THE CRYSTAL AND MOLECULAR STRUCTURES OF

SOME ORGANIC COMPOUNDS

by

THOMAS CHUNG-WAI MAK

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Chemistry

The University of British Columbia, Vancouver 8, Canada.

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T.C.W. Mak and J. Trotter: The Crystal Structure of p-Chloronitrobenzene. Acta Cryst., <u>15</u>, 1078 (1962).

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B.Sc.(Hon.), The University of British Columbia

THURSDAY, JULY 18, 1963, at 9:30 A.M. IN ROOM 261, CHEMISTRY BUILDING

COMMITTEE IN CHARGE

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		J.	Trotter	

External Examiner: E.C. Lingafelter University of Washington

THE CRYSTAL AND MOLECULAR STRUCTURES OF SOME ORGANIC COMPOUNDS

ABSTRACT

The crystal and molecular structure of biphenylene has been refined from normal and generalized projections along the c-axis. The gross features of the structure previously determined have been confirmed. A comparison of the measured bond lengths and those calculated by simple resonance theory and by molecular orbital theory indicates that the latter gives a better description of the electron distribution in the molecule. In terms of the Kekulé structures the preferred formulation is that which describes the molecule as a cyclobutane derivative. These conclusions are in agreement with the chemical behaviour of biphenylene and its derivatives.

An adduct formed by passing carbon monoxide into a solution of mercuric chloride in methanol has been shown by X-ray analysis to be methoxycarbonylmercuric chloride. The coordination around the mercury atom is exactly linear, and the molecule is planar, except for the methyl group, whose carbon atom is displaced by 0.39Å from the plane of the other atoms.

A re-examination of the crystal structure of <u>p</u>-chloronitrobenzene has established that the space group is not Pa as previously assigned, but $P2_1/a$ which implies a molecular centre of symmetry. Projections along the aand b-axes indicate that this is achieved by a disordered arrangement of molecules involving random interchange of the positions of the chlorine atom and nitro group.

A series of acenaphthene derivatives has been examined by X-rays, and the crystal and molecular structures of acenaphthenequinone, <u>cis</u>-1,2-acenaphthenediol and <u>cis</u>-1, 2-acenaphthenediol dinitrate determined with precision. In all three compounds the carbon skeleton is planar, and the strain in the <u>peri</u>-ring is almost entirely taken up by valency-angle distortions, both in the <u>peri</u>-ring and in the naphthalene rings. The variation of bond lengths in the aromatic nucleus is similar to that in naphthalene.

The acenaphthenequinone molecule is planar, and the short <u>peri</u>-bonds (average value $1.48\pm0.01_4\text{\AA}$) are indicative of conjugation between the aromatic rings and the carbonyl groups. The C₁-C₂ bond distance of $1.53\pm0.02\text{\AA}$ agrees well with the value reported for acenaphthene.

In cis-1,2-acenaphthenediol the peri-bonds are significantly shortened (mean length $1.48^{\pm}0.01_0$ Å) while the $1.60\pm0.01_4$ Å C₁-C₂ bond distance shows the effect of ring strain and steric repulsion of the non-bonded oxygen atoms. The crystal structure consists of zigzag chains of intermolecular hydrogen bonds formed between molecules related by a screw axis, the intermolecular 0.... 0 distances being 2.72 and 2.70Å.

The C_1-C_2 bond in <u>cis</u>-1,2-acenaphthenediol dinitrate has a length almost identical to that in the diol. There is no bonding between the nitroxy groups, which are planar and inclined at angles of +62.1° and +71.2° to the plane of carbon atoms.

GRADUATE STUDIES

Field of Study: Chemistry	
Crystal Structures	K.B. Harvey
,	J. Trotter
Topics in Physical Chemistry	J.A.R. Coope
	R.F. Snider
Topics in Inorganic Chemistry	Staff
Topics in Organic Chemistry	Staff
Spectroscopy and Molecular Structure	Staff
Quantum Chemistry	J.A.R. Coope
Statistical Mechanics	R.F. Snider
Theoretical Chemistry	R.F. Snider

Related Studies:W. OpechowskiClassical MechanicsW. OpechowskiQuantum MechanicsW. OpechowskiAbstract AlgebraN.J. DivinskyComputer ProgrammingMiss Charlotte Froese

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GENERAL INTRODUCTION

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This thesis is concerned with the X-ray investigation of several compounds of structural interest. It is divided into three parts. In Part I are presented some aspects of crystal symmetry and diffraction theory, and an outline of present practice of structure determination by X-ray methods. The exposition is necessarily brief, and is intended to serve as an introduction for the general reader.

Part II describes the refinement of the crystal and molecular structure of biphenylene, and the determination of the structure of methoxycarbonylmercuric chloride and <u>p</u>-chloronitrobenzene. Adequate computing facilities were not available during the analyses of these compounds; the structure factor calculations were performed on a desk calculator, and Beevers-Lipson strips were used for Fourier summations.

In the fall of 1961, an IBM 1620 computer was acquired by the UBC Computing Centre and shortly afterwards Dr. Ahmed's structure-factor and Fourier programs became available. It was now possible to tackle structures of far greater complexity. A series of acenaphthene derivatives was examined, and the analyses of acenaphthenequinone, <u>cis</u>-1,2-acenaphthenediol, and <u>cis</u>-1,2acenaphthenediol dinitrate are described in Part III.

Structure factor tables for the various compounds are collected together in Appendix I. Appendix II is a summary of the crystallographic data for <u>trans-1,2-acenaphthenediol</u>, <u>trans-1,2-acenaphthenediol</u> dinitrate, and several other organic compounds.

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PART I

.

THEORY AND PRACTICE OF

CRYSTAL-STRUCTURE ANALYSIS

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I. ELEMENTARY CRYSTALLOGRAPHY

A. Crystal Geometry

Geometrical crystallography began when the relations between the plane faces of crystals became a subject for investigation. It was discovered by Steno in 1669 that the angle between corresponding faces on crystals of a pure substance is always constant. It is thus the orientations, and not the sizes, of the faces that are characteristic of the crystal.

The faces of a crystal, and also planes within the crystal, can be described by reference to a set of crystallographic axes which may be any three non-coplanar edges of the crystal, or directions in the crystal. Once the choice of axes is made, some face intersecting all three axes may be chosen as the parametral plane. If a, b and c are its intercepts on the crystal axes, then it is found experimentally that the intercepts of any other face may be expressed as ma, nb, and pc where m, n and p are small integers or infinity. This fact, known as the law of rational intercepts, was first enunciated by Haüy in 1784.

A given crystal plane is commonly denoted by its Miller indices (hk ℓ), which are obtained by expressing the reciprocals of m, n and p as integers without a common divisor. The Miller indices are always small whole numbers for the well-developed faces of a crystal.

According to the set of axes used to describe their faces, crystals are classified into seven systems. These are summarised in Table II.

B. Symmetry of Crystals

A geometrical figure is said to possess symmetry if, by performing on it some movement or symmetry operation such as rotation about an axis, repeatedly if necessary, it can be brought into self-coincidence. The symmetry elements possessed by crystals are listed in Table I with the international symbols devised by Hermann and Mauquin.

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Table I. Symmetry Elements of Crystals

Hassel in 1830 showed that exactly 32 distinctive combinations of these symmetry elements are possible. These constitute the 32 crystal symmetry classes, also known as the 32 point groups since they are made up of a selfconsistent set of symmetry elements which leaves at least one point of the crystal invariant.

The symmetry classes may be divided into seven crystal systems, each of which is characterised by the possession of a minimum number of symmetry elements and referable to a set of crystallographic axes. The general arrangement is shown in Table II with both the Schoenflies and Hermann-Mauguin notations.

	Table II.	The	32	Point	Groups	or	Crystal	Symmetry	Classes
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System	Lattice Constants	Crystal Classes
Triclinic	a≠b≠c ≪≠ <i>β</i> ≠ ૪	l I C _l C _i
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^{\circ} \neq \beta$	$\begin{array}{cccc} 2 & m = \overline{2} & 2/m \\ C_2 & C_5 & C_{2h} \end{array}$
Orthorhombic	a≠b≠c ∝=β=γ=90 ⁰	222 mm2 mmm D ₂ C _{2v} D _{2h}
Tetragonal	a=b≠c ≪=β=¥=90 ⁰	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
Trigonal (Rhombohedral)	a=b=c ∝=β=γ≠90°	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Hexagonal	a=b≠c ∝=β=90°, γ=120°	6 6 6/m 622 6mm 6 m2 6/mmm C ₆ C _{3h} C _{6h} D ₆ C _{6v} D _{3h} D _{6h}
Cubic	$a=b=c \\ \alpha = \beta = \gamma = 90^{\circ}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

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Figure 1. The 14 Bravais lattices.

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C. Space Lattices

The characteristic geometrical form and external symmetry of a crystal point to a regular internal arrangement in which a certain unit of structure is repeated infinitely in space by regular translations. The arrangement of the crystal units may be represented by an orderly three-dimensional array of points known as a space lattice. The lattice points represent the positions occupied by the repeating unit of the crystal pattern, composed of atoms or groups of atoms. Connecting the lattice points by a regular network of line results in a number of identical parallel-sided unit cells. The choice of a unit cell for a given space lattice is dictated by considerations of convenience in visualizing the symmetry and carrying out mathematical calculations. Obviously the space lattice is completely defined by the three non-coplanar vectors representing the unit cell edges. These three basis vectors, usually denoted by \hat{a} , \hat{b} , and \hat{c} , are also referred to as the primitive translations of the lattice.

In 1848 Bravais showed that there are 14 distinct space lattices. Unit cells of the 14 space lattices are illustrated in Figure 1.

D. Space Groups

Since the atomic or molecular arrangement of a crystal is based on an infinite repetitive pattern, the symmetry operations may entail translations. Combination of rotation axes and reflection planes with translations produce two new types of symmetry elements termed screw axes and glide planes respectively. The possible groups of symmetry operations of infinite figures are called space groups, and their total number was shown to be 230 independently by Fedorov, Schoenflies, and Barlow in the latter part of the last century. A detailed account on space-group notation and nomenclature is presented in Vol. I of the International Tables for X-Ray Crystallography (1), where diagrammatic

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and analytic representation of the space groups are also given.

The space group expresses the sum total of the symmetry properties of a crystal, and therefore cannot be established uniquely by a study of external form alone. The basis for space-group determination by X-rays is that the translations of glide planes and screw axes, and the lattice centering present in non-primitive lattices, lead to the extinction of characteristic types of X-ray spectra. Unfortunately this determination is not always unique as, due to Friedel's law, a centre of symmetry is added to the structure in taking the diffraction pattern. It is possible, however, to identify the correct space group among several possibilities from a statistical analysis of the intensity distribution (2), and from other physical tests such as pyro- and piezoelectric measurements.

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II. DIFFRACTION OF X-RAYS BY CRYSTALS

A. Scattering of X-Rays by Electrons and Atoms

An electron in the path of an X-ray beam is forced into oscillation by the periodic varying electric field, and itself becomes a source of electromagnetic radiation of the same frequency and wave length. By this process the electron is said to scatter the original beam.

In an atom the scattered waves from the several electrons combine, and the ratio of the amplitude scattered by an atom at rest to that scattered by a single electron is called the atomic form factor, designated f_0 . Because of the finite size of the atom, interference can occur among waves scattered by different parts of the electron cloud, and f_0 decreases with increasing Bragg angle θ . Mathematically, f_0 is related to the electron distribution in the atom by the formula

$$f_{o} = \int_{0}^{\infty} |\psi|^{2} \frac{\sin kr}{kr} 4\pi r^{2} dr , \qquad (\underline{1})$$

where $k = 4\pi \sin\theta/\lambda$ and ψ is the atomic wave function. Tables of f_0 data have been computed for most common atoms and ions through theoretical calculations, and are conveniently tabulated as a function of $\sin\theta/\lambda$ in Vol.III of the International Tables(1).

B. Conditions for X-Ray Diffraction Maxima

Consider a parallel beam of X-rays impringing on a space lattice defined by the basis vectors $\{\vec{a}_i\}$ (i=1,2,3). The directions of the incident and diffracted beams may be represented by unit vectors \vec{u}_0 and \vec{u} which make angles $\{\alpha_i\}$ and $\{\beta_i\}$ with the lattice directions. From Figure 2, it is clear that the condition for constructive interference is

$$a_i (\cos \beta_i - \cos \alpha_i) = h_i \lambda$$
, (2)

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where the h_i 's are integers. This set of three equations, known as Laue's equations, can be written in vector form:



Figure 2. Scattering from a row of atoms in a lattice direction.



The vector $\vec{S} = \vec{u} - \vec{u_0}$ is known as the diffraction vector. It is in the direction of the bisector of the incident and diffracted beams and has magnitude 2 sin θ (Figure 3).



Figure 4. Relationship between \vec{s} and the plane $(h_1h_2h_3)$.

From equation $\underline{3}$ we deduce that

$$\frac{\vec{a}_{i}}{h_{i}} - \frac{\vec{a}_{j}}{h_{j}} \cdot \frac{\vec{s}}{\vec{\lambda}} = 0, i \neq j, \qquad (\underline{4})$$

, which shows that \vec{s} is normal to the plane of diffraction indices $(h_1h_2h_3)$ (Figure 4). The spacing $d_{h_1h_2h_3}$ of the planes $(h_1h_2h_3)$ is given by

or
$$d_{h_1h_2h_3} = \frac{\overline{a_1/h_1} \cdot \overline{S}}{|\overline{S}|} = \frac{\lambda}{2\sin\theta}$$
, (5)

which is Bragg's equation with the order n absorbed in the integers $\mathrm{h_1h_2h_3}$.

C. The Reciprocal Lattice

For each direct lattice we can define a reciprocal lattice with basis vectors $\{\vec{a}_1^*\}$ such that

$$\vec{a}_{i} \cdot \vec{a}_{j}^{*} = \delta_{ij} \quad (\underline{6})$$

From this fundamental relation it is a simple matter to deduce the following formulae:

$$\vec{a}_{i}^{*} = \frac{\vec{a}_{i} \times \vec{a}_{k}}{V} = \frac{\vec{a}_{j} \times \vec{a}_{k}}{\vec{a}_{i} \cdot \vec{a}_{j} \times \vec{a}_{k}} \quad (i, j, k \text{ in cyclic permutation}),$$
(7)

$$\vec{a}_{i} = \frac{\vec{a}_{j} * x \vec{a}_{k} *}{V *} = \frac{\vec{a}_{j} * x \vec{a}_{k} *}{\vec{a}_{i} * \cdot \vec{a}_{j} * x \vec{a}_{k} *} (" " " "),$$

$$(\underline{8})$$

$$VV* = 1 , \qquad (\underline{9})$$

$$\vec{S} = \sum_{i} (\vec{a}_{i} \cdot \vec{S}) \vec{a}_{i}^{*} = \lambda \sum_{i} h_{i} \vec{a}_{i}^{*} . \qquad (10)$$

If we take $\{\lambda \vec{a}_i^*\}$ as basis vectors in the reciprocal lattice, each vector $\vec{\rho}_{h_1h_2h_3}$ represents a diffraction vector, which in turn represents a set of planes $(h_1h_2h_3)$ in the direct lattice.

The reciprocal lattice provides a simple geometrical picture of diffraction on the basis of the Bragg law, as was first shown by Bernal. The interpretation of equation 5 in the form

$$\sin\theta = \frac{\lambda}{2d_{h_1h_2h_3}} = \frac{|\vec{s}|}{2} = \frac{|\vec{P}_{h_1h_2h_3}|}{2}$$

is obvious from Figure 5. A reciprocal lattice point P which happens to lie on the surface of the sphere of reflection will give rise to a reflection. The basis of most single-crystal techniques is to rotate or oscillate the crystal so that many reciprocal lattice points will be caused to intersect the sphere of reflection (3).

D. The Structure Factor

In general, the waves scattered in any order $hk \ell$ by the atoms in a unit cell differ in phase and must be compounded vectorially. The resultant $F(hk\ell)$ is known as the structure factor and can be expressed as an explicit function of the fractional coordinates of the N atoms in the unit cell:

$$F(hk\ell) = \sum_{j=1}^{N} f_{j} e^{2\pi i (hx_{j}+ky_{j}+\ell z_{j})}$$
(11)

The complex quantity $F(hk\ell)$ is characterised by an amplitude $|F(hk\ell)|$ and a phase $\alpha(hk\ell)$. The structure-factor formula <u>ll</u> is equivalent to the set of equations

$$|F(hk\ell)| = \sqrt{A^{2} + B^{2}},$$

$$\alpha(hk\ell) = \tan^{-1} \frac{B}{A},$$

$$A = \sum_{j=1}^{N} f_{j} \cos 2\pi (hx_{j}+ky_{j}+\ell z_{j}),$$

$$B = \sum_{j=1}^{N} f_{j} \sin 2\pi (hx_{j}+ky_{j}+\ell z_{j}).$$

$$(\underline{12})$$



Figure 5. Diffraction in reciprocal space.

In equations <u>11</u> and <u>12</u> the effect of thermal vibrations of the atoms is taken into account through the relation

$$f = f_0 e^{-Bsin^2\theta/\chi^2}$$
 (13)

where the constant B is equal to $8\pi^2$ times the mean square displacement of the atom in a direction perpendicular to the reflecting plane. In practice B is treated as an empirical parameter and refined in the course of analysis.

E. The Intensities of X-Ray Reflections

A crystal reflects X-rays over a certain angular range in the neighbourhood of the Bragg angle, and when it is turned through the reflecting position with an angular velocity ω , different portions of the crystal are successively brought into the position of maximum reflection. The ratio $E \omega/I_0$, where E is the total energy reflected during a sweep and I_0 the intensity of the primary beam, is found to give a correct measure of the

reflecting power of the crystal and is termed the integrated reflection.

The majority of real crystals appear to have a mosaic block structure, in which tiny crystal fragments of linear dimension $\sim 10^{-5}$ cm. are nearly but not quite aligned. For such a crystal block of volume δV Darwin and others have derived the following relation:

$$\frac{E\omega}{I_{o}} = \left(\frac{Ne^{2}}{mc^{2}}\right)^{2} \wedge^{3} \frac{1+\cos^{2}2\theta}{2\sin^{2}\theta} |F|^{2} \delta V . \qquad (\underline{14})$$

In equation $\underline{14}$ the term e^2/mc^2 arises from the classical formula for scattering by an electron, and N is the number of unit cells per unit volume of the crystal. The trigonometric term takes two factors into account. The polarization factor $(1 + \cos^2 2\theta)/2$ allows for the partial polarization of the reflected beam, while the Lorentz factor $1/\sin 2\theta$ occurs because the reciprocal points pass through the surface of the reflecting sphere at different speeds. For application to crystal specimens expression $\underline{14}$ must be modified according to the experimental conditions, which may introduce a different form for the Lorentz factor. For example, the intensity formula for the equi-inclination Weissenberg method is

$$\frac{E\omega}{I_0} \propto \frac{1+\cos^2 2\theta}{\xi \cos \theta} A(hk\ell) |F|^2 , \qquad (15)$$

where ξ is the cylindrical coordinate of the reciprocal lattice point. The transmission factor A(hkl) is introduced to allow for absorption in the crystal, and has the form

$$A = \frac{1}{V} \int_{V} e^{-\mu t} dV , \qquad (\underline{16})$$

where t is the total path length of the X-rays reflected from an element dV, and μ and V are respectively the linear absorption coefficient and volume of the crystal. Evaluation of this integral is in general difficult,

and values for specimens of simple shapes are tabulated as a function of Θ in the International Tables(1).

Two other factors arise when the crystal does not conform to the ideally imperfect structure. The perfect block of the mosaic may be so large that the upper layers screen the lower ones in the same block an effect known as primary extinction. Secondary extinction refers to the screening of the lower blocks by the upper blocks. Both types of extinction cause a significant diminution of intensity of the strongest reflections. Extinction corrections are usually neglected in crystalstructure analysis, and are included only when their magnitudes are suspected of being large.

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F. Representation of the Crystal as a Fourier Series

The periodic distribution of electron density in a crystal may be represented by a triple Fourier series

$$g(xyz) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} C(hk\ell)e^{-2\pi i(hx+ky+\ell_z)}$$

The Fourier coefficients $C(hk\ell)$ can be readily shown to be equal to $F(hk\ell)/V$. Thus

For convenience in calculation the structure factor is replaced by its amplitude and phase. In accordance with Friedel's law, $|F(hk\ell)| = |F(\bar{h}\bar{k}\bar{\ell})|$, so that equation <u>17</u> becomes

$$g(xyz) = \frac{1}{V} \sum_{\substack{h=\\ -\infty}}^{\infty} \sum_{\substack{k=\\ -\infty}}^{\infty} \sum_{\substack{\ell=\\ -\infty}}^{\infty} |F(hk\ell)| \cos \left[2\pi (hx+ky+\ell z) - \mathscr{A}(hk\ell)\right]. (\underline{18})$$

In a centrosymmetric crystal the value of the phase angle is restricted to

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O or $\mathcal T$, and so the electron-density expression is simplified to

$$g(xyz) = \frac{1}{V} \sum_{\substack{h=\\ -\infty}}^{\infty} \sum_{\substack{k=\\ -\infty}}^{\infty} \sum_{\substack{\ell=\\ -\infty}}^{\infty} \frac{1}{V} \left[F(hk\ell)\right] \cos 2\pi (hx+ky+\ell z) \quad (\underline{19})$$

G. The Phase Problem

Equations <u>18</u> and <u>19</u> illustrate the 'phase problem' of X-ray crystallography. The structure amplitudes can be determined experimentally, but the relative phases are lost in taking the X-ray pattern and must be recovered by indirect means.

An infinite number of electron-density distributions may be obtained by assigning arbitrary phases to the structure amplitudes. However, the number of possible phase combinations is greatly reduced by the requirement that g(xyz) must be everywhere non-negative and composed of spherically symmetric atomic functions, and that the structure postulated is chemically reasonable. In fact, a set of phases which satisfies the above criteria is almost certainly the correct one. Some of the more important methods of solving the phase problem are outlined in section III-C.

III. THE DETERMINATION OF CRYSTAL STRUCTURES

A. Two-Dimensional Projections

The summation of the triple Fourier series <u>18</u> is extremely laborious. Furthermore the collection and calculation of all $F(hk\ell)$'s involve a great deal of work. It is usual therefore to project the structure onto two or more axial planes using a double series, which can be computed from zonal data of the type F(hkO). Except for very complex structures, two-dimensional projections are sufficient to yield a fairly accurate set of atomic coordinates, expecially when special precautions to eliminate errors are taken (section III-D).

B. The Interpretation of Diffraction Patterns

The determination of the spatial relationships of the atoms in a crystal proceeds in five stages:

(a) Determination of Unit Cell Parameters and the Space Group.

- (b) Collection of Intensity Data.
- (c) Determination of the Structure.
- (d) Refinement of Atomic Parameters.
- (e) Assessment of Accuracy.

Stages (a) and (b) constitute the routine part of a crystal-structure investigation, and are described in detail in a number of treatises(3). In the paragraphs that follow, stages (c), (d) and (e) are given a brief discussion.

C. Methods for Obtaining an Approximate Structure

The various methods for solving the phase problem are conveniently classified into three categories; in general no one method is certain to lead to the correct structure.

(a) Trial and Error Methods. In these methods crystallographic, physical and chemical knowledge are combined to arrive at a trial structure which gives reasonable agreement between the observed and calculated structure amplitudes. A good indication of the correctness of the postulated structure is that the discrepancy factor, defined as $R = \sum_{i=1}^{n} |F_{o_i}| - |F_{c_i}| / \sum_{i=1}^{n} |F_{o_i}|$, should be about 0.5 and 0.4 for centrosymmetric and non-centrosymmetric space groups respectively(4). Leaving out terms for which agreement is poor, the calculated phases and the measured amplitudes are used in a Fourier synthesis, which leads to a revised set of atomic coordinates. This iterative process is repeated until all observed reflexions can be included in the series summation.

(b) Heavy-Atom and Patterson Methods. If the crystal contains an atom of high scattering power situated at a known position, it may determine a sufficient number of phases for a Fourier synthesis to reveal the lighter atoms. Sometimes it is possible to replace such a heavy atom by another at the same position without disturbing the essential nature of the structure, so that the phase relationships can be determined from a difference effect. The heavy-atom and isomorphous replacement methods are beautifully exemplified by Robertson's determinations of the structures of the phthalocyanines(5).

In an organic structure the position of the heavy atom is rarely fixed by symmetry, and a general method is needed for its location. In 1934Patterson(6) showed that the function

$$P(xyz) = \frac{1}{V^2} \sum_{\substack{h=\\ -\infty \end{array}}^{\infty} \sum_{\substack{\ell=\\ -\infty \end{array}}^{\infty} \sum_{\substack{\ell=\\ -\infty \end{array}}^{\infty}} \left| F(hk\ell) \right|^2 \cos 2\pi (hx+ky+\ell z) , \qquad (\underline{20})$$

which can be computed directly from observed data, represents a density distribution such that the vectors from the origin to the maxima correspond to vectors between all possible pairs of atoms in the crystal. Systematic procedures have been developed to derive the atomic positions from this vector distribution(7). The weight of a Patterson peak is the product of the atomic numbers of the two atoms involved, so that the method can be

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applied most successfully to structures containing heavy atoms.

(c) Direct Mathematical Methods. These methods seek to determine the phases directly from the structure amplitudes alone. The Harker-Kasper inequalities(8), derived by application of Schwarz and Cauchy inequalities to modified structure amplitudes, impose certain restrictions on the phases due to crystal symmetry. Further developments (9), based upon the limiting conditions that $\rho(xyz) \ge 0$ and is a superposition of discrete atomic functions, furnish completely general systems of inequalities as well as equalities. Sign relations between structure factors in centrosymmetric space groups have been derived by Sayre(10), Cochran(11), and Zachariasen(12). The latest development is the statistical approach of Hauptmann and Karle(13), which provides expressions for the probability of a structure factor being positive or negative.

D. Refinement Procedures

The principal methods for crystal-structure refinement are outlined in the following sections.

(a) F_0 Synthesis. Atomic parameters obtained from successive Fourier synthesis are affected by (i) errors in cell dimensions; (ii) inaccurate F_0 values; (iii) round-off errors in computation; (iv) termination of the Fourier series while the remaining coefficients are still appreciable; and (v) thermal motion of the atoms. The differential synthesis of Booth(14), which locates the atoms exactly at the electron-density maxima, is subject to the same sources of error. The effect due to series-termination is serious; it may be allowed for by computing a F_c synthesis separately and applying back-shift corrections to the atomic coordinates (15).

(b) Method of Least Squares. This procedure was first used by Hughes(16) to find the atomic parameters which give the best fit to the set of F_0 's.

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The function minimized is $\sum w(|F_0| - |F_c|)^2$, where w is a weighting factor. To each observed reflection there corresponds an observational equation, and the set of equations can be normalised and solved for the coordinate shifts. Refinement by least squares is free from series-termination errors; it is also possible to include individual isotropic or anisotropic temperature factors and a scale factor in the refinement process.

(c) Difference Synthesis. The function

$$\mathbb{D}=\mathcal{G}_{O}-\mathcal{G}_{C} = \frac{1}{V} \sum_{h=1}^{\infty} \sum_{k=1}^{\infty} \sum_{\ell=1}^{\infty} \left(|\mathbf{F}_{O}| - |\mathbf{F}_{C}| \right) \cos \left[2 \mathcal{T}(hx+ky+\ell z) - \alpha(hk\ell) \right] \quad (\underline{21})$$

was first suggested by Booth(17) as a device for refinement and its properties were fully exploited by Cochran(18). An atom of the proposed structure which deviates slightly from its true position lies on a steep slope of the difference map. From Figure 6 it is clear that the atom should be shifted up the gradient. The displacement is given by

$$\Delta r = \frac{\partial D/\partial r}{\partial^2 S_0/\partial r^2} = \frac{\partial D/\partial r}{\partial r} , \qquad (22)$$

where \uparrow is a constant in the approximation $f = f_0 e^{-\uparrow r^2}$ for the electron density at a distance r from the centre of an atom. Refinement by $(F_0 - F_c)$ synthesis automatically eliminates series-termination errors; it furnishes valuable information about the thermal motion of the atoms, and can be used to locate hydrogen atoms.



