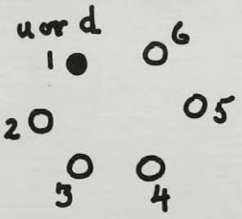


Fig. 2.

Plane Ring.

Explanation of Fig. 1. - U and D stand for "up" and "down" carbon atoms. Those encircled are saturated with hydrogen. Those left free are the ones chosen for substitution. Fig. 1 may be regarded as a "mono-substitution skeleton."

If an (OH) group is attached to that valency bond which lies nearest the average plane of the ring (i.e. lies on the edge of the disc shown in the photo), the substitution is denoted by the symbol i (inner).

If an (OH) group is attached to that valency bond which extends away from the face of the model, the substitution is denoted by the symbol o (outer).

It is of course understood that corresponding to an i (OH) substitution there must be an o (H) substitution, and vice versa.

Explanation of Fig. 2. - In the plane ring there is no distinction between "up" and "down" carbon atoms. Those carbon atoms which are to be used for substitution are shown as black discs, the others as circles. Fig. 2 is also a Mono-Substitution Skeleton. The two possible substitutions on any carbon atom are in this case represented by the symbols u (up) and d (down), meaning above or below the plane of the model.

General remarks. - The u and d symbols might have been used on the puckered model, and would have enabled an immediate transformation between the two, but for reasons which will appear later the above symbols are more efficient.

The numbers attached to the carbon atoms have the conventional significance as in the formulae of organic chemistry.

Definition of Skeleton. Such a model as is represented by Fig. 1 or Fig. 2 will be called a skeleton.

§ 2. Note on the Rigor of the Analysis.

An early attempt to derive the isomers by means of intuitive methods proved a failure. A number were missed. Although in the simpler cases the method which is here used appears somewhat cumbrous, it has turned out to be thoroughly justified in the majority of cases.

At the same time it cannot be claimed that every rule of selection has been proven with the same rigor as the propositions of mathematical crystallography. The object in view is to find the isomers, and find all of them. With this in view a method of analysis was developed, in which only rules which are proven, or can be seen intuitively, to be correct, are applied. It is believed that the agreement of the results with the findings of other workers, and with the arrays of models which were made in a number of cases, have been sufficient to prove the method sound. Throughout the analysis considerable use is made of both the symbols and methods of mathematical crystallography.

§ 3. Method of Analysis.

Briefly the method is as follows:-

(1) To determine the symmetry operations of all the skeletons on which substitutions are to be made.

(2) To take each puckered skeleton in turn and make on it all the possible substitutions, using a symbolic array of such a character that none will be missed.

(3) To apply the symmetry operations of each skeleton to its array of substitutions and so determine which substitutions are truly equivalent, and which are mirror images of one another.

Definition of Array. The rectangular arrangement of symbols in which each row represents a substitution on the skeleton will be called an array.

Definition of Form. Each row of symbols in an array represents a substitution on the skeleton. The row, or the model which it represents, will be called a form.

(4) To draw up a list of the unique arrays with their symmetry, and classify them as optically inactive, or possibly active isomers.

(5) To obtain the plane ring arrays by transforming the unique forms resulting from the puckered ring analysis, and to analyse them in the same way.

The method will be made more specific in § 4.

§ 4. Notation, Definitions, Propositions.

It has been necessary to explain certain notation and give certain definitions above. These will not be repeated here. Nor will there be any attempt made to define all the terms of mathematical crystallography used.

Definition: Symmetry Operation of the First Kind. A symmetry operation which does not involve a reflection is called a symmetry operation of the first kind.

Definition: Symmetry Operation of the Second Kind. A symmetry operation which involves a reflection or an inversion is called a symmetry operation of the second kind.

Prop. 1. No form can have a symmetry higher than that of its skeleton.

Prop. 2. No form can be brought into coincidence with another form by a symmetry operation which is not a property of the skeleton of the array.

Prop. 3. If a form can be brought into coincidence with another by an operation of the first kind, then they are truly equivalent forms (represent the same model, or isomer).

Prop. 4. Let (1), (2) be forms which possess no symmetry of the second kind. Then if (1) can be brought into coincidence with (2) only by symmetry operations of the second kind, they represent two mirror image isomers of possible optical activity.

Prop. 5. If a form can be brought into self coincidence by an operation, then it represents a model possessing the symmetry of that operation.

The models described in § 1, Fig. 1 and Fig. 2, are unsuited to the formation of an array in which it can be clearly seen that all the possible forms are present. An examination of the Plates will show the arrangement which was adopted, and its relation to the model. After all the possible forms have been listed, the analysis is carried out as follows: (See Plates)

In the upper right hand corner each symmetry operation of the skeleton is taken in turn and its effect on the symbols of a form are determined.

Example: 1 3 means that the diagonal operation interchanges the symbols in the 1st and 3rd columns of the array.

The operations are then applied to each form in turn, and the result is noted at the right of the form.

Examples: 3 i o i Cf.2 means that the diagonal axis operating on form 2 has produced form 3.

3 i o i means that the diagonal operation has produced self coincidence.

3 i o i Cf.2 1 means that the plane (1) of symmetry operating on form 2 has produced form 3.

Certain groups of forms usually turn out to be equivalent, as shown by the symmetry operations of the first kind (Prop. 3). These are listed under the heading "Equivalent Forms."

Certain of the unique forms which remain usually turn out to be related by symmetry operations of the second kind. These are listed under "Mirror Image Forms." (Prop. 4.)

Then the forms are divided into two classes:

Inactive. Those which possess planes or centres of symmetry, and which cannot therefore represent optically active molecules.

Active. The pairs which, possessing no symmetry of the second kind, represent molecules which may possess optical activity.

Note. It is clearly to be understood that the heading "Act." on the plates means "representing models which may possess optical activity." The need of an abbreviation is obvious.

The tabulation and operations have been simplified in some cases by omitting from the array certain types of forms which can be derived directly from certain types of listed forms by simply interchanging all i's and o's and vice versa. This does not affect the symmetry. A derived form is represented by the same number as the form from which it is derived, but with a bar over the top.

In cases where there are two mirror image skeletons, the analysis is carried through for one only, and the corresponding mirror image forms on the second are denoted by the same numbers dashed.

The problem of obtaining the plane ring models is greatly simplified by the following considerations.

The symmetry of any plane ring skeleton can be directly derived from that of the corresponding puckered ring skeleton by the addition of a plane of symmetry.

