

The Crystal and Molecular Structure
of
Dimethyl Ketene Dimer
and
Acedianthrone, Aceanthrono-(2'.1': 1.2)-Aceanthrone

THESIS

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Doctor of Philosophy
at
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by
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Preface

The work to be described in the following pages was carried out during a three year period in the Chemistry Department of the University of Glasgow. It is hoped that some of the work will be published.

I wish to express my sincere thanks to Professor J. Monteath Robertson for suggesting the problems and for guidance and instruction received. I would also like to thank Dr. V. Vand for assistance and most helpful discussion.

I am indebted to the Department of Scientific and Industrial Research for a Maintenance Grant.

P.H.F.

Summary

The research work described in this thesis has been separated into two parts and an appendix. These contain reports on the crystal and molecular structures of dimethyl ketene dimer and acedianthrone, determined by X-ray diffraction methods. The appendix describes a further analysis of the results of the three dimensional investigation of naphthalene, undertaken to obtain more information on the positions of the hydrogen atoms and on the effect of the π electrons on bond length. The unit cell dimensions and space group of fluoranthene have also been determined.

Part I. The crystal and molecular structure of dimethyl ketene dimer has been determined by the X-ray method. The crystals were found to have the unusual space group $C_{2h}^3 - C 2/m$ with 2 molecules per unit cell. The cell dimensions are, $a = 6.55 \pm 0.02A.$, $b = 10.26 \pm 0.03A.$, $c = 6.43 \pm 0.02A.$, $\beta = 104^\circ$. This space group requires a molecular plane of symmetry and a two-fold axis at the centre of symmetry. This symmetry is chemically possible. The structure of this compound had previously been studied by the method of electron diffraction by Lipscomb and Schomaker and it was considered interesting to repeat the work using the X-ray method, to compare the results obtained by the two methods. Fairly close agreement has indeed been obtained.

Part II. The crystal and molecular structure of aceanthrono-(2'.1': 1.2)-aceanthrone has been determined by quantitative X-ray analysis. The structure postulated by E. Clar has been confirmed and the molecule found to be planar within experimental limits. The monoclinic crystals were found to have the space group $P 2_1/c$ with two molecules per unit cell and thus use is made of the centre of symmetry in the molecule. The cell dimensions are, $a = 5.64 \pm 0.01 \text{ \AA}$., $b = 10.96 \pm 0.02 \text{ \AA}$., $c = 15.49 \pm 0.02 \text{ \AA}$., $\beta = 108.2^\circ \pm 0.2^\circ$. While the chemical structure and orientation of the molecule in the crystal have been determined, it has not been possible to obtain bond lengths with the usual accuracies as two of the projections obscure all but three of the 16 atoms of the asymmetric unit and the molecule is highly inclined to the plane of projection in the third axial projection.

Appendix Part 1. The investigation of naphthalene by Robertson has been the basis of several other investigations undertaken to determine general properties of carbon bonds in aromatic molecules. After the publication of the 3-dimensional analysis of naphthalene by Abrahams, Robertson and White (1949) it was decided to draw sections through the molecule in various planes in an attempt to obtain information on the hydrogen atoms and on the effect of the π electrons on bond length. C.A. Coulson on the basis of the molecular orbital theory has predicted, that in the naphthalene molecule as one passes from the molecular plane to a plane parallel to it

and further from the centres of the carbon atoms, there should be a foreshortening of certain carbon bonds. This effect, if it occurs, should affect the electron density in these positions and a quantitative measurement of it should thus be obtained by the Fourier method. Sections were drawn of the electron density values on planes at $1/4$ A., and $1/2$ A. perpendicular distance from the molecular plane and one on a plane at right angles to the molecular plane and through the centre of symmetry and the two central carbon atoms. The results confirm the ellipsoidal nature of the carbon atoms, but the shortening effect is not unambiguously observable by this method. The variations of shape of the electron cloud density of the α and β carbon atoms has been observed and slight shifts in the manner predicted by Coulson can be discerned.