Figure 6. Effect of a small error in atom location on D.

(d) Generalised Projections. Frequently only one clear projection of a structure, say, on (OlO), can be obtained. Without utilizing the complete $(hk\ell)$ data, approximate y-coordinates can be deduced from the Kth layer data by the method of generalised projections due to Cochran and others(19).

The expression for a structure factor belonging to the Kth layer is

$$F(hK\ell) = \sum_{j} \left\{ f_{j}(hK\ell)e^{2\pi iKy_{j}} \right\} e^{2\pi i(hx_{j}+\ell z_{j})}.$$

When the zero and Kth layers are close together, $f_j(hK\ell) \simeq f_j(hO\ell)$ so that the generalised projection

represents a projection of the structure on (OlO), with the electron density at the jth atom modified by a factor $e^{2\pi i Kyj} = \cos 2\pi Kyj + i \sin 2\pi Kyj$. Thus yj can be deduced from $2\pi Kyj = \tan^{-1} S_K/C_K$.

Elimination of series termination errors can also be achieved by the use of (F_O-F_C) Fourier coefficients. The resulting difference cosine and sine generalised projections, C_K^D and S_K^D , are used to refine the x, y, z and B parameters simultaneously in the following expressions (20):

$$\mathcal{G}_{K,o} \sin 2\pi K(y_o - y_c) = S_K^D \cos 2\pi K y_c - C_K^D \sin 2\pi K y_c , \qquad (24)$$

$$\Delta r = \frac{\partial}{\partial r} \left(s_{K}^{D} \sin 2\pi K y_{c} + c_{K}^{D} \cos 2\pi K y_{c} \right) / 2\hbar g_{K,o} , \qquad (25)$$

$$\mathcal{G}_{K,o} \cos 2\pi K(y_o - y_c) - \mathcal{G}_{K,c} = S_K^D \sin 2\pi K y_c + C_K^D \cos 2\pi K y_c . \qquad (\underline{26})$$

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E. Assessment of Accuracy

Cruickshank, among others, has investigated the standard deviation in the electron density and in atomic positions(21). His results are

$$\sigma(\varsigma_0) = \frac{1}{\nabla} \left\{ \sum \left(|\mathbf{F}_c| - |\mathbf{F}_c| \right)^2 \right\}^{\frac{1}{2}}$$
 (27)

and
$$\sigma_{j}(x) = 2\pi s \left\{ \sum h^{2} (|F_{o}| - |F_{c}|)^{2} \right\}^{\frac{1}{2}} / aVC_{jx}$$
 (28)

with similar expressions for the y and z coordinates. Here s has values 1 and 2 for centrosymmetric and non-centrosymmetric structures respectively, and $c_{jx} = \frac{\partial^2 g_c}{\partial x^2}$ is the curvature at the centre of the jth atom.

The standard deviation of the bond distance between two atoms is given by the relation

$$\sigma^{2}(d_{12}) = \sigma_{1}^{2} + \sigma_{2}^{2} , \qquad (\underline{29})$$

where σ_1 and σ_2 are the standard deviations of the positions of the atoms in the direction of the bond.

Two bond lengths measured as d_A and d_B differing by an amount δ will have a probability

$$P = \frac{1}{2} - \frac{1}{2} \operatorname{erf} \left(\frac{\delta}{\sqrt{2} \sigma_{AB}} \right) ; \sigma_{AB}^{2} = \sigma_{A}^{2} + \sigma_{B}^{2}$$
(30)

of being observed differently because of experimental errors. Cruickshank(21) has suggested the following subdivision of significance:

Comparison of δ and \mathcal{O}_{AB}	Р	Significance of observed bond length difference
$\delta \leq 1.645 \sigma_{AB}$	5% or greater	not significant
1.645 0 ≤6≤2.327 0 AB	5% - 1%	possibly significant
2.327 7AB<8<3.090 7AB	.1% - 0.1%	significant
3.090 𝒫 _{AB} ≥ δ	0.1% or less	highly significant
The standard deviation of an angle θ between two bonds d_{12} and d_{23} is given by

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$$\sigma^{2}(\theta) = \frac{\sigma_{1}^{2}}{d_{12}^{2}} + \frac{\sigma_{3}^{2}}{d_{23}^{2}} + \sigma_{2}^{2} \left(\frac{1}{d_{12}^{2}} - \frac{2\cos\theta}{d_{12}d_{23}} + \frac{1}{d_{23}^{2}}\right) . \quad (\underline{31})$$

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PART II

THE CRYSTAL AND MOLECULAR STRUCTURES OF BIPHENYLENE, METHOXYCARBONYLMERCURIC CHLORIDE, AND

p-CHLORONITROBENZENE

I. BIPHENYLENE

. A. Introduction

The structural formula (I) of this hydrocarbon was first given in 1901 by Niementowski(22), who used the name biphenylene. This name is now adopted by most American chemists, although European workers generally prefer the name diphenylene. The carbon atoms are numbered as shown in formula (I).

Biphenylene is of interest to both theoretical and organic chemists since it is the only stable derivative of the elusive cyclobutadiene. The synthesis, chemistry and structure of this unusual compound have been the subjects of many studies, and several reviews have been published (23). <u>Synthesis</u>. Genuine biphenylene was first synthesised by Lothrop(24) in 1941 by the distillation of 2,2'-diiodobiphenyl (II) or biphenylene-2,2'-iodonium iodide (III) with cuprous oxide. This synthesis has since been improved (25) and several other methods of preparation are now available (26), of which the most interesting is that due to Wittig and Pohmer. They showed that



<u>o</u>-bromofluorobenzene reacted with lithium almalgam in ether to give biphenylene and triphenylene(IV) with yeilds of 24% and 3% respectively. The reaction is

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thought to proceed via the reactive intermediate benzyne (V).

The Structure of Biphenylene. As evidence for the structure (I), Lothrop cited analytical data for the hydrocarbon and its picrate, molecular weight determinations in benzene and in camphor, oxidation to phthalic acid by chromic acid, reduction to biphenyl by hydrogenation over red-hot copper, and formation of the same compound, namely 2,7-dimethylbiphenylene (VI), by the pyrolysis of both 5,5'-dimethyl (VII) and 4,4'-dimethyl (VIII)-biphenylene -2,2'-iodonium iodides. However, it was soon pointed out by Baker (27) that such evidence did not exclude the possibility that the hydrocarbon was actually benzopentalene (IX), the formation of which could be explained by



assuming a free-radical mechanism. This view was supported by Coulson(28) who deduced that the strain energy of biphenylene was much higher than that of benzopentalene (~100 versus a few kcal./mole), while the resonance energies were about the same (90 and 86 kcal./mole, respectively). The structure was finally settled in 1943 by the electron diffraction studies of Waser and Schomaker(29), which established the dibenzocyclobutadiene formulation conclusively. Further confirmation of the structure was provided by an X-ray crystallographic analysis by Waser and Lu(30). These structural determinations indicated that the C-C bonds in the six-membered rings had an average length of 1.39 $\stackrel{o}{A}$, and that the bonds joining these rings were significantly longer (1.46 $\stackrel{o}{A}$), but the measurements were not sufficiently accurate to detect the finer details of bond-length variation in the molecule.

<u>Cyclobutadienoid Character</u>. Despite the very considerable angular strain, the four-membered ring in biphenylene is remarkably inert towards a variety of reagents, and can be cleaved only by catalytic reduction. Biphenylene undergoes many of the typical aromatic substitution reactions, including nitration, sulphonation, halogenation, mercuration, acetoxylation, and the Friedel-Crafts reaction (31). Monosubstitution occurs exclusively at position 2, in agreement with the theoretical predictions of Brown(32) and of Fernández Alonso and Domingo(33). Experiments on disubstitution of biphenylene (31) have shown that a <u>meta</u>-directing substituent such as the acetyl group (X) at position 2 directs the second substituent into position 6 by a resonance effect involving both six-membered rings, and it appears therefore that there is some cyclobutadienoid character about the central four-membered ring.



Positions 1,3,5,7 are deactivated; position 6 is β , and hence more reactive than position 8 which is α .

Interaction between the outer rings is also indicated by the ultraviolet spectrum (34), which shows two main regions of absorption: a high-intensity band at 235-260 mu corresponding to the lone intense band of biphenyl at 250 m μ ,

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and a second band of lower intensity in the region 330-370 mµ attributable to some conjugation between the rings.



Molecular centre of symmetry shown by X-ray crystal data.

On the other hand, recent attempts to prepare π -complexes of biphenylene (35) have succeeded only in getting the benzene type such as μ -biphenylenebis(tricabonylmolybdenum) (XI). The ability of biphenylene to form coordination compounds using each six-membered ring independently, but not the four-numbered ring system, is consistent with the preferred bond structure (XIIa) in which there is little or no cyclobutadienoid character in the central ring.

The foregoing evidence provides different answers to the question regarding the extent of interaction between the benzene rings. A direct and more quantitative measure of cyclobutadienoid character in biphenylene would be the mean length of the central bond 9-10, but unfortunately the uncertainty in the value 1.46 ± 0.05 Å determined by electron diffraction (29) makes it difficult to draw definite conclusions.

<u>Bond Structure</u>. For biphenylene five Kekulé structures may be drawn, one of which (XIIa) represents it as a derivative of cyclobutane, two (XIIb and XIIc) as a cyclobutene, and two (XIId and XIIe) as a cyclobutadiene. Simple resonance theory, with the five canonical forms contributing equally to the



hybrid molecule, shows that the 1-2 bond has more double-bond character than the 2-3 bond, and hence an <u>ortho,para</u>-activating group in position 2 should direct an entering substituent into position 1. This prediction is at variance with that drawn from molecular-orbital calculations which indicate that the second substituent should be directed into position 3 (36). Recently it has been shown that bromination of 2-acetamidobiphenylene gives 2-acetamido-3-bromobiphenylene (37), and that 2-aminobiphenylene couples with benzenediazonium chloride at the 3-position (38). In valence-bond terminology these results imply that the preferred Kekule structure of biphenylene is (XIIa).

Since the two theories also predict different bond-length variations for biphenylene, it should be possible to decide between them by an accurate measure of the bond distances. The present research is concerned with the determination of these distances by a detailed X-ray examination of the crystalline material.

B. Experimental

All the crystals in the original sample of biphenylene were twinned on (100), but well-formed single crystals were obtained by recrystallization from propan-l-ol (cf.ref.30). These consisted of pale yellow prisms elongated along the c-axis. The density was determined by flotation in aqueous potassium iodide. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of crystals rotating about the b- and c-axes, holl, hkO, hkl, and hk2 Weissenberg films. No

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precautions were taken to prevent the crystals volatilizing, so that they disappeared in a few days.

<u>Crystal Data</u>. Biphenylene, $C_{12}H_8$; M=152.2; m.p.110°C. Monoclinic, a = 19.66±0.06, b=10.57±0.04, c=5.85±0.01Å, β =91.0±0.5°. U=1215.5Å. $D_x(\text{with } Z=6) = 1.240$, $D_m=1.24g.\text{cm}^3$ Absorption coefficient for X-rays, $\gamma = 1.5418A$, $\mu = 6.46 \text{ cm}^{-1}$ F(000)=480. Absent spectra: hole when h is odd, OkO when k is odd. Space group is $P2_1/a-C_{2h}^{-5}$.

The intensities of the hkO and hkl reflexions were recorded on Weissenberg photographs for a crystal rotating about the c-axis, the equiinclination method being used for the upper level. CuK_X radiation was used, with multiple-film technique (39) to correlate strong and weak reflexions. The intensities were estimated visually, the range being about 5000 to 1. The values of the structure amplitudes were derived by the usual formulae for a mosaic crystal, the absolute scale being established later by correlation with the calculated structure factors. No absorption corrections were applied. 65 independent hkO reflexions with h=3n were observed (see below for discussion of "h=3n rule"), representing 71% of the total number of these reflexions theoretically observable with CuK_X radiation, but only 36 very weak reflexions with h≠3n were observed (about 20% of the possible number). 206 hkl reflexions were recorded, representing about 40% of the possible number observable.

C. Structure Analysis

[001] Projection

Since there are six molecules in the unit cell, two of them must be situated at centres of symmetry at 000 and $\frac{11}{22}$ 0, and the other four in general positions. As pointed out by Waser and Lu (30), the hk0 reflexions exhibit a distinctive feature, being very weak unless h=3n, and

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this "h=3n rule" requires that to a first approximation the atoms are grouped in threes with coordinates (x,y,z), $(\frac{1}{3} + x,y, r+z')$, $(\frac{1}{3}-x,\overline{y}, r-z')$, where z'= $\pm z$, and r is the z coordinate of the centre of a molecule which is in a general position. Waser and Lu obtained values for all the parameters from a consideration of the molecular Fourier transform, and from various trials.

Structure factors were calculated for the hkO reflections with h=3n (those with h=3n necessarily have zero calculated value), by using the x and y parameters given by Waser and Lu, with the scattering factor for carbon of Berghuis <u>et al</u>(40), with B=4.8 A2 . The discrepancy factor for the observed reflexions was R=0.204. Refinement proceeded by computing Fourier and difference syntheses, and adjusting the positional parameters. After one cycle R had been reduced to 0.182.

Further refinement then required consideration of planes for which $h \neq 3n$. The "h=3n rule" had been very useful in establishing the correct trial structure in the first instance, but at this stage of the analysis it proved troublesome, since it was very difficult to decide just what the small deviations of atomic positions were which gave rise to the observation of hkO reflexions with $h \neq 3n$. These reflections were all so weak that it was impossible to deduce from the magnitudes of these structure factors what small displacements were involved. Refinement of the hkO data was therefore terminated at this point, and attention was turned to the hkl zone in which there are no systematically weak reflexions.

The positional parameters at this stage of the analysis are listed in the second and third columns of Table III, and the measured structure factors, F_0 , are compared with the calculated values, $F_c(1)$, in Table A-1 (R=0.182). An electron-density projection along the c-axis, computed with measured structure amplitudes and calculated signs for h=3n reflexions only, is shown in Figure 7.

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Figure 7. (a) Electron-density projection along [001], computed with h=3n planes only. Contours at intervals of l e.A⁻², with the one electron line broken.

(b) Numbering of the carbon atoms.

hkl Refinement

Since no resolution of the individual atoms could be expected in projections down the a- and b-crystal axes, the problem of finding the z coordinates and of refining the y and x parameters further was approached by considering the hkl structure factors. Structure factors were calculated for these reflexions by using the x,y and B parameters from the hkO refinement and the z coordinates given by Waser and Lu. The discrepancy factor was 0.248. Refinement proceeded by computing cosine and sine difference generalised projections, refining all three positional parameters x, y, z, and the isotropic temperature parameters, B, simultaneously. The first set of difference maps indicated small shifts in x and y parameters, the new coordinates violating the "h=3n rule"; a reduction of B to 4.5^{02}_{A} for all atoms; and slightly larger z-coordinate shifts (maximum 0.09\AA). Structure factors were recalculated, and the R value had been reduced to 0.200. A second set of difference generalised projections were computed, but no further significant changes in parameters were indicated. Measured and calculated hkl structure factors are listed in Table A-2.

Structure factors were then calculated for all the hkO reflexions with the parameters determined from the hkl refinement, and these calculated values, $F_c(2)$, are compared with $F_c(1)$ and F_o in Table A-1. For the reflexions with h=3n, the R value had been reduced from 0.182 to 0.145, a significant improvement. For the h≠3n reflexions the $F_c(2)$ values differ from zero, and hence compare better with F_o than do the $F_c(1)$ structure factors, but there is no real quantitative agreement. In general the calculated values are too low, indicating that further deviations from the idealised h=3n positions are probably necessary. In addition, inclusion of other factors which have not been considered, such as thermal anisotropy, would probably help to improve

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the agreement.

Any further refinement would have to utilize the complete three-dimensional data, and since adequate computing facilities were not yet available, refinement was not carried any further, the final parameters being taken as those determined from the hkl generalised projections.

Table III.	Positional	Parameters
------------	------------	------------

	hkO,	h=3n	· I	Final, from 1	nkl	
Atom	x	У	x	У	Z	∆(Å)
l	0.0300	0.0072	0.0294	0.0047	-0.146	-0.011
2	0.0765	0.0000	0.0743	-0.0007	-0.318	+0.026
3	0.1236	-0.1001	0.1237	-0.1006	-0.302	-0.008
4	0.1275	-0.1750	0.1250	-0.1782	-0.117	-0.022
·5	0.0810	-0.1695	0.0821	-0.1696	0.062	+0.015
,6	0.0314	-0.0677	0.0313	-0.0690	0.045	· +0. 035
7	0.3633	0.0072	0.3637	0.0050	0.587	-0.025
8	0.4098	0.0000	0.4081	0.0008	0.753	+0.027
9	0.4569	-0.1001	0.4585	-0.1013	0.729	-0.021
10	0.4605	-0.1750	0.4619	-0.1731	0.541	~+0.02 4
11	0.4140	-0.1695	0.4142	-0.1675	0.364	-0.028
12	0.3647	-0.0677	, 0.3665	-0.0700	0.393	+0.006
13	0.3033	-0.0072	0.3048	-0.0035	0.282	+0.034
14	0.2568	0.0000	0.2599	0.0012	0.113	-0.012
15 [,]	0.2097	0.1001	0.2092	0.0999	0.137	+0.009
16	0.2058	0.1750	0.2058	0.1748	0.326	-0.017
17	0.2523	0.1695	0.2529	0.1684	0.511	+0.001
18	0.3019	0.0677	0.3042	0.0682	0.478	+0.001

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123

93 124

126 85

123

125

93/19

2

1<u>+</u>8

E 3

Coordinates, Molecular Dimensions, and Orientation

The final positional parameters of the carbon atoms are listed in Table III, x,y,z being coordinates referred to the monoclinic crystal axes and expressed as fractions of the unit-cell edges.

The coordinates of the atoms in each molecule can be fitted to an equation of the form $\ell X' + mY + nZ' + p=0$, where X', Y, Z' are coordinates expressed in $\stackrel{O}{A}$ and referred to orthogonal axes a, b, and c'. The equations of these mean molecular planes are:

Molecule I (atoms C_1-C_6 and $C_1'-C_6'$):

0.6109X' + 0.6353Y + 0.4718Z' = 0.

Molecule II (atoms C₇-C₁₈):

0.6035x' + 0.6582x - 0.4500z' - 2.8008 = 0.

The deviations of the atoms from these planes are listed in the last column of Table III.

The bond lengths and valency angles, calculated from the final x,y,z coordinates of Table III, are shown in Figure 8. The mean values of the distances and angles, with symmetry mmm assumed (this assumption is discussed below), are shown in Figure 9.



Figure 9. Mean bond disatances and valency angles.

The orientations of the molecules in the crystal are given in Table IV, where χ_{L} , ψ_{L} , ω_{L} ; χ_{M} , ψ_{M} , ω_{M} ; and χ_{N} , ψ_{N} , ω_{N} are the angles which the molecular axes L, M (see Figure 9) and the plane normals N make with the orthogonal axes a, b, and c'. The axes L were taken through the molecular centre and the mid-point of bond 3-4 for molecule (I), and through the midpoints of bonds 9-10 and 15-16 for molecule (II); and axes M through the molecular centre and the mid-point of 1-6', and through the mid-points of bonds 12-13 and 18-7. L, M, and N are thus not accurately mutually perpendicular, the angles being $\angle IM=90.6^{\circ}$, $\angle MN=91.9^{\circ}$, and $\angle IN=93.2^{\circ}$ for molecule (I), and 88.6°, 88.6°, 90.6° for the corresponding angles for molecule (II). The orientation angles differ from those given by Waser and Lu by a maximum of 5.3°, and a mean of 2.1°.

Table IV. Orientation of Molecules in the Unit Cell

	Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)	Molecule (I)	Molecule
$\varkappa_{\rm L}$	40.9 ⁰	37.2°	× _M	90.9 ⁰	92.0° × _N	523 ⁰	127.1°
ψ_{L}	122.4º	117.9°	\mathscr{V}_{M}	55.1 ⁰	55.8° \mathcal{V}_{N}	50.60	131.2 ⁰
ω _L	112.1 ⁰	67.6°	ω _м	145.1°	34.2° ω _N	61.8°	63.3 ⁰

Standard Deviations

The standard deviations of the atomic positions were calculated from Cruickshank's formulae. The mean values for all the atoms are $\sigma(x) = \sigma(y) = \sigma(z) = 0.022$ Å, so that the standard deviations of the individual bond distances are 0.031Å. This value may be compared with the root mean square deviation of the individual bond lengths from the mean distances, which is 0.043Å.



Figure 10. Projection of the structure along [001], showing the shorter intermolecular contacts.

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Intermolecular Distances

All the intermolecular separations correspond to normal van der Waals interactions. The shorter contacts are illustrated in Figure 10.

General Structure

Both of the crystallographically independent biphenylene molecules in the asymmetric crystal unit are completely planar within the limits of experimental error, the maximum deviation from the mean planes being 0.035\AA° and the root mean square deviation 0.02\AA , in comparison with a standard deviation in atomic coordinates of 0.02\AA° .

On the basis of the standard deviations of the measured bond distances $(0.03^{\circ}A)$, some of the differences between chemically identical but crystallographically distinct bonds are significant, particularly the large discrepancy between bonds 7-8 and 17-18. However, detailed examination of all the bond distances (Figure 8) indicates that in general bonds parallel to 7-8 all have rather short measured distances, while those parallel to 17-18 are much longer. This suggests that there are systematic errors in molecular orientation.

Since it was considered that these differences between chemically similar bonds could scarcely be real, mean values were obtained by assuming symmetry mmm-D_{2h} for the molecule. The root mean square difference between the individual bond distances and the corresponding mean values is 0.04Å, a little greater than the estimated standard deviation of bond length. Fortunately there are six independent estimates for bonds of type B and C, and three independent measurements for bond A, D, and E, so that the mean distances are considerably more accurate than the individual measurements. The standard deviations of the mean bond distances, estimated from the root mean square deviations of the individual lengths from the corresponding mean values, are: 0.01Å for bonds A, D, and E; 0.02Å for bond B; and 0.03Å for bond C.

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The mean values of the bond angles indicate that there are deviations from 120° in the six-membered rings, but that the angles in the four-membered ring do not differ significantly from 90° .

Table V. Measured and Calculated Bond Lengths ($\hat{\lambda}$)

						A	В	C	D	Е
					Measured:	1.35	1.42	1.38	i.38	1.52
Vale	ence-B	ond The	ory							
	Weig	hts of	Kekulé	é stru	ctures(XII))				
	(a)	(Ъ)	(c)	(đ)	, (e)					
a	l	l	l	l	1	1.41	1.38	1.41	1.41	1.45
<u>b</u>	l	· 1	l	l	0	1.39	1.39	1.39	1.39	1.53
<u>c</u>	4	2	2	l	l	1.38	1.41	1.38	1.43	1.48
<u>d</u>	4	2	2	-1	0	1.37	1.42	1.37	1.42	1.53
e	2	l	l	0	0	1.36	1.44	1.36	1.44	1.53
<u>f</u>	l	.0	0	0	0	1.34	1.53	1.34	1.53	1.53
Mole	ecular	-Orbita	l Theo	ory						
g						1.38	1.40	1.38	1.41	1.47
<u>h</u>						1.39	1.41	1.39	1.41	1.47
<u>i</u>						1.39	1.40	1.39	1.41	1.53

D. Discussion

Bond lengths calculated from simple resonance theory, with the five Kekulé structures given equal weight, are those listed for model <u>a</u> (Table V). In deriving these distances, the double-bond character was correlated with bond length by using a curve based on the points (0, 1.527Å), (0.33, 1.421Å), (0.50, 1.392Å), and (1.00, 1.339Å). This is similar to the original correlation curve given by Pauling(41) except for a small change in the value used for the single-bond distance. Coulson(42) has suggested that the usual 1.54Å singlebond length observed in diamond and in aliphatic molecules (sp³ hybrid orbitals) should be reduced to 1.50Å in aromatic molecules to allow for the change to sp^2 -hybridization. Recent accurate measurements (43) of the lengths of formally single bonds in quaterrylene suggest, however, that the pure single-bond distance in polynuclear aromatic hydrocarbons is greater than 1.50Å, and the mean value for the six single bonds in quaterrylene was therefore used in derving the correlation curve.

There are marked discrepancies between these bond lengths predicted by the simplest resonance theory and those observed. The predicted lengths of bonds A, B, C vary in the order long-short-long, and this is just the opposite of the measurged order.

Molecular-orbital calculations for biphenylene were first carried out twenty years ago (29), and the calculated bond distances (model <u>g</u>) do not differ significantly from those (model <u>h</u>) of a more recent calculation (44). Model <u>i</u> has been derived from the calculated bond orders (44) by using a correlation curve passing through the usual points (0.525, 1.42_1 Å), (0.667, 1.39_2 Å) and (1.000, 1.33_9 Å), and extrapolated to lower bond orders. The agreement between measured and calculated distances is much more satisfactory than for the simple valence-bond method, the variation of the predicted bond distances A, B, C being in the same order as the observed variation.

The measured bond lengths then are in agreement with the chemical reactivity in suggesting that the molecular-orbital method gives a better estimation of the electron distribution in the molecule than does simple resonance theory. In terms of the Kekulé structures, it appears that all five do not contribute equally to the hybrid molecule, but that the preferred structure is (XIIa). The bond distances for (XIIa) (model f) obviously represent too severe a fixation of double and single bonds, and by varying the weights (Table V) best agreement is obtained for model <u>d</u>, that is with maximum weight given to the cyclobutane formulation (XIIa), less weight to the cyclobutene structures (XIIb and XIIc), and only a little weight to the cyclobutadiene structures.

It is apparent that in all the models bond D has calculated values which are considerably greater than the measured distance. Now in all the bondlength calculations, no account has been taken of the strain introduced in forming the four-membered ring; it might be recalled that the correct molecular structure was previously discounted (27, 28) because of the high value expected for this strain energy. The distortion involved in decreasing two valency angles at <u>ortho</u>-positions in each benzene ring from 120° to 90° would obviously result in a considerable compressive force on bond D, and a shortening below the distances predicted by neglecting the effect of strain, in agteement with the short measured length. Best agreement with measured bond distances is obtained by using model <u>d</u> or <u>e</u> and applying a correction to bond D for compression due to the formation of the four-membered ring; the other bonds in the six-membered rings are, of course, also affected by this strain, but probably to a smaller extent.

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II. METHOXYCARBONYLMERCURIC CHLORIDE

A. Introduction

A series of compounds of the general formula XH_gCO_2R where X=Cl, Br,I, OAc, NO₃ and R=H, CH₃, C₂H₅ was first prepared by Schoeller, Schrauth and Essers fifty years ago (45). Their method of preparation is quite general. Methoxycarbonylmercuric chloride, for example, can be obtained in the form of colourless needles by passing carbon monoxide slowly into a solution of mercuric chloride in methanol:

$H_gC\ell_2$ +CH₃OH+CO $\longrightarrow C\ell_{H_gCO_2CH_3}$ +HC ℓ

The structure of these compounds was in doubt for many years, although Schoeller(45) apparently proposed the correct structural formulation (XIII) at an early date. The structure was not widely accepted because compounds of this type had been shown to yield carbon monoxide quantitatively by the action of methyl iodide or a dilute solution of hydrochloric acid. The carbon monoxide molecule thus appeared to be somewhat loosely bonded to the mercury atom, and this led to the suggestion of a structure (XIV) involving a coordinate link (46).