All of the plane ring forms can be obtained from the puckered ring forms by the transformation corresponding to the physical

Plate I

Symmetry of the Skeletons

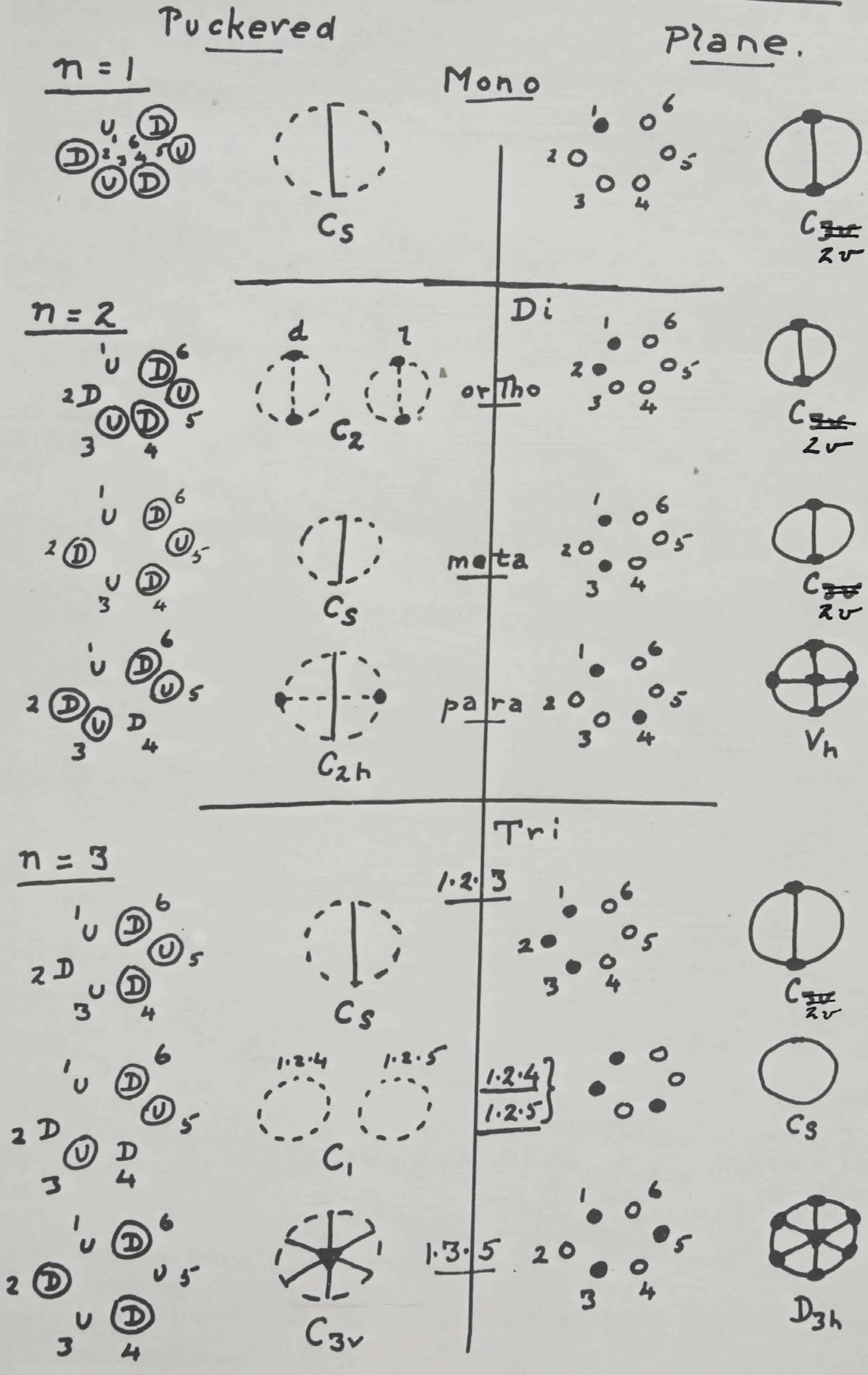


Plate II

Symmetry of Skeletons (cont'd)

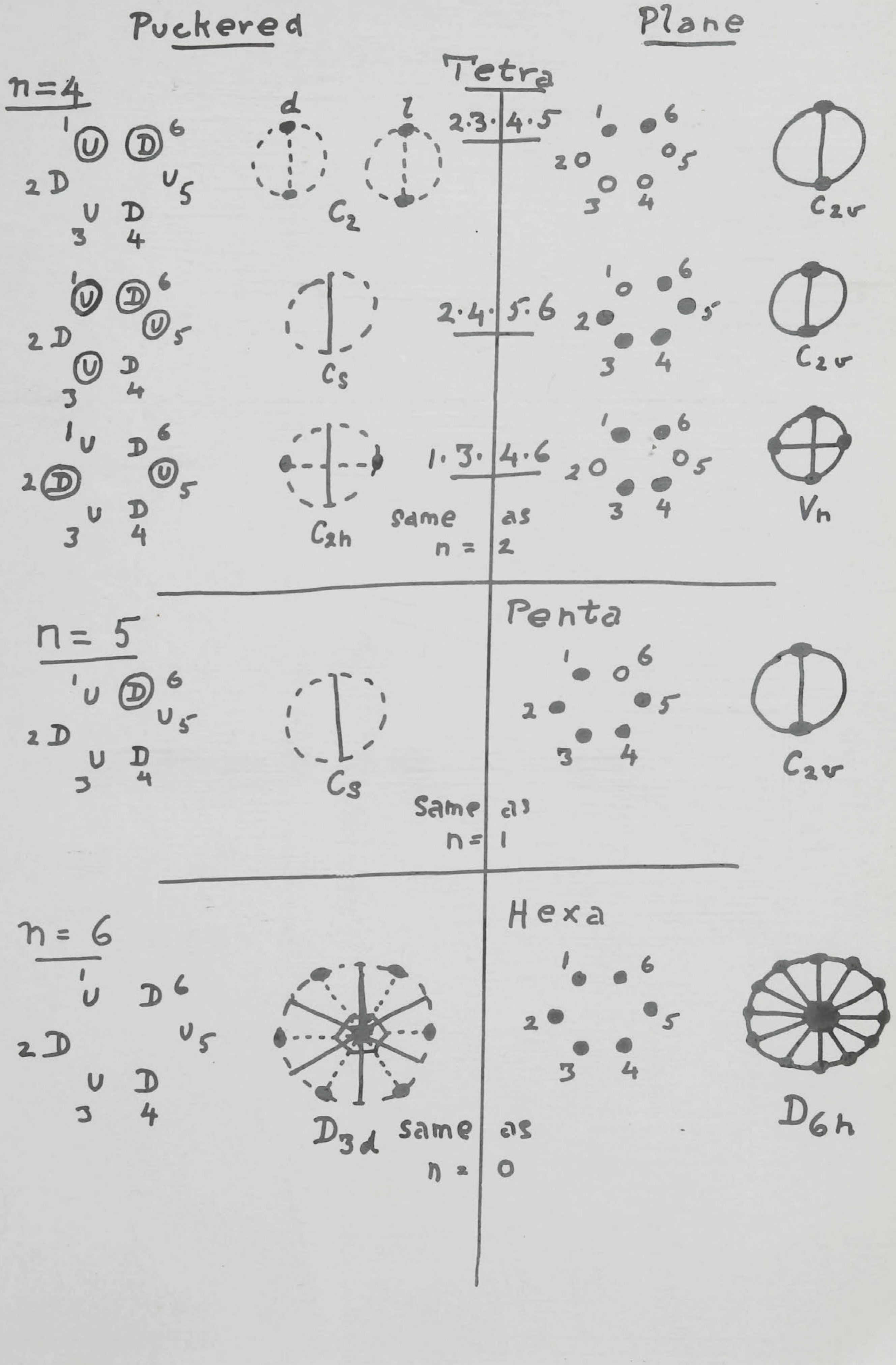
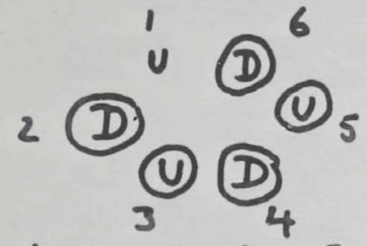


Plate III

n = 1   Mono-Substitution Forms   Puck.