Further work (47), has failed to decide between the two alternative formulations, and structure (XIV) seems to have gained general acceptance (48). Recent infrared and proton magnetic resonance measurements (49), however, furnished results which correlated well with structure (XIII), and it was felt that an X-ray investigation of the crystals would establish the structure conclusively. The present X-ray analysis indicates that the true structure is (XIII).

B. Experimental

Crystals of methoxycarbonylmercuric chloride are colourless needles elongated along the c-axis with the (100) face developed. The density was measured by displacement of carbon tetrachloride. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the c-axis, hk0 and hkl Weissenberg films, and Okℓ, lkℓ, h0ℓ and hlℓ precession films.

<u>Crystal Data</u>. Methoxycarbonylmercuric chloride, $C\ell H_g CO_2 CH_3$; M=295.1; m.p.107°C. Orthorhombic, a=8.30+0.02, b=17.20+0.03, c=7.52+0.02Å. U=1074Å³. D_x(with Z=8) =3.64, D_m=3.58g.cm⁻³. Absorption coefficient for X-rays, $\lambda = 1.5418Å$, $\mu = 610$ cm⁻¹; $\lambda = 0.7107Å$, $\mu = 336$ cm⁻¹ F(000)=1024. Absent spectra: Okl when ℓ is odd, h0 ℓ when ℓ is odd, hkO when (h+k) is odd. Space group is Pccn $-D_{2h}^{10}$.

The intensities of the hkO reflexions were recorded on Weissenberg photographs, using CuK_{α} radiation and multiple-films to correlate strong and weak reflexions. The Oké reflexions were recorded on precession films with related time exposures, using MoK_{α} radiation. All the intensities were estimated visually, the range being about 4000 to 1. The crystal used was approximately cylindrical, 2 mm. in length and 0.09 mm. in diameter, and absorption corrections were applied for a cylindrical crystal. The structure amplitudes were derived by the usual formulae, the absolute scale being established later by correlation with the calculated structure factors. 69 hkO and 76 Oké reflexions were observed, representing 68% and 64% respectively of the possible numbers observable under the experimental conditions.

C. Structure Analysis

Inspection of the hkO photographs shows that reflexions with h=0,4,8 are particularly strong while those with h=2,6,10 are either very weak or absent. Since the structure factor expression for these reflexions involves a term cos 2π hx, the mercury atom must have x coordinate approximately $\frac{1}{8}$. The Okl intensities with k odd are also weak and few in number. Consideration of the term sin 2π l z in the structure factor expression leads to the possible values z=0 or $\frac{1}{4}$ for the mercury atom.

Patterson projections along the c- and a-axes (Figure 11) confirmed the above conclusions and provided in addition coordinates for the chlorine atom. The contribution of these atoms to the hkO and Ok ℓ structure factors were calculated, the atomic scattering factors of neutral mercury and chlorine (50) being used. The signs of the majority of the structure amplitudes were correctly determined, except a few with small or no contribution from the mercury atom; for instance all Ok ℓ terms with k odd had to be omitted until the final stage of refinement.

The first hkO Fourier synthesis was computed with 67 terms. The mercury atom was well-resolved and had essentially the same coordinates as provided by the Patterson projection on (OO1). The chlorine atom, however, moved appreciably and the electron-density distribution showed a linear concentration of peaks approximately 6° long, clearly separated and lying at about 17° to the b-axis. It was obvious that the structure (XIV) must be rejected and the individual peaks corresponded to the carbonyl and methyl groups of structure (XIII)

The first Fourier synthesis for the a-axis projection was computed with 53 terms. This projection provided another view of the molecule and confirmed the correctness of structure (XIII). With the help of a ball-and-stick model, parameters for all the atoms were obtained by correlating both the a- and c-axes



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- Figure 11. (a) Patterson projection along [001]. Contours are drawn at arbitrary intervals.
 - (b) Patterson projection along [100]. Contours are drawn at arbitrary intervals.

projections. A second structure factor calculation was now carried out for the hkO and Okl reflexions. The temperature factor, $B=4.6\text{A}^2$ for both zones, was obtained by plotting $\ln \left\{ |\mathbf{F}_c| / |\mathbf{F}_o| \right\}$ against $\sin^2\theta$. The discrepancy factor R for the observed hkO reflexions was 0.195 for mercury and chlorine only, dropping to 0.153 when the lighter atoms were included; the observed intensity of the 020 reflexion was considerably lower than the calculated value, probably because of extenction, and was omitted in the evaluation of R. For Okl reflexions R was 0.169 for all atoms and 0.221 for mercury and chlorine only.

Second Fourier syntheses for both projections were now computed, utilizing all the observed structure amplitudes and their calculated signs. The electron density maps (Figure 12 and Figure 13) indicated essentially no change in the mercury and chlorine positions, and only slight shifts of the lighter atoms. A third structure factor calculation was not carried out as significant improvements were not expected by merely changing slightly the positions of the carbon and oxygen atoms. The observed and calculated structure factors are compared in Table A-3.

Molecular Dimensions

The final atomic coordinates, deduced from Figure 12 and Figure 13 and expressed as fractions of the unit-cell edges, are listed in Table VI. The bond lengths and valency angles calculated from these coordinates are shown in Figure 14.

Atom	x	У	Z
Hg	0.1256	0.0203	0.2500
cē	0.1820	-0.0785	0.0425
Cl	0.075	0.101	0.426
01	0.076	0.095	0.588
02	0.069	0.169	0.373
ି ପ _{ର୍ଚ୍ଚ}	-0.013	0.237	0,442

Table VI. Positional Parameters



- Figure 12. (a) Electron-density projection along [001]. Contours of the mercury atom are drawn at approximately 10,20,50,75,100 e.A⁻², and other atoms at 8,10,15 e.A⁻².
 - (b) The structure viewed along [001].



Figure 13. (a) Electron-density projection along [100]. Contours of the mercury atom are drawn at approximately 10,20,50,100,150 e.A⁻², and other atoms at 8,10,15 e.A⁻².

(b) The structure viewed along [100].



Standard Deviations.

The standard deviations of the atomic positions, calculated from Cruickshank's formulae, are $\sigma(x) = \sigma(y) = \sigma(z) = 0.007 \text{Å}$ for mercury, 0.044Å for chlorine, and 0.054Å for carbon and oxygen.

D. Discussion

The resolution of the lighter atoms, especially the carbonyl group, is not very good, partly because of overlap in the projections, but chiefly due to the dominating effect on the scattering of the heavy mercury atom. Both projections however indicate unambiguously that the true structure is (XIII).

The coordination around the mercury atom is exactly linear, and in addition all the atoms in the molecule, except the methyl group, lie in one plane, with equation

0.9824x + 0.1674Y + 0.0830z - 1.2392 = 0,

where X, Y, Z are coordinates expressed in Å. The methyl carbon atom is displaced from this plane by 0.39Å.

The Hg—Cl bond length (2.35Å, σ =0.04Å) and the Hg—C distance (1.96Å, σ =0.05Å) do not differ significantly from the values reported for corresponding distances in related structues (51). The other bond lengths and valency angles have been determined only rather imprecisely, but do not differ significantly from the normal values.

The packing of the molecules is illustrated in Figure 15. There are two short intermolecular distances, a Hg....Cl separation of 3.21\AA , and a Hg....O (carbonyl) contact of 3.01\AA . These distances are however very similar to corresponding contacts in crystalline mercuric chloride (52), in which the mercury atoms are surrounded by two chlorine atoms at distances of 2.25\AA (bonded distances), two at 3.34\AA , and a further two at 3.63\AA . The distances in methoxycarbonylmercuric chloride are quite similar. All the other contacts are considerably longer, the shortest Hg....Hg distance being 4.29\AA .

III. p-CHLORONITROBENZENE

A. Introduction

A preliminary investigation of the crystal structure of <u>p</u>-chloronitrobenzene by Toussaint(53) indicated that the absent reflexions corresponded to space group $P2_{1/c}$ (interchanging his a and c-axes), and the measured density to <u>two</u> molecules in the unit cell, necessitating a molecular centre of symmetry. Two types of structures were considered possible: (i) a disordered arrangement of molecules in space group $P2_{1/c}$, giving a statistically centrosymmetric structure, or (ii) an ordered arrangement in space group Pc which gives weak reflexions when k is odd. Arrangement (ii) was considered more likely, and a structure based on space group Pc was deduced from consideration of a few structure factors (which were not listed).

The present investigation was made to establish the correct structure, and the analysis described below suggests that the true space group is $P2_{1/c}$ and that a disordered arrangement of molecules exists in the crystal.

B. Experimental

Crystals of <u>p</u>-chloronitrobenzene (Eastman Kodak), obtained by crystallization from ethanol, are colourless needles elongated along the a-axis with the (OlO) face developed. The density was measured by flotation in aqueous potassium iodide solution. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the a-axis, Oké and lké Weissenberg films, and hko and hoé precession films. <u>Crystal Data</u>. <u>p</u>-Chloronitrobenzene, $C_{6H_4}NO_2C\ell$; M=157.6; m.p. 83.5°C. Monoclinic, a=3.84±0.01, b=6.80±0.01, c=13.35±0.02Å, $\beta = 97^\circ 31' \pm 5'$. U=345.6Å³. $D_X(with Z=2)=1.514$, Dm=1.52 g.cm⁻³ Absorption coefficient for X-rays, $\lambda = 1.5418Å$, $\mu = 44.1$ cm⁻¹; $\lambda = 0.7107Å$, $\mu = 5.1$ cm⁻¹ F(000)=160. Absent spectra: hoé when ℓ is odd, Oko when k is odd. Space group is $P2_{1/c}-C_{2h}^5$.

Crystals of p-chloronitrobenzene are highly volatile at room temperature so that a crystal volatilized completely in a few hours. The crystal used for intensity measurement was a needle about 3 mm. in length and 0.15X0.08 mm. in cross-section. It was sealed in a thin-walled Lindemann-glass capillary. The intensities of the Okl reflexions were recorded on Weissenberg exposures for a crystal rotating about the a-axis, using CuK_{\varkappa} radiation, and multiple-films to correlate strong and weak reflexions. The hO ℓ reflexions were recorded on precession films with MoK radiation, using multiple exposures for intensity correlation. The ranges of $0k\ell$ and $h0\ell$ intensities were about 3600 to 1 and 1800 to 1 respectively, the estimates being made visually. The structure amplitudes were derived from the usual formulae, the absolute scale being established later by correlation with the calculated structure factors. 57 independent $0k\ell$ reflexions and 35 h 0ℓ reflexions were observed, representing \cdot 48% and 44% respectively of the possible numbers observable under the experimental conditions.

C. Structure Analysis

[100] Projection

The Patterson map (Figure 16a) could be interpreted on the basis of both ordered and disordered structures, although the CL-CL interactions were much weaker than expected, suggesting that the ordered structure was less likely. Nevertheless a few structure factors were calculated using an ordered model, with atomic scattering factors from Tabellen zur Röntgenstrukturanalyse (50). The agreement between measured and calculated structure factors was rather poor, and the calculated values for OkO reflexions with k odd were significantly larger than the maximum possible observed values.

A disordered model was then set up, consisting of two half molecules, superimposed so that the carbon atoms coincided, but with the positions of

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(b) Patterson projection along [Ol0]. Contours are drawn at arbitrary intervals. Diagram of one molecule is superimposed.

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the chlorine and nitro groups interchanged. Approximate correlation between measured and calculated structure factors was obtained, the temperature factor being apparently quite high, and the electron-density projection showed good resolution of the six-membered ring and a peak of the expected shape and height at the position of the overlapping chloring atom and nitro group (Figure 17). New coordinates were obtained and the Okl structure factors recalculated, a temperature factor $B=8.5\text{A}^2$ being obtained by plotting ln $\left\{ |F_c| / |F_o| \right\}$ against $\sin^2\theta$. The strongest reflexions had consistently high F_c values, and these discrepancies were attributed to secondary extinction. An empirical correction (54), was applied using the relation

$$\frac{I}{I_0} = \frac{u+gI}{u} = 1 + \frac{g}{u} I$$

where I = intensity that would be observed in the absence of secondary extinction,

- $I_0 = observed intensity,$
- u = linear absorption coefficient,
- g = constant.

I was taken to be equal to its calculated value I_c , and a plot of I_c/I_o against I_c gave a value of 0.00173_4 for the ratio g/u. This procedure appeared to have some justification since the corrected values of the OOL structure factors agreed with those obtained from the hOL MoK_x data. Measured and calculated structure factors are listed in Table A-4 (R=0.23), both corrected (in parentheses) and uncorrected F_o values being given for the stronger reflexions.

[010] Projection

The x coordinates of the atoms were deduced from the orientation of the molecule in the (OlO) Patterson projection (Figure 16b) and the hOl structure factors calculated. A Fourier series was summed and the resulting map indicated small shifts in atomic positions. Structure factors were recalculated



Figure 17. (a) Electron-density projection along [100]. Contours are drawn at intervals of approximately 1 e.A⁻², with the lowest contour at 3 e.A⁻².
(b) The structure viewed along [100].

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Figure 18. (a) Electron-density projection along [OlO]. Contours are drawn at intervals of approximately 1 e.A⁻², with the lowest contour at 4 e.A⁻².

(b) The structure viewed along [010].

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(and are included in Table A-4, R=0.26), a temperature factor of B=8. 5^{02} again being indicated; the observed value for the 102 reflexion was considerably smaller than F_c , probably because of extinction, and this plane was omitted in evaluating R. A final electron-density projection is shown in Figure 18.

The final positional parameters of the atoms, expressed as fractions of the unit cell edges, are listed in Table VII.

Atom	x	У	Z
1 <u>2</u> Cl	0.376	0.340	0.142
₽N	0.343	0.312	0.130
1 <u>2</u> 01	0.404	0.277	0.097
¹ / ₂ 0 ₂	0.425	0.444	0.097
cl	0.167	0.153	0.064
c ₂	0.110	0.169	-0.038
C3	-0.065	0.017	-0.102

Table VII. Positional Parameters

D. Discussion

The agreement between measured and calculated structure factors is not particularly good, probably because the model used is necessarily a rather crude one, and assumes that the six-membered rings of the two orientations coincide exactly. That this is only approximately so is indicated by the temperature factor, the high value probably resulting from a smearing out of electron-density as a result of the disorder, rather than to large thermal movements. It is also quite difficult to determine the scale factor precisely, since small errors in the steep slopes of the plots of $\ln \left\{ |F_c| / |F_0| \right\}$ against $\sin^2\theta$ produce significant changes in scale. In view of these difficulties a more elegant model was not tried, and the correlation between measured and
calculated structure factors was considered sufficiently satisfactory to indicate that the disordered arrangement is the correct one.

The absence of diffuse scattering on the films indicates that the two orientations must occur randomly throughout the crystal. In p-bromochlorobenzene (55) and 1-bromo-4-chlorocyclohexane (56) similar disordered arrangements have been observed. In these structures the interchangeable atoms, chlorine and bromine, are of course very similar in size and chemical behaviour. Although at first glance the chlorine atom and nitro group, in p-chloronitrobenzene appear to be rather different in nature, closer study suggests that their sizes are not very different and that their electronegativities are similar, so that it is not surprising that the structure is disordered. A direct test of the approximate equivalence of the two orientations is provided by an examination of the packing of the molecules in the crystal. Allowing every molecule to have either arrangement, it is found that there are several intermolecular distances below 4A; the smallest being a C.... 0 contact of 3.35A; the approaches thus correspond to normal van der Waals interactions, so that both orientations apparently exist in the crystal with no undue strain.

The disorder prevents accurate determination of the molecular dimensions, but the bond distances and valency angles appear to be normal. The molecule is at least approximately planar, but a twisting of the nitro group, out of the plane of the aromatic ring, of the order of $10^{\circ}-20^{\circ}$ would probably not be detectable.

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PART III

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X-RAY STUDIES ON SOME DERIVATIVES OF ACENAPHTHENE

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I. ACENAPHTHENE AND DERIVATIVES

A. Introduction

In 1867, Berthelot(57) isolated a hydrocarbon of molecular formula $C_{12}H_{10}$ from coal tar and named it acenaphthene. Structurally it may be regarded as a derivative of naphthalene obtained by fusion of a five-membered ring into its angular position. The enumeration of the acenaphthene nucleus, which is used for all the derivatives, follows the I.U.P.A.C. 1957 Rules (58).



The structural formula (XV) assigned to acenaphthene by Berthelot was based upon its synthesis from acetylene and naphthalene (59) and from 1-ethylnaphthalene (60) by pyrolysis. The most convincing evidence was the oxidation of the hydrocarbon to give acenaphthenequinone by chromic oxide and acetic acid, naphthalic acid by potassium permaganate, and naphthalic anhydride by chromic acid (61).

As a consequence of the pioneering work of Berthelot, and particularly of Graebe(62), the reactions of acenaphthene and its derivatives have been studied in detail. For work prior to 1921 the comprehensive review by Hahn and Holmes(63) should be consulted. Recent developments have been reviewed by Csizmadia and Hayward(64).

B. The Structure of Acenaphthene

Formula (XV), which shows a CH_2-CH_2 bend length of 2.4Å (width of a benzene ring) and interior angles of 120° and 90° in the five-membered ring, is obviously not an accurate representation of the molecular structure of acenaphthene. Considerable modification of the geometry of the <u>peri</u>-ring is expected, but it is uncertain whether the carbon skeleton would remain planar. Of particular interest is the length of the aliphatic single bond which is under considerable strain, as are also the bond-length variation and angular distortion in the naphthalene nucleus. Accordingly, several attempts have been made to determine the molecular structure of acenaphthene by an X-ray analysis of the crystalline material.

Acenaphthene crystallises in the orthorhombic system; its unit-cell dimensions were first determined by $\operatorname{Bragg}(65)$ in 1921. On the basis of the systematic extinctions (Okl absent with l odd), Hertel and Kleu(66) decided that the space group was $\operatorname{Pcmm-D}_{2h}^5$, ignoring completely the other two possibilities, viz. $\operatorname{Pc2m-C}_{2V}^4$ and $\operatorname{Pcm2}_1-\operatorname{C}_{2V}^2$. Strangely enough the same conclusion was reached seven years later by Banerjee and Sinha(67), who then proceeded to solve the crystal structure using both X-ray and magnetic data. Their analysis revealed a planar molecule with the unusual length of 2.01Å for the CH_2 -CH₂ bond. Subsequently it was pointed out by Kitaigorodskii(68) that the true space group was $\operatorname{Pcm2}_1$, on the ground that the other two space groups, viz. Pemm and $\operatorname{Pc2m}$, are forbidden to hydrocarbons (69). He arrived at the correct structure from packing considerations and by constructing the centrosymmetric electron-density projection on (OO1).

The structure is interesting crystallographically. The four molecules in the unit cell fall into two independent sets and occupy special positions: the inherent symmetry plane normal to the molecular plane coincides with the

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symmetry plane in the crystal. The CH_2-CH_2 bond length therefore depends only on the y coordinate of one aliphatic carbon atom. From consideration of the OkO structure factors alone, Kitaigorodskii(68) deduced a value of $1.8\overset{\circ}{A}$ for this distance. Later, using partial hkO CuK_{ck} data collected by means of an ionization chamber, he computed the electron-density projection along [001] and obtained a CH_2-CH_2 bond length of $1.64\pm0.04\overset{\circ}{A}$ (70).

Further refinement of the structure has been carried out by Ehrlich(71) using two-dimensional (F_0-F_c) syntheses. The analysis reveals a planar molecule with dimensions as shown in Figure 19a. Contrary to previous claims, the aliphatic CH₂-CH₂ bond is not significantly stretched, its length being $1.54\pm0.01_{\rm h}$. The bond distances in the aromatic part of the molecule are still very similar to those in naphthalene (Figure 19b).(72) and the strain in the <u>peri</u>-ring is relieved by distributing the angular stress over the entire molecule.

C. Survey of Known Analyses of Acenaphthene Derivatives

Several derivatives of acenaphthene have been axamined by X-rays; the results show that the acenaphthene skeleton is essentially planar, with large deviations from 120° in the valency angles.

Of the simple acenaphthene derivatives, only 5,6-dichloroacenaphthene (Figure 19c) has been investigated (73). The molecule is slightly non-planar as a result of severe steric hindrance between the chlorine atoms.

In pyracene (Figure 19d) a value of 1.59 ± 0.03 Å has been reported for the CH₂-CH₂ bond distance (74). The bond-lengthening is possibly significant, although the authors did not consider this to be so.

The strain in 2,13-benzfluoranthene (Figure 19e) is even greater than that in acenaphthene. It has been shown (75) that the molecule has the expected symmetry, and that the longest bond is that on the open side of the $\begin{array}{c}
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(d)





Figure 19. Mean bond lengths and valency angles in (a) acenaphthene, (b) naphthalene, (c) 5,6-dichloroacenaphthene, (d) pyracene, (e) 2.13-benziluoranthene, and (f) 20-methylcholanthrene.

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five-membered ring.

The structure of 20-methylcholanthrene (XVI), which contains the acenaphthene system, has been subjected to refined three-dimensional analysis (76). The acenaphthene skeleton has almost C_{2V} symmetry, and its average dimensions are shown in Figure 19f.



The structure of an acenaphthylene-dimer (XVII) has been established by a clearly resolved projection (77). Details of the molecular dimensions for this compound are not available.

Finally, crystallographic data have been published for the following compounds (78): 5-acetylacenaphthene, 3-acetylacenaphthene, 5,6-dibromoacenaphthene, and \propto -(5-acenaphthyl)ethylamine.

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II. ACENAPHTHENEQUINONE

A. Introduction

Study of the crystal structure of acenaphthenequinone-was undertaken as part of an investigation of a series of acenaphthene derivatives.

B. Experimental

Crystals of acenaphthenequinone are orange-yellow needles elongated along the c-axis, with the (OlO) face well developed. The cell dimensions and apace group were determined from Weissenberg and precession photographs of a crystal mounted about the c-axis. The density was measured by flotation in aqueous potassium iodide.

<u>Crystal Data</u>. Acenaphthenequinone, $C_{10}H_6(CO)_2$; M=182.2; m.p. 273-274°C. Orthorhombic, a=7.81±0.01, b=27.0±0.05, c=3.851±0.005Å. U=812Å³. D_x(with Z=4) =1.49, D_m=1.48 gm.cm⁻³. Absorption coefficients for X-rays, $\lambda =1.5418Å$, $\mu=9.83$ cm⁻¹; $\lambda =0.7107Å$, $\mu=1.24$ cm⁻¹. F(000)=376. Absent spectra: h00 when h is odd, 0k0 when k is odd, 000 when ℓ is odd. Space group is $P2_12_12_1-D_2^4$.

For intensity purposes the hkO reflexions were recorded on multiple-film Weissenberg photographs, using unfiltered CuK_{α} radiation. The Okl data were collected on precession films with related time exposures, MoK_{α} radiation being used. The intensities were estimated visually. The relative values of the structure amplitudes were derived by applying the usual Lorentz and polarization factors, the absolute scale being established later by correlation with the calculated structure factors. Absorption corrections were considered unnecessary since the crystal used had a mean diameter of 0.06 mm. 152 independent hkO reflexions were observed (excluding the 020 reflexion, which was cut off by the beam trap), representing 54% of the total number theoretically observable with CuK_{α} radiation. Only 33 Okl reflexions were



Figure 20. Relation of the origin of space group P2₁2₁2₁ to the origins of its projections on the pinacoids (100), · (010), and (001). The several origins are indicated by dots. After Buerger, Barney and Hahn(79).

Table V	III.	Transform	ations	between	Space	Group	and
		Projectio	n Coor	dinates.			

Space Group Coordinates	(001)	ojection Coordina (100)	(010)
x	$x^{\dagger} = x - \frac{1}{4}$	X'''=X	x*** =x
У	y'=y	$y''=y-\frac{1}{h}$	y ''
Z	z ' = z	z"=z	$z^{\dagger \pi} = z - \frac{1}{4}$

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recorded, representing about 20% of the total number observable.

C. Structure Analysis

Space group P2₁2₁2₁ is non-centrosymmetric, but it has centrosymmetric projections (plane group pgg) in all three principal projections (Figure 20). The relations between space group and projection coordinates are those formulated in Table VIII.

[001] Projection

The shortness of the c-axis promised good resolution of all the atoms in this projection. Packing and symmetry considerations suggested that the four molecules in the unit cell must be lined up approximately in the direction of the b-axis. The search for a trial structure was guided by the observation that the OkO reflexions exhibit a distinctive feature, being relatively weak for k=4n+2 and strong for k=4n. The very strong 0,24,0 reflexion corresponds to a planar spacing of 1.13Å, which is slightly less than half the width of a benzene ring. This indicated that in the c-axis projection the aromatic carbon atoms must lie very close to the (0, 24, 0) planes. The angle between the molecular plane and the (001) plane was estimated to be about 24° by comparing the lengths of the molecule and the a-axis. (The final results show it to be 29°). The orientation of the aromatic nucleus was also in complete agreement with that deduced from the "benzene" reflections. The x and y parameters referred to the molecular origin (defined as centre of the $C_{5a}-C_{8b}$ bond) were obtained from the projection of a CENCO Petersen molecular model held in the deduced orientation.

Examination of the Patterson projection along [OO1] (Figure 21) confirmed the above deductions. From the multiple vector peak between naphthalene rings related by symmetry, the coordinates of the molecular origin were estimated as $y_0=0.125$, $x_0=0.190$ or 0.310. The former value for x_0 was taken since it gave

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Figure 21. Patterson projection along [001]. Contours are drawn at arbitrary intervals. Diagram of one molecule is superimposed.

better agreement between the observed and calculated structure amplitudes for some low-order reflexions. (The final coordinates of the molecular origin are $x_0=0.1762$, $y_0=0.1249$). Structure factors were now calculated for all hk0 reflexions using the carbon and oxygen scattering factors from Tabellen zur Röntgenstrukturanalyse (50), with an overall isotropic temperature factor $B=4.5^{O2}$. The discrepancy factor R for the observed reflexions was 0.408, but there appeared to be no serious discrepancy between the observed and calculated structure amplitudes. 123 terms (including F(000)) were used in a Fourier synthesis, which gave good resolution of all the atoms. Recalculation of the structure factors with atomic coordinates determined from the electron-density map reduced R to 0.288. Refinement of positional and temperature parameters proceeded by computing successive (F_0-F_c) syntheses, and after five cycles R dropped to 0.150.

At this point, the contributions of the hydrogen atoms were considered. The positional parameters were obtained by measurement on a molecular model. An isotropic temperature factor of $5.0\text{A}^{\circ2}$ was assigned to each of the six hydrogen atoms. The inclusion of these hydrogen-atom contributions led to a significant improvement in the agreement of the low-order data, especially the OkO reflexions, and the R factor was lowered to 0.139.

Measured and calculated structure factors are compared in Table A-5, and the final hkO F_O synthesis is shown in Figure 22.

[100] Projection

Since the number of observed Okl reflexions was smaller than the number of parameters to be determined good resolution was not expected in this projection. Approximate z coordinates for the carbon and oxygen atoms were obtained by measurement on a molecular model. The initial Okl discrepancy was 0.190 for the observed reflexions, and this was reduced by an (F_0-F_c)

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Figure 22. Electron-density projection along [001]. Contour lines are drawn at intervals of $1 e \cdot A^{-2}$ starting with $1 e \cdot A^{-2}$.