		1	2	3	4	5	6
		U	D	U	D	U	D
1	i		L^1				
2	0		L^1				

Operations

1   1↔1

Sym. of Skel.


C_s

Equiv. Forms

None. No ops. of 1st kind.

Mirror Image Forms

None

Self-Equiv. Forms

$\left.\begin{matrix}1\\2\end{matrix}\right\} C_s$

Summary

2 inact. C_s

0 act.

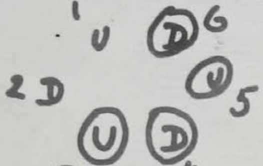
inact.	act.
$\left.\begin{matrix}1\\2\end{matrix}\right\} C_s$	

Plate IV

$n=2$ Di-Substitution Forms

Puck.

ortho 1·2



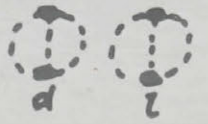
	1 U	2 D	3 U	4 D	5 U	6 D
1	i	i	L⁝			
2	i	o				
3	o	i	cf. 2 ⁝			
4	o	o	L⁝			

Summary

o inact.

3 act. prs? $\left\{\begin{array}{l} 2\ C_2 \\ 1\ C_1 \end{array}\right.$

Sym. of Skel.



C_2

Sym. Operations

⁝ 1 ↔ 2

Equiv. Forms

2 - 3

Mirror Image Forms

For every unique form here there is a mirror image on the $\overset{1}{D}\overset{2}{U}$…… skeleton.

Self-equiv Forms

$\left.\begin{array}{c} 1 \\ 4 \end{array}\right\} C_2$

Inact.	Act.
none	$\left.\begin{array}{c} 1-1' \\ 4-4' \end{array}\right\} C_2$
	$2-2'$ C_1

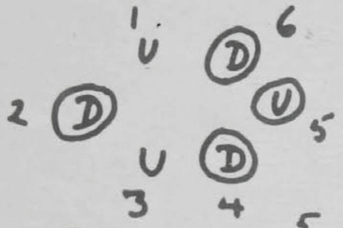
The ' refers to corres. form on $\overset{1}{D}\overset{2}{U}$···· skeleton.

Plate V

Puck.

$n = 2$ Di-Substitution Forms

meta 1·3



	1 U	2 D	3 U	4 D	5 U	6 D
1	i		i	⊥		
2	o		i			
3	i		o	cf. 21.		
4	o		o	⊥		

Summary

2 inact. C_s

1 act. pr. C_1

Sym. of Skel.

 C_s

Sym. Operations

| 1 ↔ 3

Equiv. Forms

no ops. of 1st kind.

Mirror Image Forms

2 - 3

Self-equiva Forms

$\left.\begin{matrix}1\\4\end{matrix}\right\} C_s$

Inact.

$\left.\begin{matrix}1\\4\end{matrix}\right\} C_s$

Act.

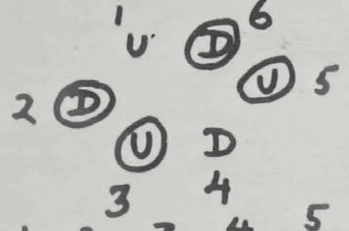
2 - 3 C_1

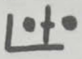
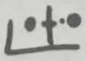
Plate VI

$n=2$ Di-Substitution Forms

Puck.

para 1.4



	$\overset{1}{U}$	$\overset{2}{D}$	$\overset{3}{U}$	$\overset{4}{D}$	$\overset{5}{U}$	$\overset{6}{D}$
1	i			i		
2	o			i		
3	i			o	cf. 2 •··•.	
4	o			o		

Summary

3 inact. $\left\{\begin{matrix}2\ C_{2h}\\1\ C_s\end{matrix}\right.$

0 act.

Sym. of Skel.

C_{2h}

Sym. Operations

•····• $1 \leftrightarrow 4$

| $\begin{matrix}1 \leftrightarrow 1\\4 \leftrightarrow 4\end{matrix}$

Equiv. Forms

2 - 3

Mirror Images Forms

None

Self-equiv. Forms

$\left.\begin{matrix}1\\4\end{matrix}\right\}C_{2h}$

2 C_s

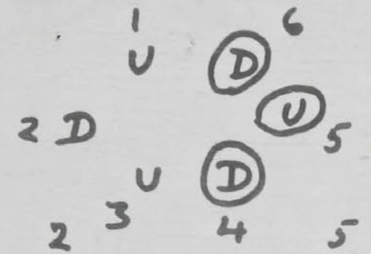
Inact.	Act.
$\left.\begin{matrix}1\\4\end{matrix}\right\}C_{2h}$	none
2 C_s	

Plate VII

$n = 3$ Tri-Substitution Forms

Puck.

1.2.3



	1 U	2 D	3 U	4 D	5 U	6 D
1	i	i	i	L'		
2	0	i	i	.		
3	i	0	i	L'		
4	i	i	0	cf. 21.		
5	0	0	i	.		
6	i	0	0	cf. 51.		
7	0	i	0	L'		
8	0	0	0	L'		

Summary

4 inact. C_s

2 act. prs. C_1

Sym. of Skel

C_s

Sym. Operations

$$1 \begin{cases} 1 \leftrightarrow 3 \\ 2 \leftrightarrow 2 \end{cases}$$

Equiv. Forms.

no ops. of 1st kind.

Mirror Image Forms

2 - 4
5 - 6

Self-equiv. Forms

$$\left.\begin{matrix} 1 \\ 3 \\ 7 \\ 8 \end{matrix}\right\} C_s$$

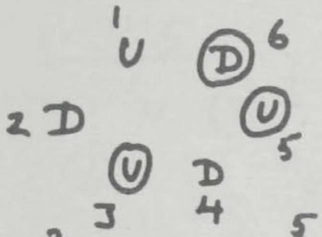
Inact.	Act.
$\left.\begin{matrix} 1 \\ 3 \\ 7 \\ 8 \end{matrix}\right\} C_s$	$\left.\begin{matrix} 2-4 \\ 5-6 \end{matrix}\right\} C_1$

Plate VIII

n = 3 Tri-Substitution Forms

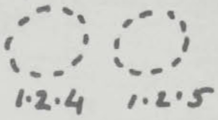
Puck.

$\left\{\begin{array}{l}1\cdot2\cdot4\\1\cdot2\cdot5\end{array}\right.$



	1 U	2 D	3 U	4 D	5 U	6 D
1	i	i		i		
2	o	i		i		
3	i	o		i		
4	i	i		o		
5	o	o		i		
6	i	o		o		
7	o	i		o		
8	o	o		o		

Sym. of Skel.



C_1

Sym. Operations

None

Equiv. Forms

no ops. of 1st kind.

Mirror Image Forms

For every unique form there is a mirror image on the 1.2.5 skeleton.

Self-equiv. Forms

None

Summary

0 inact.

8 act. prs. C_1

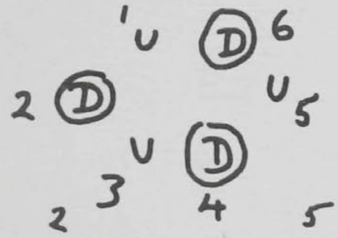
Inact.	Act.
none	1 - 1'
	2 - 2'
	⋮
	8 - 8'

Plate IX

$n = 3$ Tri-Substitution Forms

Puck.

1.3.5



	1 U	2 D	3 U	4 D	5 U	6 D
1	i		i		i	L✱
2	o		i		i	L!
3	i		o		i	cf 2 ▼
4	i		i		o	cf 2 ▼
5	o		o		i	L!
6	i		o		o	cf 5 ▼
7	o		i		o	cf 5 ▼
8	o		o		o	L✱

Summary

$4 \text{ inact.} \begin{cases} 2\ C_{3v} \\ 2\ C_s \end{cases}$

0 act.

Sym. of Skel.

C_{3v}

Sym. Operations

▼ $\overleftrightarrow{1 \leftrightarrow 3 \leftrightarrow 5}$

$\overset{1}{|}$ $3 \leftrightarrow 5$

$\overset{3}{|}$ $5 \leftrightarrow 1$

$\overset{5}{|}$ $1 \leftrightarrow 3$

Equiv. Forms

2 - 3 - 4

5 - 6 - 7

Mirror Image Forms

None

Self-equiv. Forms

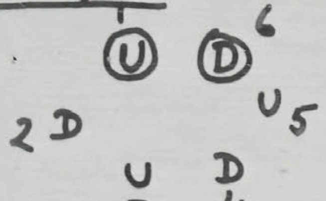
$\left.\begin{matrix}1\\8\end{matrix}\right\} C_{3v}$ $\left.\begin{matrix}2\\5\end{matrix}\right\} C_s$

Inact	Act.
$\left.\begin{matrix}1\\8\end{matrix}\right\} C_{3v}$ $\left.\begin{matrix}2\\5\end{matrix}\right\} C_s$	none

Plate X

n = 4 Tetra-Substitution Forms   Puck.

2.3.4.5

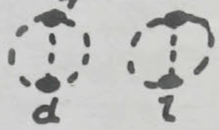


1 U		2 D	3 U	4 D	5 U	6 D
1	t_0	i	i	i	i	L⋮
2	t_1	o	i	i	i	
3		i	o	i	i	
4		i	i	o	i	cf 3 ⋮
5		i	i	i	o	cf 2 ⋮
6	t_2	o	o	i	i	
7		i	o	o	i	L⋮
8		i	i	o	o	cf 6 ⋮
9		o	i	o	i	
10		i	o	i	o	cf 9 ⋮
11		o	i	i	o	L⋮

t_3 same as t_1
with o for i

t_4 — – t_0
– o for i

Sym. of Skel.



C_2

Sym. Operations

⋮ $\begin{cases} 2 \leftrightarrow 5 \\ 3 \leftrightarrow 4 \end{cases}$

Equiv.	Forms
2 - 5	$\bar{2} - \bar{5}$ *
3 - 4	$\bar{3} - \bar{4}$
6 - 8	
9 - 10	

Mirror Image Forms

For every form There is a mirror image form on the othe skeleton.

Self-equiv. Forms

$\left.\begin{matrix} 1 \\ 7 \\ 11 \\ \bar{1} \end{matrix}\right\} C_2$

Inact.	Act.
none	$\left.\begin{matrix} 1 \\ 7 \\ 11 \\ \bar{1} \end{matrix}\right\} C_2$
	$\left.\begin{matrix} 2 \\ 3 \\ 6 \\ 9 \\ \bar{2} \\ \bar{3} \end{matrix}\right\} C_1$

Summary

0 inact.

10 act. prs. $\begin{cases} 4 & C_2 \\ 6 & C_1 \end{cases}$

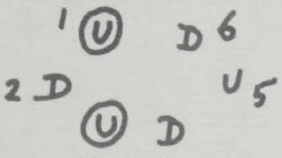
* The ¯ refers to types t_3 & t_4, obtained by putting o for i

Plate XI

$n = 4$ Tetra-Substitution Forms

Puck.

2·4·5·6



		1	2	3	4	5	6	
		$\underline{U}$	D	$\underline{U}$	D	U	D	
1			i		i	i	i	L^{1}
2	t_1		o		i	i	i	L^{1}
3			i		o	i	i	'
4			i		i	o	i	L^{1}
5			i		i	i	o	cf. 31.
6	t_2		o		o	i	i	·
7			i		o	o	i	·
8			i		i	o	o	cf. 71.
9			o		i	o	i	L^{1}
10			i		o	i	o	L^{1}
11			o		i	i	o	cf. 61.

t_3 from t_1 by i for o

t_4 from t_0 by i for o

Summary

8 inact. C_s

4 act. prs. C_1

Sym. of Skel.

C_s

Sym. Operations

$$| \quad \left\{\begin{array}{l} 2 \leftrightarrow 2 \\ 4 \leftrightarrow 6 \\ 5 \leftrightarrow 5 \end{array}\right.$$

Equiv. Forms

no sym. ops. of 1st kind.

Mirror Image Forms

3-5 $\quad \bar{3}$-$\bar{5}$
7-8
6-11

Self-equiv. Forms

$$\left.\begin{array}{cc} 1 & 4 \\ \bar{1} & \bar{4} \\ 2 & 9 \\ \bar{2} & 10 \end{array}\right\} C_s$$

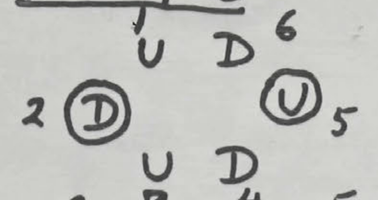
Inact.	Act.
$\left.\begin{array}{cc} 1 & 4 \\ \bar{1} & \bar{4} \\ 2 & 9 \\ \bar{2} & 10 \end{array}\right\} C_s$	$\left.\begin{array}{c} 3-5 \\ \bar{3}-5 \\ 7-8 \\ 6-11 \end{array}\right\} C_1$

Plate XII

n = 4 Tetra-Substitution Forms

Puck.

1·3·4·6



	1	2	3	4	5	6	
	U	$\underline{D}$	U	D	$\underline{U}$	D	
1 t_0	i		i	i		i	└o†o.
2 t_1	o		i	i		i	.
3	i		o	i		i	cf. 2 |.
4.	i		i	o		i	cf. 3 o···o
5.	i		i	i		o	cf. 2 o···o
6 t_2	o		o	i		i	└| .
7	i		o	o		i	└o···o .
8.	i		i	o		o	cf. 6 o···o
9	o		i	o		i	.
10.	i		o	i		o	cf. 9 o†o.
11	o		i	i		o	$\underline{\text{└o···o}}$ cf. 7 |.

t_3 from t_1 by i for o
t_4 " t_0 " . . .

Sym. of Skel.

C_{2h}

Sym. Operations

o····o $\begin{cases} 1 \rightarrow 6 \\ 3 \leftrightarrow 4 \end{cases}$

| 1 ↔ 3
6 ↔ 4

Equiv. Forms

2-5 $\bar{2}$-$\bar{5}$
3-4 $\bar{3}$-$\bar{4}$
6-8
9-10

Mirror Image Forms

2-3 $\bar{2}$-$\bar{3}$
7-11

Self-equiv. Forms

$\left.\begin{matrix} 1 \\ \bar{1} \end{matrix}\right\}$ C_{2h}
6 C_s
$\left.\begin{matrix} 11 \\ 7 \end{matrix}\right\}$ C_2
9 C_i

Summary

4 inact. $\begin{cases} 2\ C_{2h} \\ 1\ C_s \\ 1\ C_i \end{cases}$

3 act. prs. $\begin{cases} 1\ C_2 \\ 2\ C_1 \end{cases}$

Inact.		Act.	
1 $\bar{1}$	C_{2h}	7-11	C_2
6	C_s	2-3 $\bar{2}$-$\bar{3}$	C_1
9	C_i		

Plate XIII

n = 5 Penta Substitution Forms

Puck.