Figure 23. Electron-density projection along [100]. Contour lines are drawn at intervals of 1 e.A⁻² starting with 1 e.A⁻².

synthesis to 0.116. Hydrogen-atom contributions were not considered. Measured and calculated $Ok\ell$ structure factors are included in Table A-5. The final electron density projection along [100] is shown in Figure 23.

Coordinates and Molecular Dimensions

The final positional and individual temperature parameters are listed in Table IX where the atomic coordinates are referred to the space group origin and expressed as fractions of the unit-cell edges. The coordinates of the carbon and oxygen atoms can be fitted to the equation

0.3284x + 0.3548y - 0.8754z - 2.3951 = 0

where X,Y,Z are coordinates expressed in Angstrom units. The deviations of the atoms from this plane are listed in the last column of Table IX.

The bond lengths and valency angles, calculated from the x,y,z coordinates of Table IX, are shown in Table X. There are no significant differences between chemically equivalent bonds, and the average dimensions of the molecule, assuming C_{2v} symmetry, are shown in Figure 24.

The orientation of the molecule in the unit cell is given in Table XI in terms of the angles \mathcal{H}_{L} , $\mathcal{\Psi}_{L}$, ω_{L} ; \mathcal{H}_{M} , $\mathcal{\Psi}_{M}$, ω_{M} ; and \mathcal{H}_{N} , $\mathcal{\Psi}_{N}$, ω_{N} which the molecular axes L, M (see Figure 24) and the plane normal N make with the crystallographic axes. The axis L was taken through the mid-points of the C₃-C₄ and C₇-C₈ bonds, and axis M through atom C₅ and the centre of the C₁-C₂ bond. L, M and N are thus not exactly orthogonal, the angles being \mathcal{L} IM = 88.5°, \mathcal{L} MN = 90.9°, and \mathcal{L} IN = 89.9°. The angle between the plane of the molecule and the (001) plane is 28.9°.

Atom	x	У	Z	в(Å ²)	(Å)
Cl	0.7542	0.1556	0.296	5.2	+ 0.032
C ₂	0.7852	0.1025	0.170	5.2	+0.028
C _{2a}	0.6267	0.0864	-0.005	4.3	+ 0.057
c ₃	0.5745	0.0427	-0.143	4.1	-0.030
C14	0.4006	0.0407	-0.276	4.9	-0.047
c ₅	0.2910	0.0802	-0.262	4.5	+ 0.003
C _{5a}	0.3437	0.1242	-0.109	4.1	+0.044
c6	0.2390	0.1659	-0.062	4.5	+ 0.016
c ₇	0.3048	0.2052	0.118	4.9	-0.045
c ₈	0.4779	0.2097	0.253	4.1	-0.013
C _{8a}	0.5757	0.1683	0.201	4.3	+0.016
c _{8b}	0.5086	0.1256	0.037	.3.6	-0.012
ol	0.8533	0.1793	0.457	5.7	-0.029
02	0.9168	0.0805	0.223	.5.7	-0.024
^H 3	0.658	0.013		5.0	
H ₄	0.364	0.006		5.0	
н ₅	0.161	0.073		5.0	
н	0.111	0.163		5.0	
^н 7	0.237	0.236		5.0	
H8	0.517	0.240		5.0	

* Subscripts of the oxygen and hydrogen atoms indicate the carbon atoms to which they are attached.

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Atoms	Bond Lengths	Atoms	Bond Lengths
1 - 2	1.533 Å	5 - 5a	1.389 Å
2-2a	1.473	5a-6	1.403
2 a- 8b	1.413	6 - 7	1.368
8b-8a	1.415	7-8	1.452
8a-1	1.482	8-8a	1.369
2a-3	,1.357	8b-5a	1.406
3-4	1.474	1-0 ₁	1.180
4-5	1.369	2-02	1.204
Atoms	Valency Angles	Atoms	Valency Angles
1-2-2a	106.9 ⁰	8a-8b-5a	122.7 ⁰
2-2a-8b	105.5	8b-5a-6	117.4
2a-8b-8a	115.2	5 a-6- 7	118.0
8b-8a-1	105.7	6-7- 8	125.8
8 a-1- 2	106.7	7 -8- 8a	114.2
2a-3- 4	117.2	8-8a-8b	121.6
3-4- 5	122.9	1-2 -0 ₂	122.9
4-5- 5a	119.8	2a-2 -0 ₂	130.3
5-5a-8b	117.6	2-1- 0 ₁	124.7
5a-8b-2a	121.6	8a-1- 0 ₁	128.4
8 b- 2a-3	120.0		

Table X. Bond Lengths and Valency Angles



Figure 24. Numbering and average dimensions of the molecule.

Table XI. Molecular Orientation in the Crystal

$\chi_{\rm L}$ = 81.0°	$\chi_{\rm M} = 21.7^{\rm O}$	$\varkappa_{\rm N}$ = 109.2°
$\psi_{\rm L}$ = 159.3°	$\psi_{\rm M} = 89.8^{\circ}$	$\psi_{\rm N}$ = 110.8°
$\omega_{\rm L} = 108.5^{\circ}$	ω _M = 68.4°	$\omega_{\rm N} = 28.9^{\rm o}$

Standard Deviations

The standard deviations for the x and y coordinates, calculated from the hkO data using Cruickshank's formulae, are $\mathcal{T}(x) = \mathcal{T}(y) = 0.015\text{\AA}$ for carbon, 0.011Å for oxygen. $\mathcal{T}(z)$ was not calculated from the Okl structure factors, which are few in number, but is certainly somewhat greater. The standard deviation of the bond lengths are about 0.021\AA for C-C bonds and 0.019\AA for c=O bonds. These values may be compared with the root mean square deviation of the individual bond lengths from the mean distances, which is only 0.007\AA . All valency angles have a standard deviation of approximately 1.3° .

Intermolecular Distances

All the intermolecular distances correspond to normal van der Waals interactions. The perpendicular distance between molecules related by translation c is 3.37Å. Packing of the molecule and some shorter lateral intermolecular contacts are illustrated in Figure 25.

D. Discussion

The acenaphthenequinone molecule is probably planar within the limits of experimental error. The maximum deviation from the mean molecular plane is 0.057Å for carbon atom C_{2a}, but this and another apparently large deviations from planarity are due to the fact that the z coordinates have been determined somewhat imprecisely. Since the c-axis is only 3.851Å long, slight errors in z will not however have a significant effect on the measured bond lengths and valency angles.



Projection of the structure along [OO1] , showing the shorter intermolecular contacts. Figure 25.

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It is interesting to compare the dimensions of the acenaphthenequinone molecule (Figure 24) found in the present work with those of naphthalene, acenaphthene, 5,6-dichloroacenaphthene, and pyracene (Figure 19). The variation of bond lengths in the aromatic nucleus is very similar in all four molecules. Fusion of one (or two) five-membered rings) to the system causes distortion of the valency angles, which is shared out by the entire molecule. The apex $C_{8a}-C_{8b}-C_{2a}$ angle of the peri-ring has a mean value of 114° , which is just midway between the interior angles, 108° and 120° respectively, of a regular pentagon and a regular hexagon.

In acenaphthenequinone the aliphatic C_1-C_2 bond has a length of 1.53 ± 0.02 Å, which agrees well with the value reported for acenaphthene; the angles in the <u>peri</u>-ring are also similar. The length of the C_2-C_{2a} bond is 1.48Å ($\sigma = 0.01_4$ Å). On the basis of the standard deviation, this bond shrinking is possibly significant and would seem to indicate some conjugation between the aromatic nucleus and the carbonyl groups. Shortening of bonds in a strained system as a result of conjugation has been observed previously. In <u>cis</u>-1,2-dichlorobenzocyclobutene, for example, a mean length of 1.45Å has been reported for the peri-bonds (80).

The C=O distance of 1.19Å is quite similar to the length found in <u>p</u>-benzoquinone (81) and most ketones (51). The C=O bonds make exterior angles of 124° and 129° with the <u>peri</u>-ring; their orientations are such that the intramolecular distances $0_2....C_1$ and $0_2....C_{2a}$ have the same length (2.41Å), and the $0_1....0_2$ distance is 2.86Å.

III. cis-1,2-ACENAPHTHENEDIOL

A. Introduction

For <u>cis</u>-1,2-acenaphthenediol molecular models show that the oxygen-oxygen distance is less than the normal van der Waals separation. There is some evidence that an internal hydrogen bond exists between the eclipsed OH groups. Study of the infrared spectrum of <u>cis</u>-1,2-acenaphthenediol in dilute carbon tetrachloride solution by Moriconi and co-workers (82) revealed two absorption bands for bonded hydroxyl groups: a well-resolved peak at v = 3584 cm⁻¹ and a broad shoulder at v = 3543 cm⁻¹. Moriconi <u>et al</u> assigned the higher frequency to a weak OH.... \mathcal{T} interaction and the lower frequency to stronger intra-molecular hydrogen bonding between <u>vic</u>-OH groups. Similarly, Csizmadia and Hayward(64) examined the infrared spectrum of the crystalline solid and found two OH absorption bands of approximately equal intensity: the lower frequency at 3190 cm⁻¹ indicating intramolecular hydrogen bonding of considerable strength, in agreement with the assignment of Moriconi <u>et al</u>, and the higher frequency at 3333 cm⁻¹ being ascribed, more appropriately in this case, to intermolecular hydrogen bonding.

Simple considerations of molecular geometry, however, suggest that the hydrogen bond between OH groups on adjacent carbon atoms, if formed at all, can at most be a weak one. For the five-membered intramolecular chelate ring

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the angle β between the O-H bond and the 0....0 line is 35-40° if standard values ($\angle 0-C-C \simeq 112^{\circ}$, $\angle C-O-H \simeq 107^{\circ}$, $O-H \simeq 1.0$ Å, $O....O \simeq 2.7$ Å) are assumed

for the bond distances and valency angles, leading to a "contour" hydrogen bond length of at least 3^{A} . The formation of a banana-type intramolecular hydrogen bond between the oxygen atoms would seem to contradict the generally accepted view that ϕ is not greater than about $15^{\circ}(83)$. On the other hand, if the proton were actually close to the internuclear 0....0 line, a large strain energy would be expected for the excessive deformation of the C-O-H bond angle. These arguments strongly suggest that chelation is rather unlikely, especially in a crystal which affords ample opportunities for intermolecular hydrogen-bond formation. To test this hypothesis and to obtain further structural data for the acenaphthene nucleus, the crystal structure of <u>cis-1,2-acenaphthenediol</u> was determined.

B. Experimental

A sample of <u>cis-1,2-acenaphthenediol</u> consisted of colourless needles elongated along the b-axis, with the (OOl) face well developed. All the crystals examined were twinned on (100). The density was measured by flotation in aqueous potassium iodide. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal mounted about the b-axis, hole and hle Weissenberg films, and hko and Oke precession films.

<u>Crystal Data</u>. <u>cis</u>-1,2-Acenaphthenediol, $C_{12}H_{10}O_2$; M=186.2; m.p. 218-219.5°C. Monoclinic, a=12.77+0.02, b=4.845+0.003, c=15.74+0.02Å, β =111°50'+5'. U=904.0Å³. D_x(with Z=4)=1.368, D_m=1.35g.cm⁻³ Absorption coefficient for X-rays, λ =1.5418Å, μ =8.93cm⁻¹. F(000)=392. Absent spectra: h0 ℓ when ℓ is odd, OkO when k is odd. Space group is $P2_{1/c} - c_{2h}^5$.

For the collection of intensity data a needle crystal of cross-section 0.09X0.06 mm. was mounted about the b-axis. The intensities of the hOl and hll reflexions were recorded on Weissenberg photographs, using CuK_{χ} radiation, and multiple-films to correlate strong and weak reflexions. The ranges of hol and hill intensities were about 7460 to 1 and 18400 to 1 respectively, the estimates being made visually. Twinning of the crystal resulted in the appearance of two sets of reflexions on a Weissenberg film (different c* axis) with occasional overlap. Fortunately one component of the twin was appreciably bigger than the other (intensity ratio 8 to 3), so that the spots from the two components could be distinguished, although often with some difficulty. No absorption corrections were considered necessary. The structure amplitudes were derived by the usual formulae, the absolute scale being established later by correlation with the calculated structure factors. 138 independent hol reflexions and 246 hll reflexions were observed, representing 56% and 49% respectively of the possible number observable under the experimental conditions.

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C. Structure Analysis

[010] Projection

Since the b-axis is reasonably short (4.845\AA) a good view of the molecule is expected in this projection. The orientation of the aromatic nucleus was deduced first from the weighted reciprocal lattice and confirmed later from examination of the Patterson projection along the b-axis (Figure 26). The well-resolved intramolecular 0-0 vector peak indicated that the projection of the molecular axis M (see Figure 28) must be almost parallel to the a-axis. The highest peak on the Patterson map corresponded to the interaction between naphthalene rings related by symmetry and led to the coordinates $x_0=0.207$, $z_{0}=0.276$ for the molecular origin, defined as the centre of the $C_{5a}-C_{8b}$ bond. (The final coordinates of the molecular origin are $x_0=0.2008$, $z_0=0.2761$). The x and z parameters were then obtained from the projection of a CENCO Petersen molecular model held in the deduced orientation. Structure amplitudes for the hO ℓ reflexions were calculated using the carbon and oxygen scattering factors from Tabellen zur Röntgenstrukturanalyse (50) and an overall isotropic temperature factor $B=4.5 \text{\AA}$. The discrepancy factor for 193 reflexions, including 55 unobserved reflexions with intensities taken at half the minimum observable limit, was somewhat high (R=0.517). However, there were no serious disagreements between the observed and unobserved structure amplitudes and their calculated values. It was possible to allocate signs to 94 observed reflexions for a Fourier synthesis, and the resulting map showed good resolution of all the atoms. Recalculation of the hO ℓ structure factors with the x and z coordinates of the electron-density maxima lowered R (observed reflexions only) to 0.344. Refinement of the atomic parameters was carried out by means of successive (F_O-F_C) syntheses, and after six cycles R was 0.148.

The final difference map had a number of electron density maxima which could be attributed to the presence of hydrogen atoms. Although the electron



Figure 26. Patterson projection along [OlO]. Contours are drawn at arbitrary intervals. A diagram of two molecules is superimposed.

density was negative in the region between oxygen atoms in the same molecule and positive in the proximity of the intermolecular 0...0 lines, this should not be taken as definite evidence against internal hydrogen bonding since hydrogen atoms in 0-H....0 bonds are difficult to locate by X-ray methods. Since the locations of the hydroxyl hydrogens were uncertain, positional parameters were deduced only for the eight hydrogen atoms attached to the carbon skeleton. When these hydrogen atoms were included in the structure factor calculation, R was lowered to 0.131. The measured and calculated hol structure factors are listed in Table A-6, and the final electrondensity projection on (010) is shown in Figure 27.

y Parameters and Final Refinement

As good resolution of the individual atoms could not be expected in the [100] and [001] projections, the y coordinates were deduced from the hll data. Approximate y parameters referred to the molecular origin were derived from a molecular model, and the y-coordinate of the molecular origin was then varied until reasonable agreement was obtained between the calculated and observed structure factors for a few low-order hll reflexions. Structure factors were calculated for all the hll reflexions, using the y coordinates thus determined and the x,z and B parameters from the hol refinement. R was 0.342.

For further refinement it would be advantageous to use the complete three-dimensional data. However, indexing of the h2 ℓ and h3 ℓ layers was difficult as a result of the twinning, and in any case the proportion of observable reflexions on these upper levels became increasingly smaller. Since the observed h0 ℓ and h1 ℓ reflexions constituted a large part of the observable three-dimensional data, refinement was completed by computing cosine and sine difference generalised projections, using the h1 ℓ data and

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refining all the x,y,z and B parameters simultaneously. After six cycles R was 0.173 for the observed hl ℓ reflexions. The inclusion of the contributions from the eight hydrogen atoms previously considered led to a significant improvement in the agreement of the observed and calculated structure amplitudes, and R was lowered to 0.155. Measured and calculated hl ℓ structure factors are listed in Table A-7.

Molecular Dimensions and Orientation

The final positional and temperature parameters are listed in Table XII, where the atomic coordinates are expressed as fractions of the unit-cell edges, and x,z and B are the mean of hOl and hll values. The equation of the mean plane for the carbon atoms is

0.7039X'+0.7107Y+0.0152Z'-2.5902=0 ,

where X', Y and Z' are coordinates expressed in $\stackrel{o}{A}$ and referred to orthogonal axes a, b and c'. The deviations of the atoms from this plane are listed in the last column of Table XII.

The dimensions of the molecule, calculated from the atomic coordinates of Table XII, are given in Table XIII. Since differences between chemically equivalent bonds are of doubtful significance, mean values for the bond distances and valency angles were obtained by assuming symmetry C_s for the molecule (Figure 28).

The orientation of the molecule in the unit cell is given in Table XIV in terms of the angles \mathcal{H}_{L} , \mathcal{H}_{L} , \mathcal{W}_{L} , \mathcal{H}_{M} , \mathcal{H}_{M} , \mathcal{W}_{M} , \mathcal{H}_{N} , $\mathcal{H}_{$

Table	XIT.	Final	Parameters*
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Atom	x	у	Z	B(Å ²)	\triangle ($\stackrel{\circ}{\mathtt{A}}$)
cl	0.3922	0.104	0.3255	4.1	+ 0.024
c ₂	0.3366	0.110	0.2164	4.6	-0.029
C _{2a}	0.2484	0.320	0.1931	4.5	-0.008
c ₃	0.1718	0.437	0.1113	5.3	+0.025
C4	0.0948	0.648	0.1173	4.8	+ 0.036
с ₅	0.0887	0.737	0.1947	4.4	-0.014
C _{5a} ,	0.1619	0.640	0.2789	4.1 _{<}	-0.018
c ₆	0.1687	0.720	0.3705	- 4.4	-0.038
c ₇	0.2490	0.619	0.4422	5.4	+0.057
c ₈	0.3291	0.391	0.4393	5.5	+0.002
C _{8a}	0.3228	0.309	0.3522	4.1	+0.003
cab	0.2396	0.423	0.2733	4.1	-0.044
ol	0.5109	0.167	0.3596	4.6	+1.175
0 ₂	0.4182	0.170	0.1742	·4.4	+1.075
Hl	0.386	-0.100	0.351	6.0	
^H 2	0.305	-0.083	0.191	6.0	
H ₃	0.179	0.329	0.053	6.0	
^н 4	.0.040	0.750	0.055	6.0	
н ₅	0.027	0.889	0.202	6.0	
на	0.110	0.874	0.377	6.0	
^H 7	0.254	0.721	0.505	6.0	
H8	0.399	0.289	0.493	6.0	

* Subscripts of the oxygen and hydrogen atoms indicate the carbon atoms to which they are bonded.

Atoms	Bond Lengths	Atoms	Bond Lengths
1-2	1.596Å	5 - 5a	1.389 X
2-2a	1.461	5a-6	1.464
2a-8b	1.400	6-7	1.306
8b-8a	1.413	7-8	1.519
8a-1	1.493	.8-8a	1.401
2a-3	1.414	8b-5a	1.471
3-4	1.446	1-01	1.458
4-5	1.322	2-0 ₂	1.440

Atoms	Valency Angles	Atoms	Valency Angles
1-2-2a	106.0°	8a-8b-5a	122.1°
2-2a-8b	109.6	8b-5a-6	117.0
2a-8b-8a	111.5	5 a- 6 -7	119.4
8b-8a-1	110.1	6-7 -8	124.6
8a-1 -2	102.6	7-8 -8a	116.2
2a-3,-4	118.8	8-8a-8b	120.0
3-4 -5	124.5	1-2 -0 ₂	112.7
4 - 5 -5a	121.3	2a-2 -0 ₂	111.2
5-5a-8b	114.5	2-1 -0 ₁	.112.5
5a-8b-2a	126.2	8a-1 -01	114.0
8b-2a-3	114.7		, ,

Selected Intramolecular Approach Distances

Átoms	Distances	Atoms	Distances
01-02	2.71Å	8a-01	2.46Å
1 -0 ₂	2.54	2a-0 ₂	2.41
2 -0 ₁	2.53		

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Figure 28. Numbering and average dimensions of the molecule.

Table XIV. Molecular Orientation in the Crystal

$\chi_{\rm L}$ = 90.9°	$\chi_{M} = 44.5^{\circ}$	$\times_{\rm N}$ = 45.3°
$\psi_{\rm L}$ = 87.8°	$\gamma_{M} = 134.5^{\circ}$	$\Psi_{\rm N} = 44.8^{\rm c}$
$\omega_{L} = 177.6^{\circ}$	ω _M = 91.8°	ω _N = 89.1 ^c

Standard Deviations

The standard deviations of the mean x and z coordinates are $\mathcal{O}(x) = \mathcal{O}(z) = 0.010\text{\AA}$ for carbon, 0.009Å for oxygen. $\mathcal{O}(y)$ is certainly somewhat greater but since most of the bonds lie close to the (010) plane and are therefore not very dependent on y, the standard deviations of the measured bond distances are about 0.01_{4} Å, and of the valency angles about 0.9° .

D. Discussion

The packing of the molecules is illustrated in Figure 29 with the main short approach distances indicated. It is seen that molecules related by a screw axis are linked together by intermolecular hydrogen bonds to form infinite zigzag chains extending in the direction of b. The θ -H....0 distances of 2.72 and 2.70Å are similar to those found in alcohols (84). A perspective diagram, Figure 30, illustrates the mode of hydorgen bonding in the crystal.

It is evident from the zigzag chain molecular packing that there is no intramolecular hydrogen bonding between the <u>vic</u>-OH groups. The interatomic $O_1...O_2$ distance is short (2.71Å) only as a consequence of the molecular geometry. A plausible explanation of the two infrared absorption peaks may be the different angles and environments of the intermolecular hydrogen bonds (Figure 30).

The carbon skeleton of the <u>cis</u>-1,2-acenaphthenediol molecule is probably planar. Some of the apparently significant deviations from planarity (maximum value 0.057Å for atom C₇) are due to the fact that the y coordinates



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Figure 29. Projection of the structure along [OlO], showing the hydrogen bonds and the shorter intermolecular contacts.

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Figure 30. Perspective diagram showing the hydrogen bonding.

have been determined less precisely. Since the b-axis is short, this should not significantly affect the measured bond lengths and valency angles.

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Comparison of the molecular dimensions of <u>cis</u>-1,2-acenaphthenediol with the data for other acenaphthene derivatives (Figure 19) shows that the valency angles are very similar. The aliphatic C_1-C_2 bond, however, is significantly lengthened (bond length $1.59_6\pm0.01_{\mu}\text{Å}$, projection on (010) 1.59_{μ}Å) probably due to the combined effect of ring strain and steric repulsion of the non-bonded oxygen atoms. The short peri-bond length of $1.48\pm0.01_{0}\text{Å}$ is unexpected. It may be pointed out, however, that a similar bond-shortening effect has been observed in <u>cis</u>-1,2-dichlorobenzocyclobutene, which has an average <u>peri</u>-bond distance of $1.45\pm0.01\text{Å}$ (80). The C-O bend has a length of $1.45\pm0.01_{0}\text{Å}$ which is typical of aliphatic alcohols (51). In the naphthalene rings the C_3 - C_4 and C_4 - C_5 bonds are respectively the longest and the shortest, in agreement with the bond-length variations observed in all acenaphthene derivatives so far examined.
IV. cis-1,2-ACENAPHTHENEDIOL DINITRATE

A. Introduction

Recently it has been demonstrated that <u>o</u>-dinitrosobenzene (XVIII) has the benzofurazan-N-oxide (XIX) structure in the solid state (85). A tautomeric form (XX) in which the nitroxy groups are directly linked together has also been suggested for nitroglycerine to explain the mechanism of its polarographic reduction (86). Furthermore, much evidence has been found for the steric interaction of contiguous nitroxy groups in cyclic and acyclic polynitrates (64). It therefore seems reasonable to speculate that ring formation is sometimes favoured in organic structures containing -NO, -NO₂ and -ONO₂ groups on suitable oriented carbon atoms.



Relatively little is known about the crystal and molecular structures of nitrate esters. The only published X-ray work is that on pentaerythritol tetranitrate (87,88) in which no bonding between nitroxy groups was found. However, the compound is rather unique among nitrate esters, and can hardly be regarded as a typical example.

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<u>cis</u>-1,2-Acenaphthenediol dinitrate (XXI), first synthesised by Csizmadia and Hayward(64), provides a rigorous test of the possibility of intramolecular bonding between nitroxy groups. In structures (XXII) and (XXIII) the steriochemical configurations can be easily assumed by rotation about single bonds, and the non-planar eight- and seven-membered rings thus formed are completely free of strain. A strained structure (XXIV) would be analogous to one proposed for dinitrogen tetroxide (89). To decide between these structures, an X-ray investigation of the crystalline material was carried out.

B. Experimental

Crystals of <u>cis</u>-1,2-acenaphthenediol dinitrate are colourless needles elongated along the b-axis with the (OOl) face well developed. The density was measured by flotation in aqueous potassium iodide. The cell constants and space group were determined from rotation and oscillation photographs of a crystal rotating about the b-axis, hol and hll Weissenberg films, and Okl and hkO precession films. <u>Crystal Data</u>. <u>cis</u>-1,2-Acenaphthenediol dinitrate, $C_{10}H_6(CHONO_2)_2$; M=276.20; m.p.128.0-130.5°C. Monoclinic, a=17.10±0.02, b=4.242±0.005, c=19.18±0.02Å, β =122°12'±5'. U=1177.3Å³. D_x(with Z=4)=1.557, D_m=1.53 gm.cm.³ Absorption coefficients for X-rays, λ =1.5418Å, μ =12.70 cm.⁻¹ ; λ =0.7107Å, μ =1.57 cm.⁻¹ F(000)=568. Absent spectra: hole when lis odd, OkO when k is odd. Space group is P2_{1/c}-C⁵_{2h}.

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For the collection of intensity data a needle crystal of cross-section 0.07x0.11 mm. was mounted about the b-axis. Equi-inclination Weissenberg photographs of the hOl and hll layers were taken with CuK_{α} radiation. To extend the intensity range the data for each zone were collected on two sets of four films related by time exposures. The intensities of the various reflexions were estimated visually and corrected as usual for Lorentz and polarization factors. No absorption corrections were considered necessary. 246 hOl (excluding the 100 and $\overline{102}$ reflexions which were cut off by the beam trap) and 443 hll independent reflexions were found to be of measurable magnitude; these represent 75% and 76%, respectively, of the total number theoretically observable.

C. Structure Analysis

The first attempts to derive an approximate structure made use of the set of hO ℓ data. A Patterson synthesis projected down the short b-axis (Figure 31) was computed. The highest peaks on this map were readily identified as multiple vector peaks between naphthalene rings related by symmetry, leading to a position of $x_0=0.258$, $z_0=0.196$ or $x_0=0.242$, $z_0=0.304$ for the molecular origin, defined as the centre of the $C_{5a}-C_{8b}$ bond. The orientation of the aromatic nucleus indicated by the Patterson map was in agreement with that deduced from an examination of the weighted reciprocal lattice. The extended peak marked with a cross (about 3.4% from the origin)

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could be reasonably ascribed to interactions between non-bonded nitroxy groups. On this basis structure (XXII), with its many conformations involving rotations about C-O and O-N single bonds, was taken as a starting point for the precise location of atoms by Fourier methods.

[010] Projection

The shortness of the b-axis promised a good view of the structure in this projection. The x and z coordinates of the carbon atoms were obtained from the projection of a CENCO Petersen molecular model (Figure 36) held in the deduced orientation, the molecular origin being arbitrarily placed at $x_0=0.258$, $z_0=0.196$. Various sets of x and z parameters were postulated for the oxygen and nitrogen atoms, allowing for the fact that the two nitroxy groups must be approximately 3.4Å apart, and oriented in such a way that the "thickness" of the molecule in the [010] direction was not excessive. The different trial structures were tested by calculating $hO\ell$ structure amplitudes and comparing them with the observed values. The atomic scattering factors were taken from the International Tables, Vol.III, and an overall isotropic temperature factor $B=4.5^{0}A^2$ was used. Finally a structure which gave reasonable agreement with the low-order reflexions was chosen for refinement. The discrepancy factor R (observed reflexions only) was 0.618, a rather high value, but it was possible to allocate signs to 155 observed reflexions for a Fourier synthesis. All the atoms could be identified, and there were no spurious details in the electrondensity map. However, further refinement proved less encouraging and R could not be improved below about 0.40. This suggested that the molecule had essentially the correct structure and orientation, but was wrongly placed in the unit cell. New x and z coordinates for all the atoms were now deduced with the molecular origin shifted to the alternative position $x_0=0.242$, $z_0=0.304$. Recalculation of the hOl structure factors gave an R value of 0.523 and in

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Figure 32. Electron-density projection along [010]. Contour lines are drawn at intervals of $1 e \cdot A^{-2}$ starting with $1 e \cdot A^{-2}$.

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y Parameters and Final Refinement

To determine the y coordinates of the atoms, attention was turned to the hll data. Approximate y parameters referred to the molecular origin were derived from a molecular model (Figure 36), and the y coordinate of the molecular origin was chosen as that which gave the best agreement between the calculated and observed structure amplitudes for a few low order data. Structure factors were now calculated for all hll reflexions, using the y coordinates thus determined and the x, z and B parameters from the hol refinement. The initial value of R for the observed reflexions was 0.347. Refinement of all the positional and temperature parameters proceeded by computing cosine and sine difference generalized projections, and after five cycles R dropped to 0.169. The observed values for the very intense $\overline{211}$, $\overline{312}$, $\overline{212}$, $\overline{313}$, and $\overline{213}$ reflexions were considerably larger than F_c , probably due to errors in intensity estimation, and these planes were omitted in evaluating R.

Structure factors were again calculated for the hO ℓ reflexions with the parameters determined from the hl ℓ refinement; the R value was reduced slightly from 0.160 to 0.145. Measured and calculated hO ℓ and hl ℓ structure factors are listed in Tables A-8 and A-9 respectively.

Coordinates, Molecular Dimensions, and Orientations

The final positional and temperature parameters are given in Table XV, where the atomic coordinates are expressed as fractions of the unit-cell edges. The dimensions of the molecule, calculated from these coordinates, are shown in Table XVI. Mean bond lengths and valency angles were obtained by assuming symmetry C_s for the cis-1,2-acenaphthenediol portion of the molecule (Figure 33),

Table XV. Final Parameters

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Atom	x	<u>y</u>	.´ Z	в(⁰²)	$\triangle(\overset{\circ}{\mathtt{A}})$
Cl	0.3234	0.455	0.2289	4.3	-0.003
c ₂	0.2187	0.387	0.1564	4.3	+0.038
C _{2a}	0.1746	0.193	0.1941	4.4	-0.034
c3	0.0871	0.080	0.1617	5.0	· + 0.008
C ₄	0.0681	-0.081	0.2181	5.8	-0.002
C ₅	0.1336	-0.116	0.3015	5.6	-0.023
C _{5a}	0.2230	0.024	0.3341	5.2	+0.020
c6	0.2943	0.008	0.4172	5.4	+0.019
C7	0.3780	0.140	0.4400	4.9	+0.005
c8	0.3982	0.306	0.3852	4.9	+0.035
C _{8a}	0.3268	0.298	0.3019	4.7	-0.053
CSb	0.2409	0.171	0.2786	4.8	-0.006
0 ₁	0.3882	0.273	0.2168	4.6	+ 0.007
N	0.4070	0.398	0.1592	4.9	-0.030
0 ₂	0.3660	0.631	0.1230	6.1	+0.010
0 ₃	0.4675	0.262	0.1605	5.7	+0.011
oi	0.2216	0.191	0.0947	5.0	-0.015
N'	0.1530	0.257	0.0120	5.2	+ 0.058
02	0.0915	0.424	0.0009	7.2	-0.025
0'3	0.1636	0.082	-0.0333	6.8	-0.021

Table XVI. Bond Lengths, Valency Angles and Some Intramolecular Approach Distances

Atoms	Bond Lengths	Atoms	Bond Lengths	Atoms	Bond Lengths
1-2	1.603Å	4-5	1.388Å	1-0 ₁	1.467 Å
2 - 2a	1.533	5 - 5a	1.436	O _l -N	.1.408
2a-8b	1.401	5a-6	1.401	N-02	1.196
8b-8a	1.396	6-7	1.373	N-03	1.173
8a-1	1.523	7-8	1.451	2-0'1	1.468
2a-3	1.365	8-8a	1.402	O _l -N'	1.410
3-4	1.455	8b-5a	1.401	N'-02	1.189
				N'-03	1.227
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Atoms	Valency Angles	Atoms	Valency Angles	Atoms	Valency [,] Angles
1-2-2a	106.9°	8b-2a-3	121.2°	01-N'-02	,116.5°
2-2a-8b	106.5	8a-8b-5a	123.2	01-N'-03	109.2
2a-8b-8a	114.4	8b-5a-6	118.4	02-N'-03	133.1
8b-8a-1	110.9	.5 a-6 - 7	118.1	0 ₁ -1 -2	110.9
8a-1 -2	101.3	6-7 -8	125.2	0 ₁ -1 -8a	104.7
2 a-3 - 4	116.8	7-8 -8a	114.5	l -0 ₁ -N	115.7
3-4 -5	123.0	8-8a-8b	120.2	0 ₁ -N -0 ₂	117.3
4-5 -5e	118.4	01-2 -1	107.4	0 ₁ -N -0 ₃	·111.5
5-5a-8b	117.8	0 <mark>1</mark> -2 -2a	108.2	°₂-№ -°3	131.0
5a-8b-2a	122.6	2 -01-N'	115.4		

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continued on page 108



Figure 33. Numbering and average dimensions of the molecule.

and by averaging corresponding values for the two nitroxy groups (Figure 37). The equations of the mean planes are

Carbon atoms : -0.4699X' + 0.8658Y + 0.1720Z' - 0.8134 = 0, Unprimed $0NO_2$: 0.3583X' + 0.5907Y + 0.7229Z' - 4.8051 = 0, Primed $0NO_2$: 0.6638X' + 0.7454Y - 0.0616Z' - 2.3966 = 0,

where X', Y, Z' are coordinates expressed in Å and referred to orthogonal axes a, b and c'. The deviations of the atoms from these planes are listed in the last column of Table XV. The unprimed and primed ONO_2 groups (Figure 35) are inclined to the plane of carbon atoms at angles of +62.1° and +71.2° respectively.

The orientation of the molecule in the unit cell may be indicated by giving the angles \swarrow , \checkmark and \bigotimes (Table XVII), which the molecular axes L,M (Figure 33) and the carbon-plane normal N make with the a and b crystal axes, and their perpendicular c'. The axes L was taken through the mid-points of bond C₃-C₄ and C₇-C₈, and axis M through C_{5a} and the centre of the C₁-C₂ bond. L, M and N are thus not mutually orthogonal, the angles being 4 LM=90.6^o, 4 LN=90.2^o, and 4 MN=90.0^o. - 106 -

Table XVII. Molecular Orientation in the Crystal

$x_{\rm L}$ = 128.9°	$\varkappa_{\rm M}$ = 51.5°	$\varkappa_{\rm N}$ = 118.0°
$\psi_{\rm L}$ = 101.4°	$\Psi_{\rm M} = 62.5^{\circ}$	$\Psi_{\rm N} = 30.0^{\circ}$
$\omega_{L^{1}} = 138.7^{\circ}$	$\omega_{\rm M}$ = 129.1°	ω _{N =} 80.1°

Standard Deviations

The standard deviations for the x and z coordinates, calculated using Cruickshank's formulae, are $\sigma(x) = \sigma(z) = 0.010\text{\AA}$ for C, 0.008\AA for 0_1 , 0.009\AA for N, and 0.010\AA for 0_2 and 0_3 . $\sigma(y)$ is expected to be somewhat greater. The standard deviations of the measured bond distances are about 0.014\AA for C-C and N=O bonds, 0.013\AA for C-O and 0.012 for O-N bonds. All valency angles have a standard deviation of approximately 0.9° .

Intermolecular Distances

All the intermolecular distances correspond to normal van der Waals interactions. Packing of the molecules in the unit cell and some shorter lateral intermolecular contacts are shown in Figure 34.

D. Discussion

The y coordinates have not been determined to a high degree of accuracy, so that the apparent deviations from the mean planes of the acenaphthene nucleus (maximum value 0.053 for C_{8a}) and of the nitroxy groups (maximum value 0.058 for N') are probably not significant. Since the b-axis is short, small errors in the y parameters should not seriously affect the measured bond lengths and valency angles.

The molecular structure of <u>cis-1</u>,2-acenaphthenediol dinitrate is shown in perspective in Figure 35. The nitroxy groups are well separated from each other, the two shortest contacts between them being $0_1-0_1'=2.57\text{\AA}^{\circ}$ and $0_1'-0_2=2.91\text{\AA}$. The planes of the nitroxy groups are inclined in the same



Figure 34. Projection of the structure along [010].

- 107 -

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Figure 35. Perspective diagram of the molecular structure.

	Dometric -		* *		
Atoms	Distances	Atoms	Distances	Atoms	Distances
0 ₁ -0;	2.57Å	0 ₁ -2	2.53Å	l-N	2.43Å
0 '- 2a	2.43	2 -N'	2.43	1-02	2.61
0 <u>'</u> -1	2.48	2 -0 ′2	2.60	° <u>1</u> -° ₂	2.91
0 ₁ -8a	2.37				

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Selected Intramolecular Approach Distances

Fig. 36. CENCO Petersen molecular model photographed in two arbitrary directions to show its general shape.

Figure 37. Dimensions of the nitroxy group in (a) <u>cls</u>-1,2acenaphthenediol dinitrate, (b) pentaerythritol tetranitrate, and (c) nitric acid.

•

sense with respect to the plane of carbon atoms. Figure 36 shows a CENCO molecular model viewed in two arbitrary directions.

The dimensions of the acenaphthene nucleus of <u>cis</u>-1,2-acenaphthenediol dinitrate are very similar to those found in other acenaphthene derivatives. The lengths of bonds C_{2a} - C_3 , C_3 - C_4 , C_4 - C_5 vary in the order short-long-short, as do the corresponding distances in naphthalene.

The aliphatic C_1-C_2 bond has a length of $1.60_{3\pm}0.01_4$ Å (projection on (010) 1.57_8 Å), which agrees well with the value $1.59_{6\pm}0.01_4$ Å found in <u>cis</u>-1,2-acenaphthenediol. The significant lengthening of this bond, as compared to the values 1.54Å and 1.53Å found in acenaphthene and acenaphthene-quinone respectively, may be ascribed to steric repulsion of the non-bonded oxygen atoms O_1 and O_1' .

The bond lengths and valency angles of the nitroxy group found in the present study are compared with those of pentaerythritol tetranitrate (88) and nitric acid (90) in Figure 37. There is excellent agreement among corresponding values, and in both nitrates $\angle 0_1 N O_2$ is significantly larger than $\angle 0_1 N O_3$ as a consequence of steric interference between atoms C and O_2 .

The appreciably larger temperature factor for atoms O_2 and O_3 than for N and O_1 suggest torsional oscillation of the nitro group about the O-N bond, in a manner similar to the motion observed in 4-nitroaniline (91). It is also probable that the nitroxy group, as a whole, executes torsional oscillation about the C-O bond. These librational movements are expected to cause an apparent diminution of the measured N=O distance (92), and it is suggestive that the present measured value of $1.19_{4\pm}0.007^{\text{A}}$ is slightly smaller than the corresponding length $(1.21_{4\pm}0.01^{\text{A}})$ in pentaerythritol tetranitrate for which thermal motion is smaller. Since anisotropic thermal factors have not been determined in the present analysis, no attempt has been made to correct the bond distances for rotational oscillation errors.

V. GENERAL CONCLUSIONS

From a critical examination of the structural data of acenaphthene and its derivatives, the following conclusions may be drawn:

(a) The carbon skeleton is planar.

(b) The strain in the peri-ring is alleviated principally by the distortion of bond angles, both in the peri-ring and in the naphthalene rings.

(c) In <u>cis</u>-1,2-disubstituted acenaphthenes the C_1-C_2 bond is significantly longer than the corresponding distance in acenaphthene, probably as a consequence of steric repulsion between the non-bonded substituents.

(d) In acenaphthenequinone the short <u>peri</u>-bonds C_1-C_{8a} and C_2-C_{2a} suggest some degree of conjugation between the carbonyl groups and the aromatic nucleus. The significant shrinking of these bonds in <u>cis</u>-1,2-acenaphthenediol is less well understood.

(e) The average dimensions of the naphthalene moiety of the acenaphthene system, derived from the data for acenaphthene, 5,6-dichloroacenaphthene and the three compounds studied in the present work, are shown in Figure 38; their deviations from the corresponding values in naphthalene are also indicated. The standard deviations of the mean bond distances are about 0.008\AA for bond C_{5a} - C_{8b} and 0.006\AA for other bonds, and of the valency angles about 0.4° . It is seen that formation of the peri-ring results primarily in compression of the C_{2a} - C_{8b} bond, stretching of the C_{2a} - C_{3} bond, and widening of the C_{2a} - C_{8b} - C_{5a} angle. In general the bond distances are affected to a lesser extent than are the valency angles.

Figure 38. Average dimensions of the naphthalene moiety of the acenaphthene system. Deviations from the corresponding values in naphthalene are shown in brackets; for the bond distances the deviations are given in 10⁻³A. APPENDIX I

STRUCTURE FACTOR TABLES

Table A-1. Biphenylene hkO

.

<u>h</u>	<u>k</u>	<u>F</u> o	<u>F</u> (1)	<u>F</u> (2)	<u>h</u>	<u>k</u>	<u>F</u> 。	<u>F</u> _(1)	<u>F</u> (2)	<u>h</u>	<u>k</u>	F.	<u>F</u> _c (1)	<u>F</u> _c(2)
							<u>h</u>	= 3 <u>n</u>						
0 3	2468021234567890112301234567890	97.8 9.4 42.9 42.9 42.9 42.9 42.9 42.9 42.9 42.9 42.9 21.7 24.7 < 3.1 3.2 7.0 5.2 11.4 < 3.4 < 3.6 < 3.	+112.1 + 11.2 + 54.7 - 1.7 + 14.8 + 17.2 + 53.8 +134.0 + 95.5 - 26.9 + 20.6 + 3.3 + 1.9 + 3.0 - 15.9 - 1.7 + 1.8 + 4.9 - 53.2 - 48.1 + 6.6 - 28.9 - 1.2 - 4.1 + 0.7 - 2.6	+111.0 + 9.7 + 50.6 - 0.3 + 17.2 + 19.9 + 55.5 + 134.6 + 96.1 - 22.1 + 20.4 + 1.4 + 4.7 + 3.1 + 4.0 - 16.5 - 0.8 + 2.6 + 49.5 - 47.1 + 8.9 + 1.0 - 3.1 + 29.0 - 3.1 + 29.0 - 3.0.9 - 0.3 - 4.0 + 1.5 - 2.0	6 9 12	11 12 13 1 2 3 4 5 6 7 8 9 10 11 2 0 1 2 3 4 5 6 7 8 9 10 11 2 1 2	10.4 < 2.7 5.1 4.9 30.8 34.7 32.8 12.4 < 3.8 12.4 < 3.7 9.7 < 3.7 9.7 < 3.0 4 3.0 15.6 < 3.7 9.7 < 3.0 4 3.0 11.8 19.4 6.4 6.9 6.5 3.0 < 1.4 < 3.5 5.5	$\begin{array}{r} - 6.9 \\ - 4.7 \\ - 7.5 \\ + 4.4 \\ + 36.9 \\ - 28.9 \\ + 25.4 \\ - 12.8 \\ 0 \\ - 5.3 \\ - 15.3 \\ - 0.7 \\ - 5.9 \\ + 25.4 \\ - 15.7 \\ - 5.9 \\ - 27.5 \\ 0 \\ - 8.4 \\ + 7.9 \\ + 13.4 \\ + 7.9 \\ + 16.2 \\ - 4.7 \\ + 5.4 \\ - 3.5 \\ - 2.9 \\ - 3.0 \\ - 3.0 \\ - 2.5 \end{array}$	-7.5 -7.9 +1.4 +30.8 -33.0 +28.4 -14.2	15 18 21 24	345678901012345678912345670123	$\begin{array}{c} 21.9\\ 5.2\\ 3.7\\ <3.7\\ 6.2\\ 9.5\\ <2.4\\ <1.4\\ 30.2\\ 11.7\\ 14.0\\ <3.7\\ 5.8\\ 7.1\\ 10.5\\ <3.0\\ <2.6\\ <19.8\\ 5.5\\ <3.0\\ <2.8\\ 7.2\\ 19.8\\ 5.5\\ <2.0\\ 19.8\\ 5.5\\ <2.0\\ 19.8\\ 5.5\\ <2.0\\ 19.8\\ 5.5\\ <2.0\\ 10.4\\ 2.9\\ 3.7\\ 6.2\end{array}$	$\begin{array}{r} -19.1 \\ -6.7 \\ +2.6 \\ +3.1 \\ +4.1 \\ +4.8 \\ 0 \\ -2.1 \\ +2.7 \\ -28.3 \\ +11.4 \\ -11.3 \\ +2.8 \\ -6.9 \\ -10.0 \\ +1.1 \\ +0.5 \\ -13.5 \\ -13.5 \\ -13.5 \\ -13.5 \\ -11.7 \\ -2.6 \\ +2.7 \\ -2.8 \\ -1.0 \\ +2.8 \\ -1.1 \\ -2.8 \end{array}$	$\begin{array}{r} -18.4 \\ -6.1 \\ +3.7 \\ +5.7 \\ +5.7 \\ +5.7 \\ +2.2 \\ -29.6 \\ +12.5 \\ -11.4 \\ -3.0 \\ -7.1 \\ -10.2 \\ +3.0 \\ -7.1 \\ -14.0 \\ -2.9 \\ -14.0 \\ -2.6 \\ -3.5 \\ -2.7 \\ -3.1 \\ -2$
							<u>h</u>	≠ 3 <u>n</u>						
5 8 10	0	5.9 4.0 2.6	0 0 0	0 + 1.3 + 4.0	10 11 16	2	4.4 4.1 5.2	0 0 0	- 0.3 + 3.0 + 1.1	5 7 8	4	6.9 4.6 3.4	0	+ 0.8 + 0.1 - 0.5
11 2 4 7	1	2.8 2.1 2.5 2.2	0 0 0 0	0 + 1.3 + 0.9 - 1.1	2 4 5 7	3	10.6 2.1 6.2 3.5	0 0 0	-0.7 -1.3 +1.7 +1.4	5 7 8 16	5	6.7 2.1 5.3 2.7	0 0 0 0	-1.6 + 0.6 + 1.7 + 0.8
8 16 2 4	2	2.8 4.4 8.8 3.1	0 0 0 0	- 1.8 - 1.5 + 0.6 0	8 10 13 17		6.3 3.6 3.4 5.3	0 0 0	+ 1.1 - 2.1 + 1.4 - 1.5	1 5 7 10	6 8	7.0 3.7 6.0 3.8	0 0 0	- 0.8 - 0.6 - 1.3 - 0.9
5		6.2	0	+ 1.5	4	(4	1.6	0	- 1.2	11		5.3	0	- 0.3

Table A-2. Biphenylene hkl

<u>h</u>	<u>k</u>	Fo	Ēc	<u>h</u>	<u>k</u>	<u>F</u> o		Fc	<u>h</u>	<u>k</u>	Fo	Fc
-20	0	4.2	- 4.2	5	1	26.0	+	25.4	13	2	7.9	+ 7.5
-18		16.6	- 11.4	6		16.9	-	12.1	14		21.0	- 21.4
-16		12.2	- 12.6	7		2.6	+	3.5	15		13.5	- 15.7
-14		<4.0	+ 0.7	8		<2.8	+	3.1	16		9.8	- 5.9
-12		3.6	+ 6.0	9		20.6	+	19.4	17		< 4.5	+ 6.9
-10		<3.2	+ 2.8	10		< 3.2	+	1.8	18		6.3	+ 5.5
- 8		<2.7	+ 2.0	11		10.8	-	13.6	19		<4.3	- 1.1
- 6		27.6	+ 29.6	12		25.0	+	25.2	20		< 4.1	+ 2.0
- 4		16.7	+ 24.1	13		10.9	-	11.3	21		6.7	+ 6.1
- 2		Not	obs.	14		4.0	+	3.2	-19	3	4.3	+ 5.7
0		Not	obs.	15		4.2	+	3.5	-18		< 4.4	+ 3.4
2		Not	obs.	16		< 4.4	+	0.3	-17		4.4	- 2.4
4		16.0	+ 21.7	17	•	15.3	-	15.4	-16		< 4.4	- 3.1
6		29.8	- 37.5	18		< 4.4		4.7	-15		11.4	- 12.2
8		<2.8	+ 3.8	19		< 4.4	-	3.2			<4.2	+ 4.0
10		4.5	+ 6.5	20		5.1		5.4	-13		.9.9	- 14.9
.12		5.1	+ 4.1	21	•	5.6		4.9	-12		2.9	- 10*8
14		11.4	- 8,2	-18	2	4.4	***	4.7	-11		1+2	- 0.2
16		9.7	- 7.7	-17		6.3	+	0.5	-10		9.2	+ 1+1
18		30.4	+ 23.1	-16		12.4		12.8	- 9		20.I	+ 24.4
20		6.0	- 8.1	-15		7.4	+.	TOPT	- 8		0.1	+ 12.2
-22	1	8.9	- 7.2	-14		13.0	-	11.4	- 1		21.0	+ 29.0
-21		<4.0	+ 6.5	-13		2.9	+	7.9	- 0		2)•1	- 14.0U
-20		<4.2	- 3.0	-12		2•1	+	4•1			2.0	+ 0.7
-19		10.7	- 8.2	-11		5.0	-	4.2	⇒ 4 z		20.0	+ 29.2
-18		4.4	+ 1.4	-10		8.1	•0+	12.)	-)		41.1	- 52.0
-17		6.3	- 9.5	- 9		20.8	+	22.2	- 2		2.0	- 0.2 20 E
-10		< 4.2	+ 5.4	- 0		103		2+7			24+2	- 10 0
-17		4.2	+ 4•/	- 1		10+T	~	4.0	1		2107	- 13 8
		<4.0 06.E	+ 1.)	O E		4100	-	42.0	÷ 2		11 2	- 50
		20.0	- 19.0	- 2		4+1 20 6	- -	0.0	2 3		21 7	- J.J
-12 11		22.9	- 22.0 7 7	- 4		74 0	-	71 1	ן א		20 1	± 18 6
TT		4.0	- 1.2	- 2		/4•9 ∠10	_	14+4	4 5		33 0	± 12 2
-10		20 6	- 197	- 2		33 0	-	30.2	6		< 2.8	- 4.7
- 9		18.6	- 10 <u>0</u> 1	- 1		1.3	-	3.1	7		21.0	+ 19.0
- 7		18.2	T (#4	1		5.7	_	8.0	้ร่		24.5	+ 23.6
- 6		20.2	+ 1/ 1	2		9.6		14.7	q		24.5	- 24.8
- 5		56	T, 1401	3		26.2	+	36.6	10		< 3.5	+ 3.9
		50.2	+ 50.9	ן ג		44.1	+	49.5	11		11.1	- 8.1
- 3		100.0	-101.2	5		22.9	+	20.7	12		< 3.9	+ 4.6
- 2		18.2	± 26.8	6		23.2		21.4	13		9.1	- 5.9
_ 1		Not		7		3.9		6.2	14		< 4.2	+ 7.7
- <u>-</u>		Not	oba	8		8.3	+	4.3	15		32.1	+ 25.8
1		Not	obs	q		25.1		29.4	16		< 4.4	- 2.3
2		61.4	+ 60.4	10		7.0	_	9.4	17		< 4.5	- 3.6
ב א		70.2	+ 72.1	11		< 3.5	_	1.8	18		< 4.4	- 1.3
4		25.1	+ 34.3	12		3.7	+	4.8	19		< 4.2	+ 1.4