1 U   Ⓓ 6

2 D   U 5

U   D

		1	2	3	4	5	6
		U	D	U	D	U	D
1		i	i	i	i	i	$\llcorner$
2	t_1	o	i	i	i	i	·
3		i	o	i	i	i	·
4		i	i	o	i	i	$\llcorner$
5		i	i	i	o	i	cf. 3|.
6		i	i	i	i	o	cf. 2|.
7	t_2	o	o	i	i	i	·
8		i	o	o	i	i	·
9		i	i	o	o	i	cf. 8|.
10		i	i	i	o	o	cf. 7|.
11		o	i	o	i	i	·
12		i	o	i	o	i	$\llcorner$
13		i	i	o	i	o	cf. 11|.
14		o	i	i	o	i	·
15		i	o	i	i	o	cf. 14|.
16		o	i	i	i	o	$\llcorner$

$t_3 \overset{i\,o}{\longleftrightarrow} t_2$

$t_4 \longleftrightarrow t_1$

$t_5 \longleftrightarrow t_0$

Summary

8 inact. C_s

12 act. prs. C_1

Sym. of Ske?

C_s

Sym. Operations

$$\mathbf{1}\;\begin{cases} 3 \leftrightarrow 3 \\ 2 \leftrightarrow 4 \\ 1 \leftrightarrow 5 \\ 6 \leftrightarrow 6 \end{cases}$$

Equiv. Forms

No sym. ops. of 1st kind.

Mirror Image Forms

$3-5 \quad \bar{3}-\bar{5}$

$2-6 \quad \bar{2}-\bar{6}$

$8-9 \quad \bar{8}-\bar{9}$

$7-10 \quad \bar{7}-\overline{10}$

$11-13 \quad \overline{11}-\overline{13}$

$14-15 \quad \overline{14}-\overline{15}$

Self.equiv. Forms

$$\left.\begin{matrix} 1 & \bar{1} \\ 4 & \bar{4} \\ 12 & \overline{12} \\ 16 & \overline{16} \end{matrix}\right\} C_s$$

Inact.

$$\left.\begin{matrix} 1 & \bar{1} \\ 4 & \bar{4} \\ 12 & \overline{12} \\ 16 & \overline{16} \end{matrix}\right\} C_s$$

Act.

$$\underbrace{\begin{matrix} 3-5 & \bar{3}-\bar{5} \\ 2-6 & \bar{2}-\bar{6} \\ 8-9 & \bar{8}-\bar{9} \\ 7-10 & \bar{7}-\overline{10} \\ 11-13 & \overline{11}-\overline{13} \\ 14-15 & \overline{14}-\overline{15} \end{matrix}}_{C_1}$$

Plate XIV

n = 6 Hexa-Substitution Forms

Puck.

¹U D⁶
²D U₅
U D
³ ⁴

		1 U	2 D	3 U	4 D	5 U	6 D	
1		i	i	i	i	i	i	 D3d
2	t_1	0	i	i	i	i	i	⌊1
3		i	0	i	i	i	i	cf 2 ●···●
4		i	i	0	i	i	i	cf 2 ▼
5		i	i	i	0	i	i	cf 2 ●···●
6		i	i	i	i	0	i	cf 2 ▼
7		i	i	i	i	i	0	cf 2 ●···●
8	t_2'	0	0	i	i	i	i	⌊●···●
9		i	0	0	i	i	i	cf 8 |
10		i	i	0	0	i	i	cf 8 ▼
11		i	i	i	0	0	i	cf 9 ▼
12		i	i	i	i	0	0	cf 8 ▼
13	t_2''	0	i	0	i	i	i	⌊1
14		i	0	i	0	i	i	cf 13 ●···●
15		i	i	0	i	0	i	cf 13 ▼
16		i	i	i	0	i	0	cf 14 ▼
17	t_2'''	0	i	i	0	i	i	⌊●·|·●
18		i	0	i	i	0	i	cf 17 ▼
19		i	i	0	i	i	0	cf 17 ▼
20	t_2^{iv}	0	i	i	i	0	i	cf 13 ▼
21		i	0	i	i	i	0	cf 14 ▼
22	t_2^{v}	0	i	i	i	i	0	cf 9 ▼
23	t_3'	0	0	0	i	i	i	⌊●·|·●
24		i	0	0	0	i	i	cf 23 ●···●
25		i	i	0	0	0	i	cf 23 ▼
26		i	i	i	0	0	0	cf 24 ▼
27	t_3''	0	0	i	0	i	i	
28		i	0	0	i	0	i	
29		i	i	0	0	i	0	cf 27 ▼
30	t_3'''	0	i	0	0	i	i	cf 28 | cf 27 ●···●
31		i	0	i	0	0	i	cf 27 | cf 29 ●···●
32		i	i	0	i	0	0	cf 30 ▼
33	t_3^{iv}	0	0	i	i	0	i	cf 30 ▼
34		i	0	0	i	i	0	cf 31 ▼
35	t_3^{v}	0	i	i	0	0	i	cf 28 ▼
36		i	0	i	i	0	0	cf 27 ▼
37		0	0	i	i	i	0	cf 24 ▼
38		0	i	i	i	0	0	cf 23 ▼
39		0	i	0	i	i	0	cf 28 ▼
40		0	i	i	0	i	0	cf 31 ▼
41		0	i	0	i	0	i	⌊✱
42		i	0	i	0	i	0	cf 41 ●···●

$t_4 \overset{i}{\underset{0}{\leftrightarrow}} t_2$ $t_5 \overset{i}{\underset{0}{\leftrightarrow}} t_1$ $t_6 \overset{i}{\underset{0}{\leftrightarrow}} t_1$

Sym. of Skel.

D3d

Sym. Operations

▼ $1 \rightarrow 3 \rightarrow 5$, $2 \rightarrow 4 \rightarrow 6$

●···●		
1↔2	2↔3	3↔4
6↔3	1↔4	2↔5
5↔4	6↔5	1↔6

|		
1↔1	2↔2	3↔3
2↔6	3↔1	4↔2
3↔5	4↔6	5↔1
4↔4	5↔5	6↔6

Equiv. Forms

2-3-4-5-6-7
$\bar{2}-\bar{3}-\bar{4}-\bar{5}-\bar{6}-\bar{7}$
8-10-12 9-11-22
$\bar{8}-\overline{10}-\overline{12}$ $\bar{9}-\overline{11}-\overline{22}$
13-14-15-16-20-21
$\overline{13}-\overline{14}-\overline{15}-\overline{16}-\overline{20}-\overline{21}$
17-18-19
$\overline{17}-\overline{18}-\overline{19}$
$\overline{23}-\overline{24}-\overline{25}-\overline{26}-37-38$
27-29-36
28-35-39
30-32-33
31-34-40
41-42