<u>h</u>	k	Fo	<u>₽</u> c	<u>h</u>	<u>k</u>	<u>F</u> .	<u>F</u> c	<u>h</u>	k	Fo	<u>F</u>	C
20	3	4.0	- 3.3	- 7	5	22.2	+ 17.5	- 6	7.	< 4.1	- 7.	8.
-19	4	5.9 ·	- 4.4	- 6		28.4	- 17.2	5		9.8	- 8.	2
-18		<4.3	+ 1.1	- 5		9.8	- 16.2	- 4		3.7	+ 7.	7
-17		<4.4	- 3.4	- 4		3.2	- 2.9	3		13.5	- 13.	2
-16		<4.5 ·	- 1.3	- 3		8.2	- 15.8	- 2		12.2	+ 8.	8
-15		4.4	+ 3.3	- 2		4.3	- 12.1	- 1		< 3.8	0	
-14		7.5 ·	- 9.9	- 1		9.1	+ 15.8	0		10.8	+ 12.	4
-13		5.9 ·	+ 9.0	0		7.4	+ 10.8	l		< 3.8	- 0.	3
-12		<4.0 ·	+ 2.3	1		9.6	+ 9.4	2		21.8	+ 22.	0
-11		5 . 5 ·	+ 5.6	2		21.0	- 19.9	3		26.6	+ 19.	6
-10		7.4	- 8.3	3		23.1	+ 23.6	4		5.6	+ 3.	6
- 9		< 3.5	- 3.4	4		< 3.2	- 2.1	5		8.0	- 7.	2
- 8		<3.3 .	+ 4.1	5		18.0	- 20.1	- 8	8	< 4.2	- 0.	8
- 7		31.2 .	+ 41.0	6		< 3.4	+ 2.9	- 7		14.0	- 11.	0
- 6		58.5	- 57.2	7		10.0	+ 10.0	- 6		12.4	- 16.	1
- 5		11.0	+ 5.3	8		18.7	+ 15.8	- 5		<4.3	- 1.	1
- 4		23.9	+ 27.2	9		< 3.8	- 0.6	- 4		12.7	+ 13.	7
- 3		3.9	+ 1.3	10		7.9	+ 5.1	- 3		< 4.2	- 0.	4
- 2		6.0	- 2.0	11		< 4.1	- 3.1	- 2		< 4.2	- 7.	6
- 1		24.0	- 26.9	12		16.9	- 15.4	- 1		9.3	+ 10.	4
ō		9.8	+ 6.8	13		< 4.3	- 1.0	Õ		< 4.2	0	
.1		9.8	- 11.6	14		< 4.4	+ 1.9	i		7.2	+ 6.	2
2		10.7	- 2.6	15		6.3	+ 7.6	2		5.9	- 11.	9
3		8.2	+ 13.8	<u> </u>	6	5.8	- 5.3	3		10.3	- 6.	9
á		14.4	+ 18.7	- 8	-	4.0	+ 1.2	4		7.4	+ 9.	0
5		17.4	+ 18.9	- 7		< 3.8	+ 2.7	5		6.1	- 3.	0
6		37.1	+ 43.6	- 6		26.7	- 19.8	6		17.3	+ 13	2
7		24.5	+ 22.3	- 5		< 3.6	+ 0.1	- 4	q	8.9	- 5	7
8		10_1	+ 12.5	÷ Á		14.3	_ 19.1	- 3	<i>Y</i>	16.5	- 18.	q
ä		< 3.5	- 5.3	- 7			- 1.0	- 2		< 4.4	- 2.	7
10		3.7	- 6.9	- 2		×3.5	- 3.2	_)		15.3	- 14.	1
11		78	+ 0.8	_ 1		6.8	- <i>J</i> .2	·		< A . A		
12		57.	+ 30	- 1		8.1	- 68	้า			Ő	
17		1.2	+ 20	1		1 8	± 6.6	2		6.2	- 5.	0
1/		130.	- 13 7			4.0	_ 0.0	2 		17 7	- 16	A I
- 15			- 2.0			235	- 202	ر ۸		AA	- 1	р т 2
16	•	\[4 \circ 4 \circ	- 2.0 - 0.7	ر ۸		63.6	- 57			7.7	- 4 .	Л
10		1405	- Q /	4 5		5.2	- 201		10	6.2	T 7	N
エ/ ニコム	F	4.4	- 53	2		2.4	T 101	- 3	τŅ		T /	0
∾10	2	A.A.		7		<2.2 Q	+ 22.4	- 2				0
-17		404 4	- 10°T				T 1.0	- 2		> 4 • 4 A A	· - 4.	2 5
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-17 19		<u>、4</u> •ク ' 10 マ	- 2.0 1 01	ע סו		<u> </u>		-)	TT		~ 2	ショ
-12		- 10°2 .		<u>רר</u>			T)•4	- 2		< 4.⊥< 	-). - 2	5
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- 9)•0 ·	- 201	- 0 - 7		<u> </u>	- 4.0 - 1 4	⊥		۲.1 ۲.0	्म 4,• ∖ <u> </u> 7	14 7
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0 64 0 64	468 -383 463 -379	301 -281 255 -127	123 -127 70 - 60		< 5 + 29	40 + 47	55 + 45	46 + 43	< 5 - 14	24 + 41	86 +109	110 +148	128 +148	611+ 111	82 + 73	67 + 58	25 + 27 25 + 27		ר ה ר ר	< 5 + 11	< 5 + 20	< 5 - 27	 1 2 1 2 3 4 4 5 4 4 5 4 4 5 5 6 6 6 6 6 7 6 7 6 7 7	∨ 10.1 4.4		<pre> 4 + 4 × ×</pre>	∧ / k ↓ 1		25 + 25	58 + 69	63 + 71	42 + 71	40 + 56	41 + 56	55 + 54	45 + 47		107 +106	108 +106	96 +119	79 + 92	59 + 59	21 + 1 3
<u>e</u> <u>e</u> <u>e</u>	0 468 -383 0 463 -379	0 501 -281 0 255 -127	0 123 -127	02 02 0	0 < 5 + 29	0 40 + 47	0 55 + 45	0 46 + 43	0 < 5 - 14	0 24 + 41	0 86 +109	0 110 +148	0 128 +148	611+ 111 0	0 85 + 73	0 67 + 58	0 2 5 + 27		0 < 5 + 5	0 < 5 + 11	0 <5 + 20	0 <5 - 27	0 0	0 < 7 5 1 1 1 4	a + c > 0	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0) (0 25 + 25	0 58 + 69	0 63 + 71	0 42 + 71	0 40 + 56	0 41 + 56	0 55 + 54	0 45 + 47		0 107 +106	0 108 +106	0 <u>96</u> +119	0 79 + 92	0 59 + 59	U 18 + 13
फ्र <i>ि</i> म _्	0 0 468 -385 2 0 463 -379	4 0 <i>5</i> 01 -281 6 0 255 -127	8 0 123 -127	12 0 30 - 7	14 0 < 5 + 29	16 0 40 + 47	18 0 55 + 45	20 0 46 + 43	10 < 5 - 14	3 0 24 + 41	5 0 86 +109	7 0 110 +148	9 0 128 +148	611+ 111 0 11	13 0 85 + 73	15 0 67 + 58	1/ 0 40 + 44 19 0 25 + 27		00 < 5 + 5	20 < 5 + 11	4 0 < 5 + 20	6 0 < 5 - 27	80 < 2 1 5 1 5 1 5 1 5 1 5 1 5 1 5 1 5	10 0 < 5 - 4					1 0 25 + 25	3 0 58 + 69	5 0 63 + 71	70 42 + 71	9 0 40 + 56	11 0 41 + 56	13 0 55 + 54	I5 0 45 + 47		901+ LOI 0 0	2 0 108 +106	4 0 96 +119	6 0 79 + 92		51 + 81 0.0T
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<u>म</u> ्द म <u>ह</u> <u>म</u> ्द	1024 4 0 0 468 -387 +625 4 2 0 467 -379	+397 4 4 0 301 -281 +227 4 6 0 255 -127	+163 4 8 0 123 -127 +128 4 10 0 70 - 60	+72 $+120$ 30 -7	-34 4 14 0 < 5 + 29	- 80 4 16 0 40 + 47			- 42 - 24 5 1 0 < 5 - 14	5 3 0 24 + 41	- 44 5 5 0 86 +109	- 90 5 7 0 110 +148	-146 5 9 0 128 +148	-255 5 11 0 111 +119	-261 5 13 0 85 + 73	-218 5 15 0 67 + 58	-120 5 $1/0$ 40 $+$ 44		- 40 6 0 0 < 5 + 5	- 26 6 2 0 < 5 + 11	6 4 0 <5 + 20	+ 44 6 6 0 <5 - 27	- 70 6 8 0 < 5 - 2	+ 4 6 10 0 < 5 - 4	9 + 6 > 0 75 0 91 +	+ + + > 0 + 1 0 - C + + + 7 - 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2 -	1 4 0 10 0 10 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		- 2 7 1 0 25 + 25	+12 7 3 0 58 + 69	+ 8 7 5 0 63 + 71	7 7 0 42 + 71	-136 7 9 0 40 + 56	-194 7 11 0 41 + 56		-1 63 7 15 0 45 + 47	-144	-146 8 0 0 107 +106	-151 8 2 0 108 +106	- 96 8 4 0 96 +119	- 50 8 6 0 79 + 92		- 13 8 IO 0 IB + 13
म् जिस्ति म् भ	1024 4 0 468 -383 352 +625 4 2 0 463 -379	561 +59/ 4 4 0 501 -281 244 +227 4 6 0 255 -127	186 +163 4 8 0 123 -127 135 +128 4 10 0 70 - 60	89 + 72 4 12 0 30 - 7	< 5 - 34 4 14 0 < 5 + 29	66 - 80 4 16 0 40 + 47		80 - 63 4 20 0 46 + 43 25 42	73 - 42 78 - 24 5 10 < 5 - 14	5 3 0 24 + 41	59 - 44 5 5 0 86 +109	88 - 90 5 7 0 110 +148	114 -146 5 9 0 128 +148	243 -255 5 11 0 111 +119	712 -261 5 13 0 85 + 73	290 -218 5 15 0 67 + 58	211 -120 2 1/ 0 40 + 44 103 - 85 5 19 0 25 + 27	68 I 50	56 - 40 6 0 0 < 5 + 5	<i>3</i> 7 − 26 6 2 0 < 5 + 11	6 4 0 <5 + 20	70 + 44 6 6 0 <5 - 27	74 - 70 6 8.0 < 5 - 2	<4 + 4 6 10 0 $<5 - 4$	0 + 6 > 0 T 0 0 + 6 > 0 + 0 > 0 + 0 > 0 + 0 > 0 + 0 + 0 + 0			<5 - 25	<5 - 2 7 10 25 + 25	<pre><4 + 12 7 3 0 58 + 69</pre>	< 2 + 8 7 5 0 63 + 71	7 7 0 42 + 71	112 -136 7 9 0 40 + 56	188 -194 7 11 0 41 + 56	149 -162 7 13 0 55 + 54	155 -163 7 15 0 45 + 47	161 -144	142 -146 8 0 0 107 +106	127 -151 8 2 0 108 +106	108 - 96 8 4 0 96 +119	68 - 50 8 6 0 79 + 92	52 - 31 8 8 0 59 + 59	< 5 - 13 8 10 0 18 + 13
$\frac{\mathcal{L}}{\mathcal{L}} = \frac{\mathcal{L}}{\mathcal{L}} = \frac{\mathcal{L}}{\mathcal{L}} = \frac{\mathcal{L}}{\mathcal{L}} = \frac{\mathcal{L}}{\mathcal{L}}$	0 1024 4 0 0 468 -387 0 352 +625 4 2 0 467 -379	0 261 +397 4 4 0 201 -281 0 244 +227 4 6 0 255 -127	0 186 +163 4 8 0 123 -127 0 135 ±128 x 10 0 79 - 69	0 89 + 72 4 12 0 30 = 7	0 < 5 - 34 4 14 0 < 5 + 29	0 66 - 80 4 16 0 40 + 47		0 80 - 63 4 20 0 46 + 43 0 25 ± 42	0 38 - 24 5 10 < 5 - 14	5 3 0 24 + 41	0 59 - 44 5 5 0 86 +109	0 88 - 90 5 7 0 110 +148	0 114 -146 5 9 0 128 +148	0 243 -255 5 11 0 111 +119	0 312 -261 5 13 0 85 + 73	0 290 -218 5 15 0 67 + 58	0 211 -120 2 1/ 0 40 + 44 0 103 - 85 5 19 0 25 + 27	0 68 = 50	0 56 - 40 6 0 0 < 5 + 5	0 37 - 26 6 2 0 < 5 + 11	6 4 0 <5 + 20	0 70 + 44 6 6 0 <5 - 27	0 74 - 70 6 8 0 < 5 - 2	$0 < 4 + 4 = 6 \ 10 \ 0 < 5 - 4$				$\mathbf{O}_{1} < \mathbf{S}_{1} = \mathbf{S}_{2}$	0 <5 = 2 7 1.0. 25 + 25	0 <4 +12 7 3 0 58 +69	0 < 3 + 8 7 5 0 63 + 71	7 7 0 42 + 71	0 112 -136 7 9 0 40 + 56	0 188 -194 7 11 0 41 + 56	0 149 -162 7 13 0 55 + 54	0 155 -163 7 15 0 45 + 47	0 161 -144	0 142 -146 8 0 0 107 +106	0 127 -151 8 2 0 108 +106	0 108 - 96 8 4 0 96 +119	0 68 - 50 8 6 0 79 + 92		U < 2 - 13 8 10 0 18 + 13
<u> हि</u> हि में ही है है है	0 0 1024 4 0 0 468 -383 2 0 352 +625 4 2 0 463 -379	4 0 261 +59/ 4 4 0 201 -281 6 0 244 +227 4 6 0 255 -127	80 186 +163 4 80 123 -127 100 135 -128 4 100 70 - 60	12 0 89 + 72 4 12 0 30 - 7	140 < 5 - 34 + 140 < 5 + 29	16 0 66 - 80 4 16 0 40 + 47		20 0 80 - 63 4 20 0 46 + 43 22 0 25 - 42	24 0 38 - 24 5 1 0 < 5 - 14	5 3 0 24 + 41	10 59 - 44 5 5 0 86 +109	30 88 - 90 5 70 110 +148	50 114 -146 5 90 128 +148	7 0 243 -255 5 11 0 111 +119	9 0 312 - 261 5 13 0 85 + 73	11 0 290 -218 5 15 0 67 + 58	15 0 103 - 85 5 10 0 25 + 27	17 0 68 - 50	190 56 - 40 6 00 < 5 + 5	210 37 - 26 6 2 0 < 5 + 11	6 4 0 < 5 + 20	00 70 + 44 6 60 <5 - 27	2 0 74 - 70 6 8 0 < 5 - 2		0 < 4 + T0 0 T2 0 < 4 + T0 0 T2 0 < 7 + 0	80 < 5 + 75 0 14 0 < 4 + 12 30 0 × 5 + 5 5 0 × 5 + 12		14 0 < 5 - 25	160 < 5 - 2 7 1.0 25 + 25	1 80 < 4 + 12 7 30 58 + 69	200 < 3 + 8 7 5 0 63 + 71	7 7 0 42 + 71	10 112 -136 7 9 0 40 + 56	30 188 -194 7 11 0 41 + 56	5 0 149 -162 7 13 0 55 + 54	7 0 155 -163 7 15 0 45 + 47	9 0 161 -144	11 0 142 -146 8 0 0 107 +106	13 0 127 -151 8 2 0 108 +106	15 0 108 - 96 8 4 0 96 +119	17 0 68 - 50 8 6 0 79 + 92	19 0 52 - 31 8 8 0 59 + 59	21 U < 2 - 13 8 10 0 18 + 13

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Table A-3. Methoxycarbonylmercuric Chloride hkO and $Ok\ell$

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Table A-4. 1	o-Chloronitrobenzene	0kl	and	hOl
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<u>h k</u>	<u></u>	<u>F</u> 。	<u>F</u> c		<u>h k</u>	Ł	Fo	<u>F</u>	C	<u>h</u>	<u>k</u>	Ł	Fo	<u>F</u> c
00	0		160		03	1	2.0	- 0.	9	1	0	0	9.3	- 7.3
00	2	12.6	+24.3		03	2	1.7	- 1.	6	2	0	0	<1.1	+ 5.8
		(21.1)			03	3	19.6	-25.	6	3	0	0	3.4	+ 2.1
00	4	18.3	-34.3				(23.2)			4	0	0	3.0	- 3.1
		(28.9)			03	4	10,3	- 6.	.9	5	0	0	<1.5	+ 0.3
00	6	4.8	- 9.2		03	5	6.1	- 4.	9	-3	0	2	2,5	+ 3.2
00	8	< 0.6	+ 3.7		03	6	<0•6	+ 2.	3	-2	0	2	4.2	-15.7
00	10	3.6	- 2.4		03	7	9.8	+ 9.	9	-1	0	2	37.0	+70.0
01	1	13.6	+12.4		03	8	2,8	- 1.	1	0	0	2	23.0	+24.3
		(16.3)			03	9	0.7	+ 4.	1	1	0	2	11.7	-10.3
01	2	<u>_</u> 19•4	-43.4		04	0	4.7	- 3.	.4	2	0	2	9.0	+12.6
		(42.5)			04	1	1.3	- 6.	6	3	0	2	5.5	- 8,5
01	3	<u>_</u> 11.6	+21.2		04	2	6.1	- 4.	5	4	0	2	2.1	- 0.3
		(15.0)			04	3	1.6	+ 2.	.0	-3	0	4	4.9	- 6,2
01	4	16.2	+12.4		04	4	1.7	+1.	4	-2	0	4	3.9	+ 5.5
		(16.8)			04	5	4.0	. + 5.	0	-1	0	4	2.2	+11.8
01	5	4.8	- 0.8		04	6	1.3	- 3.	1	0	0	4	34.7	-34.3
01	6	7.5	+10.3		04	7	7•4	- 3.	1	1	0	4	9.1	+11.8
01	7	12.9	- 8.9		04	8	1.1	+ 0.	4	2	0	4	6.0	- 7.6
01	8	0.6	+ 2.5		04	9	4.3	- 4.	8	3	0	4	3.2	- 1.9
01	-9	1.6	- 2.1		04	10	2.5	+ 2.	2	-4	0	0	2.1	- 1.2
01	10	2.1	- 1.3		05	Ţ	1.7	+ 1.	4	-2	0	0	< 1.4	- 1,5
	11	1.3	+ 1.3		05	2	2.7	+ 4.	9	~2	0	о с	2.1	+ 0,8
01	12	4.7	+ 2.5			2		+ 2.	4	~1	0	6	10.1	~⊥/•/
02	0	(10, C)	-10.9			4	< 0.0	- 0.	6	י ז	0	6	41/	- 7.4
0 0	•	(18.0)	105 9			2	< U.0	- 1. 7	0 7	2 T	0	6	2.5	т 2.0
0 2	T	(50.0)	+27.0			7	209	- J.	- I Z	ے ح	0	6-	51	- J•9 - 2 4
0.0	2	(22.62)	17 F		05	ା ନ	<0.8	- +•	r A	~2	ñ	8	5 A	- 3 8
02	2	12 5	- 1.0J		05	a	2.1	+ 0	.4 7	_]	õ	8	5.8	- 9.0
02	ר א	10 3	- 2 8		06	0	20.8	+ 6.	0	ō	õ	8	<1.2	+ 3.7
02	ት 5	15 1	-13.6	;	06	ĩ	<0.8	+ 2.	õ	ĩ	õ	8	2.2	- 2.7
02	6	12.4	_ Q.T		06	2	<0.8	+ 2.	Õ.	2	õ	8	6.3	+ 4.0
02	7	0.6	- 1.8		06	3	2.5	+ 1.	7	3	õ	8	3.4	+2.4
02	ิ่ร	2.1	+ 0.8		06	á	0.8	- 2.	6	ó	ō	10	3.7	- 2.4
02	ģ	5.8	+ 7.3		06	5	1.1	+ 0-	9	ì	Õ	10	3.9	- 2.4
02	10	5.3	+ 4.9		07	í	<0.8	+ 1.	í	2	0	10	4.2	+ 4.2
02	11	0.8	+ 1.9		07	2	<0.8	- 1.	0	-1	0	12	3.5	- 1.9
					07	3	1.8	+ 0.	6	Ō	0	12	<1.5	- 2.4
					07	4	<0.8	+ 0.	.4	1	0	12	2.1	+ 2.1
					07	5	0.7	_ 0	x					

Table A-5. Acenaphthen equinone hkO and $\mathrm{Ok}\ell$

<u>h</u>	<u>k l</u>	Fo	<u>F</u> c	<u>h</u>	<u>k l</u>	<u>F</u> o	Fc	<u>h</u>	<u>k</u>	<u>l</u>	<u>F</u> ,	<u>F</u> _c	<u>h</u>	<u>k</u>	<u>e</u>	<u>F</u> o	<u>F</u> c =
0	00	Not	376	1	27 0	<1.3	- 4.1	3	9	0	25.2	-22.5	4	23	0	<1.3	1.6
0	20	obs.	- 4.6	1	28 0	<1.2	1.3	3	10	0	< 0.9	- 2.3	4	24	0	<1.3	0.3
0	40	75.9	-85.8	ì	29 0	<1.2	1.5	3	11	0	26.0	26.0	4	25	0	<1.2	- 2.9
0	60	< 0.6	1.8	l	30 0	<1.1	- 0.5	3	12	0	5.5	6.4	4	26	0	<1.2	- 2.2
0	80	60.8	-55.6					3	13	0	15.5	16.0					
0	10 0	10.6	12.2	2	00	17.5	21.4	3	14	0	4.2	- 2.9	5	1	0	7.9	- 8.5
0	12 0	14.6	16.6	2	10	38.8	-38.9	3	15	0	<1.2	- 2.5	5	2	0	5.0	- 5.2
0	14 0	6.0	- 8.4	2	2 0	16.3	-15.2	3	16	0	13.7	-14.0	5	3	0	<1.1	- 3.1
0	16 0	16.2	-16.1	2	30	8.9	-12.7	3	.17	0	<1.2	0.7	5	4	0	6.0	7.3
0	18 0	2.7	- 1.4	2	40	30.8	-28.1	3	18	0	<1.2	2.9	- 5	5	0	17.6	13.5
0	20 0	9.5	-12.2	2	50	2.6	- 2.3	3	19	0	12.1	-12.7	5	6	0	<1.2	1.5
0	22 0	<1.3	1.7	2	60	11.1	13.4	3	20	0	<1.3	4.7	5	7	0	7.6	-10.1
0	24 0	29.5	29.4	2	70	<0.7	1.8	3	21	0	3.9	- 6.5	5	8	0	17.7	20.5
0	26 0	<1.3	1.8	2	80	3.7	- 4.8	3	22	0	<1.3	1.1	5	9	0	2.5	- 2.7
0	28 0	<1.2	- 2.9	2	90	21.4	20•4	3	23	0	10.4	11.3	5	10	0	<1.2	- 2.1
0	30 0	<1.2	- 0.9	2	10_0	4.1	6.9	3	24	0	2.2	4.0	- 5	11	0	12.8	13.0
0	32 0	<0•9	- 2.3	2	11 0	17.7	-16.8	3	25	0	4•9	6.5	5	12	0	6.5	5.0
0	34 0	<0.7	- 0.3	2	12 0	30.7	29.4	3	26	0	3.0	- 4.3	5	13	0	<1,3	3.0
				2	13 0	7.0	6.6	3	27	0	2.1	- 3.5	5.	14	0	7.0	7.2
j	10	14.7	-15.9	2	14 0	<1.0	- 2.2	3	28	0	3.4	- 3.1	5	15	0	<1.3	- 1.2
1	20	62 <u>.</u> 3	-55.7	2	15 0	3.1	4.5	- 3	29	0	<1.1	- 0.3	5	16	0	19.3	-18.6
1	30	9•7	11.4	2	16 0	6.8	- 8.1		_	_			5	17	0	<1.4	- 1.1
1	4 0	<0.5	- 1.3	2	17 0	12.7	-11.8	4	0	0	<0.9	- 1.5	5	18	0	9.1	- 8,0
1	50	19•4	21.0	2	18 0	3.5	3.4	4	1	0	26.2	-24.0	5	19	0	4.0	- 1.9
1	60	20.2	-20.5	2	19 0	<1.2	- 1.1	4	2	0	22.8	-21.6	<u>ຼ</u> ້າ	20	Ū.	2.8	- 2.3
1	70	6.5	- 8.4	2	20 0	5.7	5.5	4	3	0	2.8	- 5.5	5	21	0	<1.3	0.2
1	80	13.7	-13.2	2	21 0	2.2	4.3	4	4	0	5.9	- 6.7	5	22	0	5.2	4.9
1	90	15.5	17.0	2	22 0	4.5	- 5.8	4	5	0	15.7	14.5	<u>ל</u>	.23	0	<1.2	1.4
1	10 0	52.1	-48.4	2	23 0	<1.3	3.2	4	6	0	5.9	6.1	2	24	0	< 1.2	2.3
1	11 0	30.6	-29.8	2	24 0	9.1	- 6.5	4	7	0	2.7	- 6.1	ר ד	25	0	2.2	- 3.1
1	12 0	2.0	4.0	2	25 0	<1.3	2.0	4	8	0	10.2	14.4	୍ ୨	26	0	< T°O	- 2.1
1	13.0	6.3	- 6.9	2	26 0	1.0	101	4	.9	0	< 1.1	- 0.4	6	^	0	0 5	, ,
1	14 0	19.6	20.6	2	27 0	2.2	1.1	4.	10	0	< 1.1	- 1.0	0 2	<u>י</u>	ó	0.) 7 7	1.4
· 1	15 0	21.9	20.0	2	20 0	< 1.c		4	10	0		= 0.4	. 0	: Т Т	0	201	- 4+2
Ţ	-TP 0	4.0	5.4	2	29 0) ショフ マョコ	- 2.02	4	12	0	2.2	- 2+2	6	2	0	0,0 E 7	10°T
1	17 0		- 1.1	2	50 0	<1.1	0.9	4	12	0	~1.2	10 6	. 0 	2	0	2.1.2	- 2.2
1	18 0	12.1	12.0	7	1 0	77 5	71 0	4	14	0	120	10.0	6	4		>⊥•∠	- 7.4
- <u>1</u>	19 0	$< 1 \cdot 2$	- 0.0	ファ	- 1 O	2102	0+דל ו וו	4	16	0	12.0		6	5	0	2.2	20
۲ ۲	20 0	10 6	-10 7	ファ	20	0•4 15 7		4 1	17	0	4+) ス に	9+0 	6	7	0	11 1	11 1
. т г т	21 U	10.0	-10.0	ファ		20 0 20 1		4	19:	0	202 A D	6.0	6	י 2	0	11 0	_11 6
1 7	22 0	⊿ 	12.0	ファ	4 U 5 A	ס,•ס, קי∵ב	- <u>-</u>	4	10	0	7 6	- 21	6	0	0	15.2	14.6
L r	27 0	< 1 2	_ 1 O) マ	60	201	- 202 9 1 8	4 1	20	0	6.5	- 2.1 1.6	6	10	0	14.2	-13.3
ר ר	24 0	×⊥•⊅ ∧ ⊑	- 1.U	ノス	7.0	~ 0.9 07 x	-26 7	4 A	20	0	<1.A	1.1	6	11	õ	2.2	- 2.0
ר ר	29 0	4•2 10 7	0+1	ノマ	80	ריו <u>ר</u> ייון	ייבט+ <i>ו</i>	н Л	22	ñ	10 4		6	12	õ	16.3	13.8
	20 0	TO \$ 2	-TC + O)	0.0	على ه على ح	TT 0	- +	~~	. U	TA++		v	هيئة بكير	~	~~,• J	

<u>h kl</u> <u>F</u>, E_c <u>h k l</u> P. E. Fc Fc <u>h k l</u> E. Fc Not obs. 20 6 13 0 <1.4 0.8 7 16 0 4.1 3.9 0 5.3 0 19 1 < 5.7 0.3 6 14 O 7 17 0 5.3 40 86.7 -95.9 0 20 1 13.9 -14.7 3.2 - 4.94.9 0 60 <2.8 - 1.4 0 21 1 < 5.9 - 2.9 6 15 0 14.7 -12.3 7 18-0 <1.1 2.0 0 0 8 0 65.7 -60.6 0 22 1 < 5.9 2.6 6 16 0 14.5 -12.3 7 19 0 <1.0 - 1.0 0 23 1 12.9 6 17 0 <1.3 - 0.7 7 20 0 <1.0 1.6 0 10 0 14.1 -13.2 11.0 0 24 1 < 6.2 0.1 6 18 0 <1.3 2.9 7 21 0 3.3 1.2 0 12 0 15.5 10.9 6 19 0 6.5 7 22 0 < 0.9 - 0.3 0 14 0 6.9 9.6 0 25 1 10.7 9.9 5.0 0261 < 6.4 - 1.56 20 0 2.9 4.0 0 16 0 18.2 -17.1 0 27 1 < 6.5 - 5.9 6 21 0 < 1.2 - 3.2 0 0 <1.3 3.0 0 18 0 < 4.5 2.0 8 6 22 0 <1.1 10 1.5 2.7 0 20 0 12.3 -12.1 0.8 8 0 2 16.7 -21.0 6 23 0 < 1.0 2.0 2.2 - 1.9 0 22 0 < 5.1 - 1.8 1.3 8 0 12 < 5.2 - 2.6 1.2 8[.] 3.0 6.1 - 6.20 24 0 34.9 29.3 0 6 24 0 < 0.9 6 25 0 < 0.9 - 0.5 8 40 4.3 - 4.5 0 2 2 < 5.2 13.0 32 < 5.2 - 2.5 50 5.2 - 5.3 43.8 43.3 0 6 26 0 4.2 3.3 8 0 11 8.6.0 4.2 2.2 21 33.9 40.1 0 4 2 < 5.2 - 8.3 0 • 5 2 < 5.3 - 6.1 70 5.1 0 31 47.0 -49.0 0 7 4.0 - 3.2 8 5.2 10 41 67.6 58.6 0 62 12.3 -15.3 7 20 5.0 4.8 8 8 0 6.5 . 3..2 0 51 < 3.9 - 2.1 72 14.7 30 90 2.2 0 0 15.6 7 8 1.4 3.2 4.9 61 < 4.0 - 4.84 0 8 10 0 < 1.2 - 0.5 0 0 82 10.5 13.5 7 7.2 4.0 71 0.92 10.6 15.0 8 11 0 < 1.2 0 27.5 29.0 7 50 <1.4 1.5 0.9 7. 8 12 0 <1.1 81 32.8 30.7 0 10 2 < 5.4 - 3.5 60 13.8 -12.7 1.2 0 7 70 4.5 6.0 8 13 0 <1.1 - 0.9 0 91 < 4.4 4.5 0 11 2 7.5 - 7.8 0 12 2 < 5.5 - 1.8 0 10 1 18.5 -21.1 7 ·8 0 10.4 - 8.8 8 14 0 <1.0 . 0.5 3.5 - 2.9 0 11 1 14.3 -13.3 0 13 2 <5.8 2.3 90 <1.3 - 4.4 8 15 0 7 0 14 2 7 10 0 10.4 6.7 8 16 0 < 1.2 0.2 0 12 1 < 4.7 - 4.4 7.8 9.3 0 15 2 < 5.9 - 4.1 8 17 0 <1.0 0 13 1 9.6 - 9.0 7 11 0 <1.3 - 1.8 0.0 18.8 16.1 0 16 2 16.2 15.6 7 12 0 <1.3 - 0.2 8 18 0 <0.9 0.2 0 14 1 7 13 0 3.8 - 3.4 8 19 0 4.0 3.1 0 15 1 7.0 - 4.5 0 17 2 < 5.9 - 6.8 0 18 2 <6.0 - 1.2 0 16 1 11.5 -11.5 7 14 0 <1.3 - 0.4 8 20 0 <0.7 - 1.3 0 19 2 <6.1 - 2.0 0 17 1 < 5.4 - 2.6 7 15 0 3.7 - 4.0 6.7 - 5.5 0 20 0 8.5 - 6.2 0 18 1

The phases of the <u>hk</u>0 and <u>Ok</u> ℓ structure factors are referred to the respective origins of the (OO1) and (100) projections. The calculated <u>Ok</u>0 structure amplitudes are not the same since hydrogen-atom contributions are not included in computing <u>Ok</u> ℓ structure factors.