Mirror Image Forms

$8-9$ 30-28
$\bar{8}-\bar{9}$

Self-equiv. Forms

$\left.\frac{1}{1}\right\}$ D3d $\left.\frac{17}{17}\right\}$ C2h 41 C3v $\left.\frac{8}{8}\right\}$ C2 $\left.\begin{matrix}\frac{2}{2}\\ \frac{13}{13}\\ 23\end{matrix}\right\}$ Cs

Summary

10 inact $\left\{\begin{matrix}2\ D3d\\ 1\ C3v\\ 2\ C2h\\ 5\ Cs\end{matrix}\right.$

3 act. prs. $\left\{\begin{matrix}2\ C_2\\ 1\ C_1\end{matrix}\right.$

Inact

$\left.\frac{1}{1}\right\}$ D3d
41 C3v
$\left.\frac{17}{17}\right\}$ C2h
$\left.\begin{matrix}\frac{2}{2}\\ \frac{13}{13}\\ 23\end{matrix}\right\}$ Cs

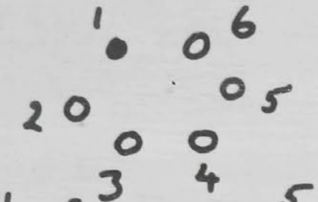
Act.

$\left.\begin{matrix}8-9\\ \bar{8}-\bar{9}\end{matrix}\right\}$ C_2
30-28 C_1

Plate XV

$n = 1$ Mono-Substitution Forms

Plane



1 2 3 4 5 6
● o o o o o

1 d ·———

2 u cf. 1 ⋮.

Summary

1 inact. C_s

0 act.

Sym. of Skel.

$C_{\substack{\cancel{3v}\\ 2v}}$

Sym. Operations

⋮ $\overset{|}{u} \leftrightarrow \overset{|}{d}$

| 1 ↔ 1

O $\overset{|}{u} \leftrightarrow \overset{|}{d}$

Equivalent Forms

1 - 2

Mirror Image Forms

None

Self-equivalent Forms

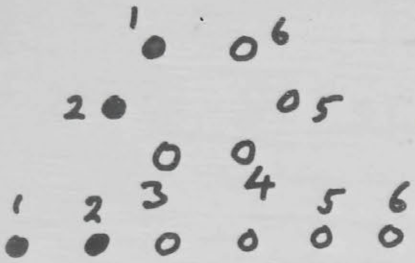
1 C_s

Inact.	Act.
1 C_s	none

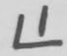
Plate XVI

n = 2 Di-Substitution Forms Plane

ortho 1·2



1 d u 

2 d d 

3 u d  cf. 1 ①

Sym. of Skel.

① $C_{\substack{\cancel{3v}\\2v}}$

Sym. Operations

⋮ 1 ⟷ 2
u ←--- d
d ---- u

| 1 ⟷ 2

○ u ⟷ d

Equiv. Forms

None

Summary

1 inact. C_s

1 act. pr. C_2

Mirror Image Forms

1 - 3

Self-equiv. Forms

1-3 C_2

2 C_s

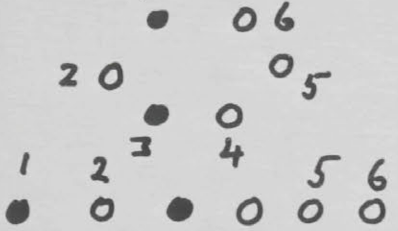
Inact.	Act.
2 C_s	1-3 C_2

Plate XVII

$n = 2$ Di-Substitution Forms

Plane

meta 1·3



	1	3	
1	d	d	
2	d	u	
3	u	d	cf. 2 ⦶
4	u	u	cf. 1 ⋮

Summary

1 inact C_s

1 act. pr. C_2

Sym. of Skel.

$C_{\cancel{3v}\ 2v}$

Sym. Operations

⋮	$1 \leftrightarrow 3$ u . . . . d d . . . . u
|	$1 \leftrightarrow 3$
○	$u \leftrightarrow d$

Equiv. Forms

1 - 4

Mirror Image Forms

2 - 3

Self. equiv. Forms

1 C_s
2 C_2

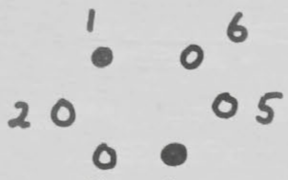
Inact.	Act.
1 C_s	2 - 3 C_2

Plate XVIII

$n = 2$ Di-Substitution Forms

Plane

para 1.4



	1	2	3	4	5	6	
	●	○	○	●	○	○	
1	d			u	∟·+·		
2	d			d	∟+		
3	u			d	cf. 1	⁝	

Sym. of Skel.

Vh

Sym. Operations

$\bullet\ 1 \leftrightarrow 4 \quad \vdots \begin{cases} \overset{1}{u} \leftrightarrow \overset{1}{d} \\ \overset{4}{u} \leftrightarrow \overset{4}{d} \end{cases}$

$\bullet\cdots\bullet\ \overset{1}{u} \leftrightarrow \overset{4}{d}$

$| \begin{matrix} 1 \leftrightarrow 1 \\ 4 \leftrightarrow 4 \end{matrix}$ — $1 \leftrightarrow 4$ O $u \leftrightarrow d$

Equiv. Forms

1 - 3

Mirror Image Forms

None

Self-equiv. Forms

1 C_{2h}
2 C_{2v}

Summary

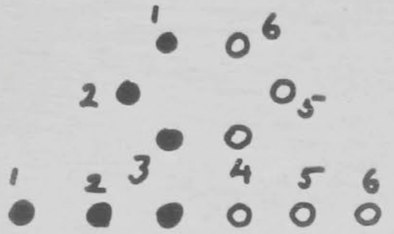
2 inact. $\begin{cases} 1\ C_{2v} \\ 1\ C_{2h} \end{cases}$

0 act.

Plate XIX

n=3 Tri-Substitution Forms Plane

1·2·3



1	d	u	d	⊔ ·
2	u	u	d	·
3	d	d	d	⊔ ·
4	d	u	u	cf. 2 |.
5	u	d	d	cf. 2 ⋮.
6	d	d	u	cf. 4 ⋮.
7	u	u	u	cf. 3 ⋮.
8	u	d	u	cf. 1 ⋮.

Summary

2 inact. C_s

1 act. pr. C_1

Sym. of Skel.

 $C_{\underset{2v}{\cancel{3v}}}$

Sym. Operations

$\vdots \begin{cases} \overset{2}{u} \leftrightarrow \overset{2}{d} \\ \overset{1}{u} \leftrightarrow \overset{3}{d} \end{cases}$ | 2 ↔ 2, 1 ↔ 3

○ u ↔ d

Equiv. Forms

2-5
3-7
4-6
1-8

Mirror Image Forms

2-4

Self-equiv. Forms

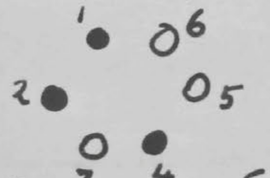
$\left.\begin{matrix}1\\3\end{matrix}\right\} C_s$

Inact.	Act.
$\left.\begin{matrix}1\\3\end{matrix}\right\} C_s$	2-4

Plate XX

n = 3 Tri-Substitution Forms Plane

{1.2.4
{1.2.5



	1 ●	2 ●	3 ○	4 ●	5 ○	6 ○	
1	d	u		u			
2	u	u		u			
3	d	d		u			
4	d	u		d			
5	d	d		d			cf. 21.
6	u	d		u			cf. 41.
7	u	u		d			cf. 31.
8	u	d		d			cf. 11.