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Table A-6. <u>cis</u>-1,2-Acenaphthenediol $hO\ell$

<u>h</u>	<u></u>	F	<u>P</u> c	<u>h</u>	$\underline{\ell}$	<u>F</u> o	Fc	<u>h</u>	Ł	<u>F</u> o	<u>F</u> c	<u>h</u>	Ľ	Fo	Fc
0	0	not	392	-10	4	32.2	-26.1	-12	8	4.1	- 4.7	- 9	12	< 2.3	- 3.1
1	0	obs.	-30.1	- 9	4	13.4	12.7	-11	8	3•3	4•7	- 8	12	< 2.3	- 0.1
2	0	52.8	-61,5	- 8	4	24.5	24.4	-10	8	< 2.2	2.7	- 7	12	4.5	4 . Q
-3	0	22.3	-22.5	- 7	4	12.8	12.5	- 9	8	< 2.0	- 2.5	- 6	12	12.6	-14.8
4	0	14.2	-19.4	- 6	4	8.4	- 9.2	- 8	8	5.0	5.6	- 5	12	12.4	15.5
5	0	7.4	- 7.3	- 5	4	18.8	-16.4	- 7	8	13.5	- 9.9	- 4	12	< 2.2	- 1.1
6	0	2.3	2.1	- 4	4	7.2	- 7.7	- 6	8	39.6	32.4	- 3	12	42.2	3.2
7	0	13.4	- 9.4	- 3	4	35.6	36.6	- 5	8	6.0	6.4	- 2	12	12.5	16.5
8	0	2.5	2.3	- 2	4	2.3	- 5.7	- 4	8	32.4	-27.4	- 1	12	11.5	13.0
9	0	4.6	- 3.5	- 1	4	13.4	-18.6	- 3	8	35.8	-38.6	0	12	11.7	-12.9
10	0	< 2.2	- 1.2	0	4	53.2	-51.0	- 2	8	11.9	17.2	1	12	29.9	-31.2
11	0	11.6	<u>- 5</u> .5	: 1	4	44.0	44.4	- 1	8	<1.7	2.0	2	12	<2.3	- 0.2
12	0	29.4	24.4	2	4	52.6	-55.2	0	8	8.1	- 9.0	3	12	7.5	10.6
13	0	42.0	2.4	3	4	31.2	27.6	1	8	20.2	20.4	-14	. 14	6.3	- 4.3
14	0	10.9	- 7.5	4	4	28.4	25.7	2	8	<1. 8	- 1.2	-13	14	<1. 8	- 2.7
15	0	4.2	- 2.8	5	4	32.9	30.1	3	8	16.3	-19.3	-12	14	9.2	5.2
-15	2	10.1	6.9	6	4	22.9	-19.5	4	8	15.1	17.4	11	14	<2.2	- 4.9
-14	2	41.8	- 0.5	7	4	42.0	- 4.6	5	8	15.0	-15.2	-10	14	3.2	- 2.9
-13	2	< 2.1	- 1.3	8	4	3.3	- 4.7	6	8	16.5	18.3	- 9	14	<2.3	2.6
-12	2	4.6	- 3.0	9	4	4.6	5.8	7	8	<2.3	0.4	- 8	14	< 2.3	5.7
-11	2	3.3	5.6	10	4	5.7	- 3.6	8	8	5.0	- 6.0	7	14	<2.3	1.0
-10	2	22.1	- 2.9	11	4	6.2	- 5.9	9	8	4.2	- 5,7	- 6	14	17.4	17.9
- 9	2	3•7	- 4.9	12	4	41.8	0.5	-14	10	4.8	- 3:7	- 5	14	16.6	-16.8
- 8	2	13.4	-13.3	13	4	3.7	3.3	-13	10	<2.1	1.9	- 4	14	4.1	4.9
- 7	2	5.3	- 8.2	-13	6	42.3	- 3.5	-12	10	3.3	0.8	- 3	14	< 2.3	- 0.6
- 6	2	21.6	- 0.0	-12	6	4.7	5.8	-11	10	24.0	21.5	- 2	14	9.5	-11.5
- 5.	2	30.9	25.6	-11	6	10.5	-10.7	-10	10	<2.3	- 5.3	- 1	14	5.3	- 6.7
- 4	2	×1,2	4.4	-10	6	24.9	22.2	- 9	10	42.2	1.7	0	14	3.6	4.6
- 3	2	60.5	55.9	- 9	6	18,5	-16.6	- 8	10	15.1	-15.3	1	14	<.2₀2	2.0
- 2	2	37.5	41.4	- 8	6	42.0	1.2	- 7	10	42.1	3.8	2	14	42.1	0.5
- 1	2	40. 8	- 1.7	- 7	6	11.6	9.4	- 6	10	14.6	-14.7	3	14	<2.0	1.3
0	2	93.5	-93.1	- 6	6	14.0	-14.4	- 5	10	<2.0	- 2.1	4	14	<1.8	4.9
1	2	22.5	25.3	- 5	6	<1.6	- 0.3	- 4	10	8.6	8.0	5	14	<1.6	- 2.2
2	2	24.7	-25.9	- 4	6	9•7	9.8	- 3	10	<1.9	1.2	6	14	5.6	6.6
3	2	30.5	-31.8	- 3	6	10.0	15.6	- 2	10	9•4	-12.0	-11	16	2,6	5.3
4	2	17.7	19.7	- 2	6	16.0	19.0	- 1	10	14.3	13.2	-10	16	<2.0	- 0.4
5	2	38.8	-33.7	- 1	6	48.4	-45.9	0	10	<2.1	- 2.7	- 9	16	4.7	6.2
6	2	17.3	17.4	0	6	30.9	26.6	1	10	17.8	21.6	- 8	16	<2.2	- 2.2
7	2	8.5	8 .6	1	6	34.0	-31.2	2	10	<2.2	6.0	- 7	16	4.7	- 6.6
8	2	3.1	5.8	2	6	39•9	39.0	3	10	6.8	- 6.5	- 6	16	<2.2	- 5.0
9	2	4.3	5.1	3	6	2.4	- 2.2	4	10	12.5	-16.7	- 5	16	4.7	3.9
10	2	4.3	4.6	4	6	15.6	-18.1	5	10	42.3	6.3	- 5	18	5.4	7.0
11	2	L 2.3	1.3	5	6	4.1	7.5	6	10	5.7	- 7.2	- 4	18	3.7	- 2.6
12	2	14.4	-11.5	6	6	7.9	- 9.6	-14	12	8.2	8.4	- 3	18	<1.8	2.2
13	2	4.5	- 2.6	7	6	42.2	- 0.7	-13	12	10.1	8.0	- 2	18	<1.7	- 3.1
-14	4	7.7	6.4	-16	8	4.9	- 5.3	-12	12	8.3	- 7.5	- 1	18	41.5	- 1.2
-13	4	42.2	- 2.2	-15	8	<1.7	- 0.9	-11	12	26.3	-21.0	0	18	3.2	3.0
-12	4	8.8	- 8.9	-14	8	<1.9	1.8	-10	12	11.5	10.0	- 5	20	4.2	- 6.9
<u>-11</u>	4	8.7	9.2	-13	8	< 2.0	- 2.3					·.			

Table A-7. <u>cis</u>-1,2-Acenaphthenediol hl ℓ

<u>h</u>	<u>e</u>	<u>F</u> 。	₽ _c	<u>h</u>	<u></u>	F.	Fc	<u>h</u>	<u>e</u>	<u>P</u> o	<u>F</u> c	. <u>h</u>	<u></u>	<u>F</u> 。	Fc
1	0	14.2	- 21.3	12	1	42.5	0.5	- 1	3	34.2	-32.5	-10	5	5.6	- 6.7
2	Ō	112.7	106.1	13	1	2.9	3.0	0	3	13.7	16.2	- 9	5	2.6	- 0.6
3	0	16.6	17.8	14	1	4.8	3.0	1	3	23.1	20.2	- 8	5	13.5	-13.9
4	0	<1.0	- 3.2	-14	2	3.2	2.2	2	3	4.6	- 4.0	- 7	5	17.0	15.8
5	0	3.2	2.7	-13	2	< 2.4	Ò.2	3	3	< 1.2	0.6	, 6	5	4.3	1.5
6	0	12.2	- 11.2	-12	2	< 2.9	- 0.9	4	3	13.1	14.7	- 5	5	12.7	- 8.9
7	0	3.1	2.5	-11	2	< 3.0	0.6	5	3	15.7	-15.3	- 4	5	6.6	2.1
8	0	3.0	- 4.6	-10	2	<2.9	4.8	6	3	5.8	- 5.2	- 3	5	12.1	-10.8
9	0	<2.7	3.3	- 9	2	<2.6	1.5	7	3	22.4	1.9	- 2	5	6.5	11.8
10	0	21.1	- 18.9	- 8	2	4.9	4.0	8	3	22.7	4.4	- 1	5	13.7	-16.1
11	0	5.8	4.0	- 7	2	9.7	-10.7	9	3	8.7	- 8,8	0	5	27.9	32.0
12	0	3.0	3.2	- 6	2	3.5	2.8	ìo	3	<3.0	3.6	1	5	22.0	26.0
13	0	<2.1	0.2	- 5	2	81.6	-75.0	-13	4	42.6	- 1.7	2	5	12.7	-13.0
14	0	5.4	4.4	- 4	2	8.5	7:1	-12	4	4.6	4.6	3	5.	12.1	-14.6
15	0	<0.8	3.2	- 3	2	46.0	47.3	-11	4	<3.0	- 1.2	4	5	6.6	-11,2
-15	ì	3.3	2.0	- 2	2	93.1	83.9	-10	4	14.4	-13.7	5	5	4.6	5.6
-14	1	4.0	- 4.0	. - 1	2	39.3	-38.4	- 9	4	9.5	10.4	6	5	7.8	10.4
-13	1	8.2	- 4.5	. 0	2	10.3	11.2	- 8	.4	20.1	-20.0	7	5	7.1	- 8.1
-12	1	42.8	3.3	1	2	6.5	i1.8	- 7	4	9.7	13.4	8	5	< 3.0	1.0
-11	1	23.0	1.4	2	2	1.9	0.8	- 6	4	く1.5	0.4	-14	6	< 2.1	- 0.3
-10	1	<2.9	- 1.5	3	2	2.0	1.9	- 5	4	25.8	24.3	-13	6	4.4	4.7
- 9	1	42.6	0.8	4	2	<1.3	- 1.9	- 4	4	12.1	-10.8	-12	6	8.2	- 6.0
- 8	1	42.4	1.8	5	2	26.6	-21.4	- 3	4	5.0	9.0	-11	6	4.7	3.8
- 7	1	<1.8	- 0.2	6	2	10.4	12.7	- 2	4	4.2	7.7	-10	6	8.5	7.9
- 6	1	5.7	5.5	7	2	35.6	-32.7	- 1	4	9.3	- 9.2	- 9	6	7.5	- 8.3
- 5	1	9.0	- 8.3	8	2	7.1	5.0	0	4	6.9	6.2	- 8	6	2.4	3.9
- 4	1	15.2	13.7	9	2	8.5	9.0	l	4	11.2	-15.2	- 7	6	7.6	- 7.4
- 3	1	74.4	70.3	10	2	14.9	17.2	2	4	19.2	-21.8	- 6	6	< 1.7	0.7
- 2	.1	95.2	- 81.9	11	2	3.9	- 4.3	3	4	1.9	2.9	- 5	6	22.2	22.7
- 1	1	35.7	- 51.2	12	2	42.4	- 2.4	4	4	3.4	- 4.8	- 4	6	29.6	-30.2
0	. 1	4.4	5.3	-13	3	< 2.5	- 2.3	5	4	4.6	7.0	- 3	6	11.5	10.9
1	1	22.5	20.2	-12	3	5.0	- 3.3	6	4	<2.3	3.3	- 2	6	23.6	-20.3
2	1	25.7	26.8	-11	3	< 3.0	3.2	7	4	9.8	11.3	· - 1	6	37.8	39.6
3	1	5.6	- 5.9	-10	3	5.6	5.6	8	4	42.9	1.8	Ó	6	18.6	-21.3
4	1	<2.4	- 1.3	- 9	3	<2.5	- 3.6	9	4	< 3.0	- 1.8	1	6	8.5	8.0
5	1	5.8	6.3	- 8	3	20.8	18.4	10	4	<2.8	- 1.2	2	6	11.7	14.9
6	1	5.7	- 7.9	- 7	3	22.6	-22.5	11	4	<2.4	- 2.5	3	6	5.7	- 6.9
7	1	6.8	6.4	- 6	3	3.9	- 3.2	12	4	<1.8	1.0	4	6	3.4	- 3.0
8	1	6.9	- 6.9	- 5	3	8.5	9.5	13	4	2.8	- 3.3	5	6	6.4	5.9
9	ī	10.9	13.8	- 4	3	9.1	- 8.7	-13	5	<2.7	- 2.2	6	6	3,8	- 2.6
10	1	10.5	- 9.0	- 3	3	26.9	-23.9	-12	5	7.4	8.6	7	6	8.0	7.0
11	1	9.6	- 7.7	- 2	3	24.1	21.8	-11	5	3.8	5.0	8	6	8.7	-10.7

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<u>h</u>	<u></u>	Fo	Ēc	<u>h</u> <u>l</u>	<u>F</u> o	<u>F</u> c	<u>h l</u> Fa	<u>F</u> _c	<u>h</u> <u>l</u>	<u>F</u> o	<u>F</u> c
9	6	42.8	0.5	48	5.2	- 9.7	-11 11 < 2.	9 0.2	- 8 13	3.7	3.0
-13	7	2.7	2.6	5 8 [.]	42.9	- 5.5	-10 11 17.	6 13.4	- 7 13	2.9	- 4.5
-12	7	8.2	- 7.6	68	12.7	13.1	-911 < 3.	0 2.1	- 6 13	<3.0	- 0.6
-11	7	4.1	4.0	78	2.8	- 1.7	- 8 11 11.	4 - 9.7	- 5 13	3.6	3.6
-10	7	<2.9	0.7	8 8	<2.7	2.9	- 7 11 7.	8 6.2	- 4 13	б.4	- 5.6
- 9	7	8.5	- 7.9	-99	∠2.8	- 1.6	- 6 11 < 2.	6 - 1.9	- 3 13	<3.0	0.7
 8 [.]	7	<2.4	1.9	-89	5.1	8.7	-511 3.	3 - 4.6	- 2 13	8.6	-11.3
- 7	7	5.6	5.8	-79	8.8	- 7.1	- 4 11 14.	2 12.2	- 1 13	9.7	10.9
- 6	7	2.8	- 3.4	-69	2.4	2.6	- 3 11 12.	6 -12.1	0 13	7.7	10.3
- 5	7	<1.7	2.8	-59	9.2	8 .6	-211 3.	7 7.8	1 13	< 3.0	- 3.3
- 4	7	19.9	-23.8	-49	< 2.0	3.1	- 1 11 < 2.	6 - 4.8	-14 14	4.3	- 2.6
- 3	7	20,8	23.4	- 39	5.5	- 5.7	0 11 11.	0 -11.4	-13 14	く1:6	0.1
- 2	7	9.8	10.4	-29	2.8	3.2	1 11 ∠ 2.	8 - 0.4	-12 14	<2.1	1.6
- 1	7	16.6	19.9	-19	5.2	- 6.9	2 11 19.	7 18.0	-11 14	<2.4	- 1.9
0	7	37.0	-32.0	09	42.1	- 1.2	3 11 く3.	0 1.1	-10 14	<2.7	- 0.5
1	7	2.6	- 5.9	19	٤. 3	1.6	411 5.	0 - 4.7	- 9 14	<2.9	- 4.2
2	7	3.6	4.8	29	4.2	- 5.5	511く2.	8 - 1.8	- 8 1 4	6.5	- 5.5
3	7	9.7	- 9.7	39	4.7	5.3	-13 12 8.	5 6.8	- 7 14	5.1	4.6
4	7	7.5	7.5	49	<2.9	- 0.5	-12 12 2.	6 - 2.3	- 6 14	<3.0	- 0 <u>.</u> 8
5	7	4.7	5.2	-13 10	<2.5	- 3.8	-11 12 14.	5 9.2	- 5 14	< 3.0	27
6	7	5.7	- 6.3	-12 10	2.5	0.1	-10 12 < 3.	0 - 3.6	- 4 14	19.6	21.2
7	7	4.1	5.8	-11 10	7.8	- 6.1	- 9 12 14.	3 - 9.1	- 3 14	3.7	- 4.6
8	7	4.0	- 6.6	-10 10	4.1	- 0.1	- 8 12 4.	6 4.2	- 2 14	8.7	9.7
9-	-7	2.6	2.2	- 9 10	16.7	19.8	-71242.	9 - 1.7	- 1 14	く3.0	- 2.3
10	7	3.4	3.4	- 8 10	11.5	12.5	-61222.	8 - 6.5	0 14	2,.8	0.3
-13	8	3.4	- 3.5	- 7 10	3.9	- 3.9	-512 3.	5 3.0	1 14	< 2.8	0.0
-12	8	3.7	3.5	- 6 10	14.3	-18.2	- 4 12 14.	6 -19.3	2 14	3.4	- 5.1
-11	8	43.0	- 2.7	- 5 10	3.7	3.6	- 3 12 6.	6 10.6	3 14	< 2.3	1.6
-10	8	<2.9	- 0.9	- 4 10	1.9	1.7	- 2 12 < 2.	8 4.8	4 14	∠1.8	- 3.2
- 9	8	< 2.7	- 4.2	- 3-10	11.3	-11.8	- 1 12 13.	5 19.3	5 14	2.8	4.0
- 8	8	4.1	- 6.3	- 2 10	6.6	7.6	0 12 4.	6 - 4.7	-14 15	2.1	- 1.9
- 7	8	4.2	- 5.6	- 1 10	7.4	- 9.9	1 12 4.	0 4.6	-13 15	2.4	1.4
- 6	8	30.1	31.2	0 10	4.3	1.6	2 12 2 3.	0 - 2.1	- 8 15	7.4	- 5.8
<u>∽</u> .5	8	8.9	- 8,6	1 10	6.4	- 7.6	3 12 7.	0 - 9.3	4 15	4.7	- 4.0
- 4	8	16.9	17.8	2 10	4.9	6.8	4 12 < 2.	8 - 2.1	-13 16	3.7	- 3.6
- 3	8	5.9	- 9.5	3 10	5.5	7.8	-15 13 1.	4 - 2.0	-10 17	3.0	- 3.I
- 2	8	5.5	4.8	4 10	11.9	16.6	-14 13 2.	0 - 2.7	- 8 17	3.0	3.5
- 1	8	20.8	-24.2	5 10	7.4	- 6.7	-13 13 8.	4 6.0	- 3 18	4.2	4.9
0	8	9.7	12.5	6 10	6.3	-10.2	-12 13 42.	j ⊥•3	5 I9	2.3	2•4
1	8	<2.0	2.8	7 10	< 2.4	0.3	~ <u>⊥⊥ 1</u> 3 <u>∠</u> 2.	b = 0.1	:		
2	8	8.8	- 9.8	-13 11	5.7	- 5.4	-10 13 <2.	y - 5.0			
5	R	3.1	/_h	-12 11	5.5	- 4.9		C T'R			

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Table A-8. <u>cis</u>-1,2-Acenaphthenediol Dinitrate $hO\ell$

<u>h</u>	Ł	Po	<u>₽</u> c	<u>h</u>	<u></u>	<u>P</u> °	<u>P</u> c	h	<u>e</u>	<u>F</u> o	<u>F</u> c	<u>h</u>	Ŀ	<u>F</u> 。	Fc
0	0		568	4	2	9.6	12.4	10	4	33.6	-33.7	14	6	2.3	2.2
1	0	obs.	-20.6	5	2	34.7	- 28.9	11	4	7.2	7.4	15	6	<1.1	2.1
2	0	88.9	89.7	6	2	17.0	- 12.5	12	4	6.2	9.1	-21	8	<1.2	- 0.9
3	0	29.6	-31.3	7	2	17.3	17.4	13	4	5.0	5.8	-20	8	2.4	3.6
4	0	106.4	-95.1	8	2	29.3	29.4	14	4	<u>ک</u>	- 1.8	-19	8	8.0	- 8.1
5	0	37.1	43.4	9	2	4.7	- 10.5	15	4	<1.7	- 0.8	-18	8	< 2.1	1.2
6	0	19.2	-19.5	10	2	3.2	6.3	16	4	4.3	4.0	-17	8	<2.4	- 0.5
7	0	35.5	-39.9	11	2	8.4	10.2	-20	6	く1.5	- 0.9	-16	.8	5.1	- 5.9
- 8	0	9•7	9.8	12	2	4.8	- 2.6	-19	6	5.2	3.7	-15	8	4.8	5.9
<u></u> 9	0	3.3	- 8.5	13	2	3.3	- 2.1	-18	6	<2.1	- 0.1	-14	8	<2.4	- 3.5
10	0	8,9	9.2	14	2	6.0	5.8	-17	6	<2.3	- 3.6	-13	8	8.9	8.5
11	0	14.3	-12.5	15	2	9.9	- 10.4	-16	6	7.1	- 8.1	-12	8	4.5	8.8
12	0	< 2.6	2,8	16	2	く1.7	- 2.2	-15	6	<2.4	- 3.3	-11	8	8.7	13.2
13	0	26.8	29.0	-18	4	< 2.0	- 0.1	-14	6	< 2.4	- 6.7	-10	8	3.0	3.2
.14	0	4.8	- 3.9	-17	4	3.1	- 4.3	-13	6	10.3	14.8	- 9	8	5.0	5.2
15	0	42.3	- 0.4	-16	4	7•4	8.0	-12	6	8.4	11.9	- 8	8	3.3	9.3
16	0	5.5	- 6.4	- 15	4	2.4	3.1	-11	6	10.7	14.7	- 7	8	16.0	-20.6
17	0	<1.7	- 1.1	-14	4	7.8	- 14.7	-10	6	20.6	-17.2	- 6	8	76.0	-72.4
18	. 0	2.0	3•4	-13	4	6.1	- 7.3	- 9	6	25.5	-27.3	- 5	8	35.1	26 <u>, </u> 3
-18	2	<1.7	- 1.9	-12	4	21.8	27•3	- 8	6	24.5	20.2	- 4	8	23 .1	-19.2
-17	2	2.1	- 2.6	-11	4	14.9	- 11.9	- 7	6	7.1	4.3	- 3	8	20.9	26.3
-16	2	5.0	- 5.8	-10	4	26.4	37.1	- 6	6	4•3	0.0	- 2	8	<1. 5	3.0
15	2	<2.4	- 4.1	- 9	4	8,8	6.7	- 5	6	3.5	2.4	. – 1	8	7.1	0.1
-14	2	11.6	12.3	- 8	4	39.5	- 48.2	- 4	6.	17.8	-14.6	0	8	<1.7	- 2.1
-13	2	٤.4	- 1.1	- 7	4	24.6	21.5	- 3	6	59•4	-57.7	1	8	6.9	5.2
-12	2	5.0	- 3.2	- 6	4	23.3	22.3	- 2	6	29.5	33.0	2	8	13.5	15.2
-11	.2	16.4	21.6	- 5	4	52.6	- 51.5	- 1	6	6.5	- 6.0	3	8	4.3	- 2.1
-10	2	16.9	-14.2	. – 4	4	36.6	- 32.3	. 0	6	59.9	55.7	4	8	7.4	- 7.2
÷ 9	2	15.2	-15.3	- 3°	4	113.5	-114.9	1	6	63.6	58.3	5	8	9.6	-11.4
- 8	2	29 . 8	-35.1	- 2	4	43.2	41.0	2	6	28.0	28.2	6	8	9.2	11.6
- 7	2	35.8	26.9	- 1	4	30.2	38.9	3	-6	72.1	-67.6	7	8	<2.4	0.4
- 6	2	52.6	54.0	0	4	2.4	2.0	4	6	18.5	-18.3	8	8	3.4	3.2
- 5	2	22.6	24.4	1	4	115.5	108.7	5	6	11.2	-10.7	9	8	<2.4	- 0.7
- 4	2	59.1	-59.2	2	4	41.2	- 37.1	6	6	.3.6	- 1.9	-17	10	<2.4	2.9
- 3	2	4.3	3.2	3	4	56.1	53•4	7	6	< 2.2	- 0.8	-16	10	14.4	. 9.5
- 2.	. 2.	$\frac{14}{n0t}$	10.9	4	4	47.1	- 39.9	8	6	13.3	-15.7	-15	10	3.4	- 5.7
- 1	2	obs.	80.0	5	4	36.1	- 33.1	9	6	14.3	15.2	-14	10	4.0	5.3
0	2	73.3	-70.3	6	4	18.6	24.0	10	6	7.9	5.0	-13	10	19.7	-18.7
1	2	11.2	16.2	7	4	21.6	19.9	11	6	<2.4	1.1	-12	10	<2.1	3.4
2	2	<1.0	3.2	8	4	9.3	8.6	12	6	5.7	5.8	-11	10	<2.1	1.7
3	2	75.7	-73.5	9	4	16.2	- 20.3	13	6	3.3	- 2.5	-10	10	8.6	- 6.3