Sym. of Skel.

○ C_s

Sym. Operations

○ u ↔ d

Equiv. Forms

No sym. ops of 1st Kind.

Mirror Image Forms

1 - 8
2 - 5
3 - 7
4 - 6

Self-equiv. Forms

None

Summary

0 inact.

4 act. prs. C_1

Inact.	Act.	
none	1 - 8 2 - 5 3 - 7 4 - 6	C_1

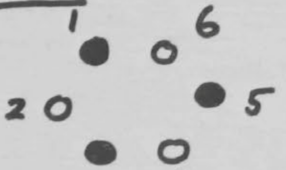
The 1.2.5 Skeleton gives identical forms.

Plate ~~XXI~~

Plane

n = 3 Tri-Substitution Forms

1·3·5



	1	2	3	4	5	6	
	●	○	●	○	●	○	
1	d		d		d		$\underline{\lfloor *}$
2	u		u		d		$\underline{\lfloor ^{15}}$
3	d		d		u		cf. 2 $^{5}\vdots$
4	u		u		u		$\underline{\lfloor *}$ cf. $^{1}\vdots$.

Sym. of Skel.

D_{3h}

Sym. Operations

$\blacktriangledown\quad \overset{\longrightarrow}{1 \leftrightarrow 3} \leftrightarrow 5$

$^{1}\vdots \begin{cases} \underset{u}{1} \leftrightarrow \underset{d}{1} \\ \underset{u}{3} \leftrightarrow \underset{d}{5} \end{cases}$ $^{3}\vdots \begin{cases} \underset{u}{3} \leftrightarrow \underset{d}{3} \\ \underset{u}{1} \leftrightarrow \underset{d}{5} \end{cases}$

$^{5}\vdots \begin{cases} \underset{u}{5} \leftrightarrow \underset{d}{5} \\ \underset{u}{1} \leftrightarrow \underset{d}{3} \end{cases}$ $^{1}| \begin{cases} 1 \leftrightarrow 1 \\ 3 \leftrightarrow 5 \end{cases}$

$^{3}| \begin{cases} 3 \leftrightarrow 3 \\ 1 \leftrightarrow 5 \end{cases}$ $^{5}| \begin{cases} 5 \leftrightarrow 5 \\ 1 \leftrightarrow 3 \end{cases}$

Summary

2 inact. $\begin{cases} 1\ C_{3v} \\ 1\ C_s \end{cases}$

0 act.

Equiv. Forms

1 - 4
2 - 3

Mirror Image Forms

None

Self-equiv. Forms

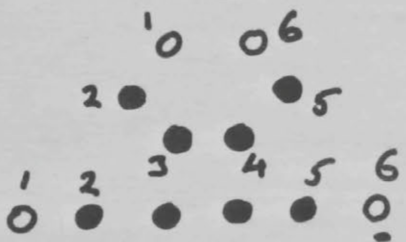
1 C_{3v}
2 C_s

Inact.	Act.
1 C_{3v} 2 C_s	none

Plate XXII

n = 4 Tetra-Substitution Forms Plane

2·3·4·5



	2	3	4	5	
1	u	d	u	d	
2	d	d	u	d	
3	u	u	u	d	
4	d	u	u	d	
5	u	u	d	d	
6	d	d	u	u	cf.5⦶.
7	d	d	d	d	
8	d	u	d	d	cf.2|.
9	d	d	d	u	cf.3○.
10	d	u	d	u	cf.1⦶

Summary

2 inact. C_s

4 act. prs. $\begin{cases} 2\ C_2 \\ 2\ C_1 \end{cases}$

Sym. of Ske


$C_{\overset{\cancel{3v}}{2v}}$

Sym. Operations


$\underset{u}{2} \leftrightarrow \underset{d}{5}$
$\underset{u}{3} \leftrightarrow \underset{d}{4}$

| 2 ↔ 5
3 ↔ 4

○ u ↔ d

Equiv. Forms

none

Mirror Image Form

5 - 6
2 - 8
3 - 9
1 - 10

Self-equiv. Forms

$\left.\begin{matrix}1\\5\end{matrix}\right\} C_2$ $\left.\begin{matrix}4\\7\end{matrix}\right\} C_s$

Inact.

$\left.\begin{matrix}4\\7\end{matrix}\right\} C_s$

Act.

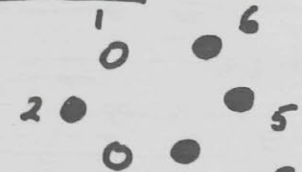
$\left.\begin{matrix}1-10\\5-6\end{matrix}\right\} C_2$
$\left.\begin{matrix}2-8\\3-9\end{matrix}\right\} C_1$

Plate XXIII

$n = 4$ Tetra-Substitution Forms

Plane

2·4·5·6.



	1 ○	2 ●	3 ○	4 ●	5 ●	6 ●	
1		u		u	d	u	⊥
2		d		u	d	u	⊥
3		u		d	d	u	
4		u		u	u	u	⊥
5		u		u	d	d	cf.3 |
6		d		d	d	u	
7		u		d	u	u	cf.6 ⁝
8		u		u	u	d	cf. 6 ○.
9		d		u	d	d	cf.8 ⁝. cf.6 |
10		u		d	d	d	⊥
11		d		u	u	u	cf.10 ÷

Sym. of Skel

$C_{\cancel{3v}\,2v}$

Sym. Operations

⁝ $\left\{\begin{array}{l} \underset{u}{2} \leftrightarrow \underset{d}{2} \\ \underset{u}{4} \leftrightarrow \underset{d}{6} \\ \underset{u}{5} \leftrightarrow \underset{d}{5} \end{array}\right.$ | $\left\{\begin{array}{l} 2 \leftrightarrow 2 \\ 4 \leftrightarrow 6 \\ 5 \leftrightarrow 5 \end{array}\right.$

○ u ↔ d

Equiv. Forms

6 - 7
8 - 9
10 - 11

Mirror Image Forms

3 - 5
6 - 8

Self-equiv. Forms

$\left.\begin{array}{c} 1 \\ 2 \\ 4 \\ 10 \end{array}\right\} C_s$

Summary

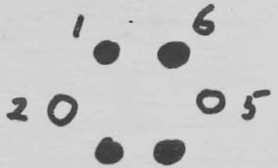
4 inact. C_s
2 act. prs. C_1

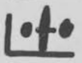
Inact.	Act.
$\left.\begin{array}{c} 1 \\ 2 \\ 4 \\ 10 \end{array}\right\} C_s$	$\left.\begin{array}{c} 3-5 \\ 6-8 \end{array}\right\} C_1$

Plate XXIV

$n = 4$ Tetra-Substitution Forms Plane

1.3.4.6



	1 ●	2 ○	3 ●	4 ●	5 ○	6 ●	
1	d		d	u		u	
2	u		d	u		u	
3	d		u	u		u	cf2 —
4	u		u	u		u	
5	d		u	d		u	
6	u		d	u		d	 cf5 ⊕
7	u		d	d		u	
8	u		u	d		u	cf.3 ● cf21
9	u		u	u		d	cf.2 ●
10	u		u	d		d	cf. 1●-●-●

Sym. of Skel.

V_h

Sym. Operations

$\bullet\begin{cases}1 \leftrightarrow 4\\ 3 \leftrightarrow 6\end{cases}$ $\vdots\begin{cases}\underset{u}{1} \leftrightarrow \underset{d}{6}\\ \underset{u}{3} \leftrightarrow \underset{d}{4}\end{cases}$

$\bullet\cdots\bullet\begin{cases}\underset{u}{1} \leftrightarrow \underset{d}{3}\\ \underset{u}{6} \leftrightarrow \underset{d}{4}\end{cases}$ $|\begin{cases}1 \leftrightarrow 6\\ 3 \leftrightarrow 4\end{cases}$

$—\begin{cases}1 \leftrightarrow 3\\ 6 \leftrightarrow 4\end{cases}$ ○ u ↔ d

Equiv. Forms

1 - 10
2 - 9
3 - 8

Mirror Image Forms

2 - 3
5 - 6

Summary

3 inact. $\begin{cases}1\ C_{2v}\\ 2\ C_{2h}\end{cases}$

2 act. prs. $\begin{cases}1\ V\\ 1\ C_1\end{cases}$

Self-equiv. Forms

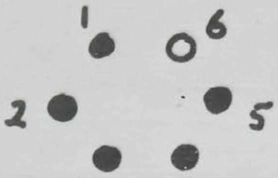
5 V
4 C_{2v}
$\left.\begin{matrix}1\\7\end{matrix}\right\}C_{2h}$

Inact.	Act.
4 C_{2v}	6-5 V
$\left.\begin{matrix}1\\7\end{matrix}\right\}C_{2h}$	2-3 C_1

Plate XXV

n = 5 Penta-Substitution Forms

Plane



Sym. of Skel.

C_{3v}

	1	2	3	4	5	6
	●	●	●	●	●	○
1	d	u	d	u	d	L|
2	u	u	d	u	d	
3	d	d	d	u	d	
4	d	u	u	u	d	L|
5	d	u	d	d	d	cf. 3 |.
6	d	u	d	u	u	cf. 2 |.
7	u	d	d	u	d	
8	d	d	u	u	d	
9	d	u	u	d	d	cf. 8 |.
10	d	u	d	d	u	cf. 7 |.
11	u	u	u	u	d	
12	d	d	d	d	d	L|
13	d	u	u	u	u	cf. 11 |.
14	u	u	d	d	d	
15	d	d	d	u	u	cf. 14 |.
16	u	u	d	u	u	L|

Sym. Operations

⋮ $\begin{cases} 3_u \leftrightarrow 3_d \\ 2_u \leftrightarrow 4_d \\ 1_u \leftrightarrow 6_d \end{cases}$

| $\begin{cases} 3 \leftrightarrow 3 \\ 2 \leftrightarrow 4 \\ 1 \leftrightarrow 5 \end{cases}$

○ u ↔ d.

Equiv. Forms

None

Mirror Image Forms

2-6
3-5
8-9
7-10
11-13
14-15

Self-equiv. Forms

1
4
12
16

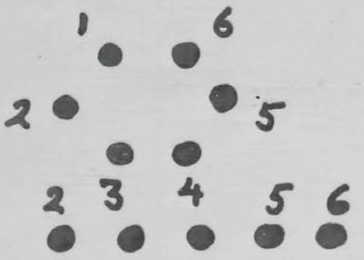
Inact.		Act.	
1	C_s	2-6	C_1
4		3-5	
12		8-9	
16		7-10	
		11-13	
		14-15	

Summary

4 inact. C_s
6 act. prs. C_1

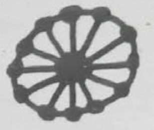
Plate XXVI

$n = 6$ Hexa-Substitution Forms   Plane



	1	2	3	4	5	6	
1	d	u	d	u	d	u	
2	u	u	d	u	d	u	
3	u	u	u	u	d	u	
4	u	u	d	d	d	u	
5	u	d	u	u	d	u	thr.
6	u	u	u	u	u	u	
7	d	d	u	u	d	u	betw.
8	u	d	d	u	d	u	cf 7l.
9	u	d	d	d	d	u	
10	d	d	u	u	u	u	cf. 9

Sym. of. Skel.



D_{6h}

Sym. Operations

● $\begin{cases}1 \leftrightarrow 4\\ 2 \leftrightarrow 5\\ 3 \leftrightarrow 6\end{cases}$ ▼ $$\begin{tikzcd} 1 \arrow[r] & 3 \arrow[r] & 5 \arrow[ll, bend right] \\ 2 \arrow[r] & 4 \arrow[r] & 6 \arrow[ll, bend left] \end{tikzcd}$$

⬢ $1 \to 2 \to 3 \to 4 \to 5 \to 6 \to 1$

thr. $\overset{1}{u} \leftrightarrow \overset{1}{d}$, $\overset{2}{u} \leftrightarrow \overset{6}{d}$ etc.   thr.| $1 \leftrightarrow 1$, $2 \leftrightarrow 6$ etc

betw. $\overset{1}{u} \leftrightarrow \overset{2}{d}$, $\overset{3}{u} \leftrightarrow \overset{6}{d}$ etc.   Betw.| $1 \leftrightarrow 2$, $3 \leftrightarrow 6$ etc.

Equiv. Forms

9 - 10

Mirror Image Forms

7 - 8

Self-equiv. Forms

1 C_{6v}
6 D_{3d}
5 C_{2v}
4 C_{2h}
7 C_2
2, 3, 9 } C_s

Summary

7 inact. $\begin{cases} 1\ C_{6v}\\ 1\ D_{3d}\\ 1\ C_{2v}\\ 1\ C_{2h}\\ 3\ C_s \end{cases}$

1 act. pr. C_2

Inact.	Act.
1 C_{6v}	7-8 C_2
6 D_{3d}	
5 C_{2v}	
4 C_{2h}	
2, 3, 9 } C_s	

Plate XXVII

Summary of Forms and Symmetry

Puckered						Plane			
Inact.		Poss. Act. Prs.		n	Subst.	Inact.		Poss. Act. Prs.	
2	C_s	0	—	1		1	C_s	0	—
0	—	3	2 C_2 1 C_1	2	ortho 1·2	1	C_s	1	C_2
2	C_s	1	C_1		meta 1·3	1	C_s	1	C_2
3	2 C_{2h} 1 C_s	0	—		para 1·4	2	1 C_{2v} 1 C_{2h}	0	—
4	C_s	2	C_1	3	1·2·3	2	C_s	1	C_1
0		8	C_1		[1·2·4 1·2·5]	0	—	4	C_1
4	2 C_{3v} 2 C_s	0	—		1·3·5	2	1 C_{3v} 1 C_s	0	—
0	—	10	4 C_2 6 C_1	4	2·3·4·5	2	C_s	4	2 C_2 2 C_1
8	C_s	4	C_1		2·4·5·6	4	C_s	2	C_1
4	2 C_{2h} 1 C_s 1 C_i	3	1 C_2 2 C_1		1·3·4·6	3	1 C_{2v} 2 C_{2h}	2	1 V 1 C_1
8	C_s	12	C_1	5		4	C_s	6	C_1
10	2 D_{3d} 1 C_{3v} 2 C_{2h} 5 C_s	3	2 C_2 1 C_1	6		7	1 C_{6v} 1 D_{3d} 1 C_{2v} 1 C_{2h} 3 C_s	1	C_2