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<u>h l</u>	Fo	<u>F</u> c	<u>h</u> <u>l</u>	<u>F</u> _	<u>F</u> _c	<u>h</u> <u>l</u>	<u>F</u> o	<u>F</u> c	<u>h</u> .	<u>e</u>	<u>F</u> .	Fc
- 9 10	∠1. 9	1.7	5 12	7.5	- 5.1	-16 16	6.9	6.4	-19 2	0	3.3	- 2.9
- 8 10	1.8	2.5	6 12	9.2	- 8.2	-15 16 4	< 2.4	- 2.9	-18 2	0 <	1.7	0,8
- 7 10	12.0	3.7	7 12	42.1	- 0.0	-14 16	5.4	4.4	-17 2	0 <	1.8	- 1.7
- 6 10	23.8	20.2	8 12	3.4	- 3.4	-1 3 16	17.3	-13.1	-16 2	0 <	2.0	- 1.9
- 5 10	40.4	-41.9	9 12	2.1	1.2	-12 16 /	2.4	- 1.6	-15 2	0	8.2	7.1
- 4 10	25.7	17.8	10 12	5.6	4.5	-11 1 6	11.4	13.2	-14 2	0 <	2.1	1.6
- 3 10	8.7	11.2	-20 14	く1.8	1.3	-10 16	12.0	-11.2	-13 2	0 <	2.1	- 1.6
- 2 10	45.4	-45.4	-19 14	2.8	- 0.9	- 9 16 4	< 2.4	- 2.9	-12 2	0	3.9	- 2.7
- 1 10	33.2	31.6	-18 14	4.9	- 6.5	- 8 16	10.2	13.6	-11 2	0	2.3	- 1.5
0 10	21.4	19.0	-17 14	6.2	-10.5	- 7 16 -	L2.4	0.0	-10 2	0	4.5	- 3.4
1 10	6.4	7.5	-16 14	28.1	22.3	- 6 16	24.6	26.0	- 9 2	0	3.9	3.6
2 10	6.0	4.8	- 15 1 4	5.4	7.7	- 5 16	6.2	- 6.0	- 8 2	0	2.3	0.6
3 10	4.9	- 4.8	-14 14	8.6	- 7.7	- 4 16	29.7	-28.0	-72	0	2.2	1.5
4 10	22.1	-24.7	-13 14	17.8	16.3	- 3 16	6.8	5.5	- 6 2	0	5.3	- 3.8
5 10	7.1	8.1	-12 14	28.2	-25.8	- 2 16	14.4	10 .1	- 5 2	0 く	2.1	0.6
6 10	2.4	1.3	-11 14	5.1	6.5	- 1 16 4	∠2.4	0.4	- 4 2	0	2.1	0.7
-20 12	く1.8	0.0	- 10 1 4	16.5	18.3	0 16	11.3	-11.7	- 3 2	0 <	2.0	0.5
-19 12	3.0	2.4	- 9 14	5.9	- 7.7	1 16 4	<2.3	1.4	- 2 2	0	1.8	1.2
-18 12	3.1	- 3.5	- 8 14	22.1	- 5.6	2 16	< 2.1	- 0.4	- 1 2	0	3.8	3.1
-17 12	5.8	4.7	- 7 14	10.4	- 8.3	3 16	2.9	2.4	0 2	0 <	1.4	0.7
-16 12	30.3	-32.3	- 6 14	11.1	-16.4	4 16	<1.9	0.2	-18 2	2 <	1.2	2.2
-15 12	22.4	- 3.1	- 5 14	6.2	- 7.3	-17 18	< 2.1	1.1	-17 2	2	4.4	- 4.3
-14 12	19.8	24.0	- 4 14	8.0	-10.3	-16 18	3.8	- 4.5	-16 2	2 <	1.6	- 1.7
-13 12	2.3	~ 3.3	- 3 14	27.4	27.6	-15 18	< 2.3	0.5	-15 2	2 <	1.7	0.6
-12 12	5.5	8.7	- 2 14	4.0	- 1.3	-14 18	3.3	~ 3.2	-14 2	2	4.0	3.2
-11 12	12.0	- 8.1	- 1 14	14.1	13.7	-12 18	9.4	12.2	-13 2	2 <	1.8	0.7
-10 12	12.0	12.1	0 14	107		-12 18	4.L	0.0	-12 2	2 <	1.9	0.8
- 9 12	44.4	44.8	1 14	4.2	-11.4	-11 10	14.4	~12.0 E 0	-11 2	2	2.2	- 2.0 1 0
- 8 12	12.8		2 14	0,0 7 0	4.0	-10 18	4.2	2•9 6 0	-10 2	2 <	1.0	1
- 1 12	10.9	-17 C	2 14 1 11	1.0	- 4.7	- 9 18	0.0 15 5	134	- 92	2 < 0 /	1.0	0.4
- 5 12	75	15 8	5 74	~~~) /) 1	- 1 7	-718	1 8	~ 3 0	- 7 2	2 \	エ•フ ス 1	- 0.0
- 1 12	22 6	10 1	5 14	2 1	_ 1 0	- 6 18	28 3	- 2.5 2		2	ער ו 1 יד	J•4 0 2
- 3 12	200	-13.4	7 14	/17		- 5 18	20°) / 1	-67	- 0 2	5/	16	- 1 2
- 2 12	21 7	17 8	8 14	23	3.0	- / 18 /	19.1	- 0.7	- / 2	2 \ 9 /	1 1	- 1,2
- 1 12	2101	20	-22 16	2.0	0	- 4 10 -	1 0	2.0	- 42	2 ~	エ • サ ら て	- 38
- 1 12	~ • i /]	2.0J 1 B	-22 10	21	- 0.9 5.0	= 218	23	63	- 22	5 /	$\int a$	- 2.0
210	4°-	4.0 8.6	-21 10 -20 16	1.7	1.8	- 2 10	53	- 5 5	- 2 2		1.2	_ 0 2
2 12	10.2	_ 0.6	-10 16	2.7	1.0	0 18	7.A	- J•J 8.1	_12 2	т с И	5.2	_ / 0
3 12	12.1	- 5.0	-18 16	22.1	- 2.8	1 18	0.75	. 1.0	<u>רו</u> ב ב		1.2	- 4+9
1 10	15.5	18.5	-17 16	7.9	- 8.1	_20 20 -	\[\lambda = \] \[\lambda = \	- 1.9	_1 0 2	 - A	2.5	2.0
7 10	±/0/	100J		100			~ * • *	- 196	- 92	4 2	1.1	0.2
									, , ,	· · · ·		U # C

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<u>h</u>	Ł	Fo	<u>₽</u> c	<u>h</u>	Ł	<u>F</u> o	<u>F</u> c	<u>h</u>	Ł	<u>F</u> o	Fc	<u>h</u>	L	<u>F</u> o	<u>F</u> c
1	0	148.0 -1	148.9	12	1	5.7	7.1	- 6	3	5.0	6.9	10	4	12.4	11.4
2	0	19.5	15.4	13	1	3.4	4.2	- 5	3	58.4	57.2	11	4	11.1	12.4
3	0	20.9 -	18.6	14	1	6.0	- 6.0	- 4	3	43.2	40.1	12	4	4.5	- 6.2
4	0	69.6	68.1	15	1	<1.3	- 0.2	- 3	3	61.4	-49.9	13	4	<1.4	0,8
5	0	10.8 -	6.3	-17	2	<1.2	- 0.7	- 2	3	125.2	-90.5	14	4	1.5	- 6.3
6	0	20.5 -	20.9	-16	2	5.6	5.5	- 1	3	30.8	-33.9	15	4	2.5	3.2
7	0	5.9	4.8	-15	2	6.3	5.7	0	3	33.3	31.9	16	4	< 0.6	0.0
8	0	2.8	3.1	-14	2	<1.5	1.4	1	3	39.9	-37.4	-19	5	<1.0	- 0.6
9	0	2.6	4.8	-13	2	15.3	-15.9	2	3	6.7	- 5.6	-18	5	2.2	2.0
10	Ó	<1.4 ⁻	2.4	-12	2	4.7	5.4	3	3	5.4	7.0	-17	5	<1.4	4.1
11	0	4.4 -	5.9	-11	2	2.4	- 2.0	4	3	8.6	-11.1	-16	5	<1.5	1.0
12	Ō	22.0	20.0	-10	2	3.7	- 7.3	5	3	36.5	34.6	-15	5	2.7	- 3.2
13	ō	15.3 -	15.0	- 9	2	4.2	- 8.1	6	3	19.1	20.1	-14	5	<1.5	- 0.3
14	ŏ	6.2 -	7.3	- 8	2	20.3	19.9	7	ź	<1.2	1.4	-13	5	4.7	-10.1
15	ō	< 1.4	0.3	- 7	2	L1.0	0.6	. 8	3	7.4	12.0	-12	5	< 1.4	- 4.1
16	ŏ	21.3 -	2.3	- 6	2	5.1	- 5.6	9	ŝ	8.3	10.3	-11	5	32.8	28.6
17	ō	6.4	6.9	- 5	2	21.9	-23.8	10	3	9.1	- 9.0	-10	5	9.0	-11.1
18	ŏ	20.7	0.4	- 4	2	32.1	-35.1	11	3	19.3	-17.8	9	5	27.5	-23.2
-18	1	2.2	3.1	- 3	2	121.0	87.6	12	3	< 1.5	- 3.2	- 8	5	5.1	- 7.5
-17	ī	<1.2	1.8	- 2	2	83.7	70.8	-19	4	×1.0	- 0.5	- 7	5	19.7	-17.7
<u>-</u> 16	ī	<1.3 -	2.1	- 1	2	23.9	-23.1	-18	4	2.3	- 3.5	- 6	5	48.5	48.5
-15	1	2.5	3.8	ō	2	37.2	-35.2	-17	4	<1.4	3.6	- 5	5	5.1	10.5
. –14	ī	3.1	2.0	1	2	2.4	- 3.8	-16	4	<1.5	- 1.4	- 4	5	13.6	- 8.7
-13	ī	6.1 -	7.9	2	2	67.3	-65.9	-15	4	2.2	- 3.3	- 3	5	35.8	33.8
-12	ī	6.2	8.8	3	2	42.9	45.4	-14	4	<1.5	0.9	- 2	5	40.3	-40.7
-11	ī	<1.4 -	2.9	4	2	36.5	-30.5	-13	4	5.6	8.0	- I	5	2.2	- 2.2
-10	ī	17.9 -	16.3	5	2	10.1	11.8	-12	4	4.5	- 1.2	0	5	11.8	-11.3
- 9	ī	2.9 -	4.3	6	2	19.1	16.6	-11	4	<1.3	0.3	1	5	8.1	- 8.6
- 8	ī	20.5 -	18.6	7	2	2.9	1.0	-10	4	3.1	- 1.9	2	5	32.8	35.8
- 7	1	7.3	0.6	8	2	41.3	- 1.6	- 9	4	14.9	-15.0	3	5	6.5	4.8
- 6	1	14.4	14.8	9	2	11.2	-11.7	- 8	4	35.4	29.0	4	5	2.5	1.0
- 5	1	41.6	39.4	10	2	2.1	- 1.9	- 7	4	7.5	11.9	5	5	9.1	-11.1
- 4	1	22.3	20.5	11	2	5.7	6.8	- 6	4	2.8	5.2	6	5	2.7	2.0
- 3	1	42.1 -	45.2	12	2	1.9	1.2	- 5	4	36.7	-32.8	7	5	8.8	12.6
- 2	1	120.8	84.7	13	2	6.7	5.0	- 4	4	33.6	-28.8	8	5	11.3	-10.8
- 1	ī	34.8	34.4	14	2	2.8	- 2.2	- 3	4	22.0	-17.3	9	5	11.0	-12.4
0	1	46.8 -	47.8	15	2	3.6	- 5.1	- 2	4	38.0	39.0	10	5	<1.5	- 0.5
ľ	1	17.4	13.5	16	2	2.4	3.9	- 1	4	9.0	- 8,9	11	5	2,6	3.0
2	1	70.7 -	67.1	17	2	<0.7	- 1.6	.0	4	56.2	51.7	12	5	<1.4	0.7
3	1	20.1 -	21.8	-15	3	<1.5	- 1.1	1	4	50.9	-46.6	13	5	<1.3	2.7
4	1	1.6	0.3	-14	3	2.7	5.0	2	4	28.8	24.7	14	5	1.6	2.1
5	1	20.2 -	17.5	-13	3	2.1	1.0	3	4	30.9	-22.5	15	5	< 0.8	- 1.6
6	1	22.1	23.7	-12	3	6.8	- 9.5	4	4	47.6	-42.9	-16	6	<1.5	- 1.0
7	1	16.8	16.7	-11	3	10.5	- 8.9	5	4	49.3	49.0	-15	6	5.3	5.2
8	1	1.6 -	3.3	-10	3	2.2	0.9	6	4	∠1.2	2.0	-14	6	2.1	2.4
9	1	6.2 -	6.1	- 9	3	7.7	- 8.1	7	4	7.6	6.1	-13	6	8.9	10.3
10	1	<1.4 -	2.1	- 8	3	13.0	8.9	8	4	3.5	- 3.3	-12	6	8.0	7.9
11	1	2.1	2.4	- 7	3	21.3	22.0	9	4	20.4	-22.0	-11	6	14.2	-14.9

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	-10	6	22.7	-24.9	3	7	1.7	0.7	-13	9	9.2	6.9	11	0	10.8	-11,5
	- 9	6	26.7	25.3	4	7	6.6	- 9.5	-12	9	<1.4	- 5.6	21	0	2.2	- 3.3
	- 8	6	19.2	-22.7	5	7	2.4	- 4.5	-11	9	19.4	-21.0	31	0	<1.4	0.6
	- 7	6	16.3	14.3	6	7	5.7	5.2	-10	9	5.6	7.0	41	0	5.0	6.4
	- 6	6	44.4	-40.7	7	7	10.9	13.0	- 9	9	6.7	- 5.7	5 1	0	3.1	6.6
	- 5	6	29.7	-25.2	8	7	5.5	7.0	- 8	9	11.5	-11.8	61	0	8.8	- 7.5
	- 4	6	43.8	43.5	9	7	2.2	- 3.3	~ 7	9	9.0	- 7.8	71	0	3.7	- 4.6
	- 3	6	31.1	29.0	10	7	< 1.5	0.4	- 6	9	16.4	-13.9	81	0	<1.4	- 2.3
	- 2	6	11.4	12.5	11	7	く1.4	- 0.1	- 5	9	53.2	50.8	9,1	0	2.6	3.4
	- 1	6	30.1	26.1	-20	8	<1.0	- 2.4	- 4	9	37.0	29.9	10 1	0	<1.1	- 1.4
	0	6	7.0	- 8,2	-19	8	4.2	- 4.8	- 3	9	7•7	- 6.4	11 1	0	1.3	1.9
	1	6	7.9	1.7	-18	8	5.4	6.8	- 2	9	9.3	- 7.3	-19 1	1	<1.2	1.6
	2	6	34.3	-28.3	-17	8,	4.2	- 5.9	- 1	9	45.1	-42.7	-18 1	1	3.9	4.8
	3	6	19.6	-23.1	-16	8	7.2	8.2	0	9	<1 <u>,</u> 2	- 0.8	-17 1	1	1.9	- 2.1
	4	6	43.8	35.2	-15	8	<1.5	1.4	1	9	18.0	17.2	-16 1	1	< 1.5	5.2
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	7	6	18.2	-19.1	-12	8	17.5	-17.5	4	9	3.5	3.4	-13 1	1	<1.5	- 1.4
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	11	6	<1.5	0.4	- 8	8	24.3	21.1	8	9	<1.5	3.4	- 91	1	7.4	8.0
	12	6	<1.3	1.6	- 7	8	16.1	-15.3	9	9	2.0	- 1.4	- 81	1	9.2	11.4
	13	6	<1.2	- 2.0	- 6	8	8.7	-10.6	10	9	<1.3	1.3	-71	I	13.2	- 8.8
	14	6	1.6	1.4	- 5	8	37.9	35.1	11	9	2.0	- 2.1	- 6 1	1	3.7	4.5
	15	6	< 0.4	- 2.4	- 4	8	22.1	-18.7	12	9	< 0.9	- 3.9	- 51	1	22.4	24.7
	-19	7	<1.2	- 1.4	- 3	8	8.8	7.6	-21	10	< 0.8	- 0.7	- 4 1	1	3.9	- 6.6
	-18	7	3.8	- 3.5	- 2	8	5.8	9•4	-20 (10	2.0	- 1.9	- 3,1	1	8.2	9,•0
	-17	7	<1.4	0.4	- 1	8	4.1	0.0	-19	10	2.2	2.4	- 21	1	<1.3	- 2.0
	-16	7	6.4	9.1	0	8	9.0	-12.4	-18	10	3.9	- 4.1	-11	1	17.6	-20.5
	-15	7	2.9	- 3•7	1	8	12.9	12.9	-17 :	10	4.2	3 •6	01	1	1.9	- 0.7
	-14	7	2.3	- 4.9	2	8	34.8	-31.5	-16	10	3.1	- 2.7	11	1	2.4	- 5.7
	-13	7	<1.5	- 0,9	3	8	く1.3	1.0	-15 :	10	4.9	- 4.0	2 1	1	6.2	- 8,0
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	-10	7	1 <u>.</u> 7	- 2.9	6	8	7.7	10.8	-12 :	10	2.5	1.6	51	1	<1.5	1.0
	- 9	7	く1.1	- 0.3	7	8	4.1	4.8	-11	10	2.7	- 3.6	61	1	<1.5	3.4
	- 8 °	7	14.1	-11.1	8	8	<1.5	- 1.5	-10 :	10	<1.3	1.0	71	1	2.5	- 3.0
	- 7	7	23.0	17,•8	9	8	<1.5	- 1.9	- 9	10	1.8	- 4.3	81	l	<1.3	0.2
	- 6	7	27.6	31.2	10	8	<1.4	- 1,1	- 8 :	10	4.8	3.4	-21 1	2	3.1	- 3.3
	- 5	7	35.3	-28.2	11	8	2.2	0.7	- 7 :	10	13.1	-13.5	-20 1	2	4.1	4.8
	- 4	7	13.8	17.1	12	8	1.8	- 0.2	- 6 .	10	<1.1	2.6	-19 1	2	<1.2	- 3.0
	- 3	7	32.4	29.3	-19	9	<1.2	- 0.6	- 5	10	3.6	- 9.1	-18 1	2	<1.4	- 0.1
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APPENDIX. II

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CRYSTALLOGRAPHIC DATA: FOR SEVERAL ORGANIC COMPOUNDS
trans-1,2-Acenaphthenediol

Crystals obtained by crystallization from aqueous methanol are thin colourless plates parallel to (001) and bounded by (100) and (010).

Crystal Data

<u>trans</u>-1,2-Acenaphthenediol, $C_{12}H_8(OH)_2$; M=186.20; m.p. 160.0-163.0°C. Orthorhombic, a=11.37±0.02, b=11.37±0.02, c=28.94±0.03Å. U=3741Å³. $D_x(with Z=16) = 1.322$, $D_m=1.29$ gm.cm⁻³ F(000)=1568. Absent spectra: hkl when h+k is odd, h0l when l is odd, hh0 when h is odd. A possible space group is Cmcm- D_{2h}^{17} provided the last condition for systematic absences is regarded as accidental.

The tentative space group assignment to <u>trans</u>-1,2-acenaphthenediol requires some comment. Weissenberg and precession phtotgraphs were taken, with $CuK_{c\zeta}$ and $MoK_{c\zeta}$ radiations respectively, of a crystal mounted about the c-axis. Since the hkO and hkl films displayed perfect tetragonal symmetry, a primitive tetragonal lattice with a=b=8.04Å was chosen initially. Systematic absences were hhl for ℓ odd, hOO for h odd, and OkO for k odd. However, it was soon discovered that $I(hh\ell) \neq I(\bar{h}h\ell)$ so that the crystal system could not be tetragonal. Accordingly, the photographs were indexed in terms of a centered orthorhombic lattice with a=b= $\sqrt{2} \times 8.04Å = 11.37Å$.

It is possible to visualize the general arrangement of molecules in the unit cell, although an accurate analysis will probably prove to be difficult. In the crystal the arrangement of the carbon skeleton must conform closely to tetragonal symmetry, the small deviations being due to the presence of the hydroxyl groups. An idealised structure can be obtained in the following way. Since the c-axis is 28.94A long, it has enough room to accommodate a set of four molecules stacked on top of one another. The sixteen molecules in the unit cell may be divided into four such sets, each lying on a screw axis parallel to the c-axis and midway between mirror planes. The molecules have their molecular planes (planes containing carbon atoms) on $\{220\}$ so that perfect tetragonal symmetry is achieved in the [OO1] projection. In such an arrangement the structure will only be slightly different when viewed along the [100] and [O10] directions. This explains rather well the fact that the Okl and hol precession films bear a striking resemblance.

trans-1,2-Acenaphthenediol Dinitrate

Crystals obtained from heptane solution are transparent plates parallel to (010). Other faces such as (100) and (110) are also well developed. Crystal Data

<u>trans</u>-1,2-Acenaphthenediol dinitrate, $C_{10}H_6(CHONO_2)_2$; M=276.20, m.p. 98.0-99.5°C. Monoclinic, a=10.56±0.03, b=7.77±0.02, c=7.85±0.02Å, $\beta = 113^{\circ}14' \pm 5'$. U=591.9Å³. D_x (with Z=2)=1.550, $D_m=1.53$ gm.cm⁻³. F(000)=284. Absent spectra: OkO when k is odd. Space groups is $P2_1-C_2^2$. (The possible space group $P2_1/m$ is ruled out because it requires the molecule to have symmetry m or $\overline{1}$).

p-Chloroaniline

Crystals of <u>p</u>-chloroaniline (Eastman Kodak), obtained by slow crystallisation from aqueous ethanol, are sand-coloured octahedra bounded by $\{111\}$. They are highly volatile and must be sealed in Lindemann-glass capilliaries for measurements lasting a day or longer.

Crystal Data

<u>p</u>-Chloroaniline, Cl C₆H₄NH₂; M=127.57; m.p.71°C. Orthorhombic, a=8.66 +0.01, b=9.26+0.01, c=7.39+0.01Å. U=592.6Å³. D_x (with Z=4)=1.427, D_m =1.43 gm.cm⁻³ F(000)=248. Absent spectra: Okl when k+l is odd, hOl when h is odd. Space group is either Pna2₁-C_{2v} or Pnam-D_{2h}.

N, N-Dimethyl-p-nitroaniline

Crystals of N,N-dimethyl-<u>p</u>-nitroaniline (Eastman Kodak) grown from ethanol solution are yellow prisms with the (100) and (010) faces well developed.

Crystal Data

N,N-Dimethyl-p-nitroaniline, $(CH_3)_2NC_6H_4NO_2$; M=166.18; m.p. 163°C. Monoclinic, a=9.73±0.01, b=10.56±0.01, c=3.964±0.005Å, β =91°28'±5'. U=407.2Å³. D_x(with Z=2)=1.355, D_m=1.33 gm.cm⁻³ F(000)=176. Absent spectra: OkO when k is odd. Space group may be either P2₁-C₂² or P2₁/m-C_{2h}².

A preliminary investigation of the crystal structure (93) has established the correct space group as $P2_1/m$, which requires that the molecule possesses a mirror plane of symmetry perpendicular to the plane of the benzene ring. A clearly resolved electron-density projection along the short c-axis shows that the molecule (neglecting the hydrogen atoms of the methyl groups) probably has symmetry mm2-C_{2v}.

Naphtho [b] cyclobutene (94)

Crystals grown from ethanol solution by slow evaporation occur as transparent plates, the principal face being (100); twinning on (100) is common. The crystals are highly volatile and slowly turn milky on exposure to air, presumably due to surface decomposition. The high-angle reflexions were all too weak to be recorded on Weissenberg photographs, and this indicates unusually large thermal vibrations of the atoms in the crystal. Crystal Data

Naphtho [b] cyclobutene, $C_{12}H_{10}$; M=154.20; m.p. 84.5-86°C. Monoclinic, a=18.04+0.02, b=5.91+0.01, c=8.13+0.01Å, β =92°0'+6'. U=866.3Å³. D_x(with Z=4) =1.181, D_m=1.19 gm.cm⁻³. F(000)=328. Absent spectra: hkl when h+k is odd, h0l when l is odd. Space group is Cd-C⁴_s. (The possible space group C2/c-C⁶_{2h} is excluded since it requires the two-fold symmetry axis of the molecule (length ~ 6.3 Å) to be parallel to the b crystal axis).

Benzocyclobutadienoquinone (95)

Crystals obtained from <u>n</u>-propanol solution are yellow prisms bounded by $\{100\}$. The $\{110\}$ faces are also well developed. The crystals slowly decompose into a powder on prolonged exposure to X-rays.

Crystal Data

Benzocyclobutadienoquinone, $C_{6}H_{4}(CO)_{2}$; M=132.11 ; m.p. 132.5°C. Orthorhombic, a=10.72+0.01, b=7.94+0.01, c=7.15+0.01Å. U=608.6Å³. $D_{x}(with Z=4)=1.442$, $D_{m}=1.45$ gm. cm⁻³ F(000)=272. Absent spectra: hol when h is odd, Okl when l is odd. Space group is $Pca2_{1}-C_{2v}^{5}$ or $Pcam-D_{2h}^{11}$.

cis-1,2-Benzocyclobutenediol Dinitrate (95)

Crystals grown from a benzene/petroleum ether mixture are transparent prisms elongated along the a-axis, with the (OlO) and (OOl) faces well developed.

Crystal Data

<u>cis</u>-1,2-Benzocyclobutenediol dinitrate, $C_{6}H_{4}(CHONO_{2})_{2}$; M=226.14; m.p.110 C. Monoclinic, a=7.41+0.01, b=15.71+0.02, c=8.14+0.01Å, β =98°2'+5'. U=938.3Å³. D_x(with Z=4)=1.601, D_m=1.57 gm.cm⁻³ F(000)=464. Absent spectra: h0ℓ when h+ℓ is odd, OkO when k is odd. Space group is P2₁/n- c_{2h}^{5} . REFERENCES

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12. SIMPLE CUBIC

13. BODY-CENTERED



14. FACE-CENTERED

11. BODY-CENTERED TETRAGONAL

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Figure 1. The 14 Bravais lattices.

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Figure 8. (a) Measured bond lengths and (b) valency angles.







1.55 104.9 4 109.7 109-8 1.₃₈ 118.4 119.0 1248 -4 N 121.4 114 122.2 130 113.8 124.1 1.75 Ċe Ċl



(C)







Figure 19. Mean bond lengths and valency angles in (a) acenaphthene, (b) naphthalene, (c) 5,6-dichloroacenaphthene, (d) pyracene, (e) 2.13-benzfluoranthene, and (f) 20-methylcholanthrene.



Figure 20. Relation of the origin of space group P2₁2₁2₁ to the origins of its projections on the pinacoids (100), (010), and (001). The several origins are indicated by dots. After Buerger, Barney and Hahn(79).

Table VIII.	Transformations	between	Space	Group	and
	Projection Coor				

Space Group Coordinates	(001)	ates (010)	
x	$\mathbf{x}^{\dagger} = \mathbf{x} - \frac{1}{4}$	x"=x	x**** =x
У	у¹=у	$y'' = y - \frac{1}{4}$	$\lambda_{\mu u} = \lambda$
Z	z ^t =z	Z ^{tt} =Z	$Z^{\dagger \dagger} = Z - \frac{1}{4}$



Figure 24. Numbering and average dimensions of the molecule.

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Figure 25. Projection of the structure along [001] , showing the shorter intermolecular contacts.



Figure 28. Numbering and average dimensions of the molecule.



Figure 29.

Projection of the structure along [OlO], showing the hydrogen bonds and the shorter intermolecular contacts.



Figure 30. Perspective diagram showing the hydrogen bonding.



Figure 33. Numbering and average dimensions of the molecule.



Figure 34. Projection of the structure along [010].



Figure 37. Dimensions of the nitroxy group in (a) cis-1,2acenaphthenediol dinitrate, (b) pentaerythritol tetranitrate, and (c) nitric acid.



Figure 38. Average dimensions of the naphthalene moiety of the acenaphthene system. Deviations from the corresponding values in naphthalene are shown in brackets; for the bond distances the deviations are given in 10^{-3} A.

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