Appendix Part 2. The cell dimensions and space group of fluoranthene have been determined by X-ray methods. The monoclinic crystals have space group $P 2_1/n$ with 8 molecules per unit cell. The cell dimensions are, $\underline{a} = 18.48 \pm 0.02 \text{A.}$, $\underline{b} = 6.27 \pm 0.01 \text{A.}$, $\underline{c} = 20.03 \pm 0.03 \text{A.}$, $\beta = 110.2^\circ \pm 0.2^\circ$

General Introduction

The usefulness of X-ray analysis in Chemistry is being widened to an ever greater extent, both in its practical and theoretical applications. In this thesis more by accident than by deliberate choice, three different aspects of the chemistry of the three compounds studied illustrate the wide adaptability of this method.

In the first compound, dimethyl ketene dimer, the structure was not in doubt. Chemical and especially electron diffraction evidence had shown the structure to be 2,2,4,4,-tetramethylcyclobutadione-1,3. Such a molecule may be expected to crystallize in a space group with a high symmetry. It was hoped that the space group would provide some information on this point. The space groups of crystalline organic compounds indicate the presence of a centre of symmetry, which is very common and the presence of two-fold axes or planes of symmetry. The presence of two different types of molecule present in a crystal can also be inferred from the space group (c.f. Bunn, Chemical Crystallography p.251).

In the second compound studied, acedianthrone, the chemical structure itself was in doubt. Acedianthrone is of interest as an important industrial compound and also for its theoretical connection with pentalene and dibenzopentalene, substances which are being studied from several aspects. Figure 1 shows the proposed structure of pentalene, Figure 2 the structure of dibenzopentalene.



Figure 1

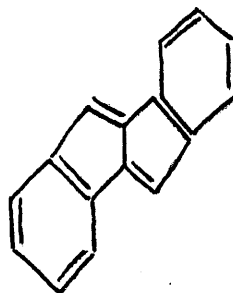


Figure 2

It is generally more difficult to disprove a chemical structure than to confirm it, or even to choose from one of a few postulated structures, except in cases where it is possible to use direct methods of solving the phase problem. These are the heavy atom and inequalities techniques. Acedianthrone was found, however, to have the structure which had been assigned to it based on organic evidence. The transition from non-aromatic to aromatic character in passing from the so far unknown pentalene, to the known but unstable dibenzopentalene and to the stable aromatic acedianthrone, has been confirmed by a determination of the bond lengths of acedianthrone and by the fact that the atoms of the molecule are co-planar.

In the third investigation described in Part 1 of the appendix an attempt was made to link the results of X-ray crystallography with the predictions of the molecular orbital and valence bond theories. At first sight, electron density maps prepared by the Fourier series method would appear to supply a complete answer to the problem of electron distribution in a molecule. The

method, however, is subject to severe limitations and great caution is required in interpreting the results. At the normal temperatures at which the intensity measurements are made the atom undergoes considerable thermal movement and the results can only give a time average picture. If an electron density function as obtained by a most elaborate 3-dimensional analysis is to give results accurate enough to give information on the probability of finding an electron ψ^2 , at positions where ψ^2 is small, the temperature effect, which may mask the real electron density, must be considered further. The Fourier sections or projections would show the shape of the atom and the electron density around it provided all the signs are correct, but the picture obtained may differ considerably from the one expected on the basis of the molecular orbital theory.

The quantitative effect of the π orbitals on bond shortening is at present not known with any precision (C.A. Coulson private communication) so it is not possible to say whether the tendency for the centres of the atoms to move in the anticipated direction is either proof of the predicted effect or that it is a quantitative measure of it.

Part IThe Crystal and Molecular Structure of Dimethyl Ketene DimerIntroduction

The structure of dimethyl ketene dimer has previously been investigated by Lipscomb and Schomaker (1) using the electron diffraction method. This method studies the compound in the vapour phase and determines in suitable cases the geometry of the molecule. It is held by some, that there is an element of bias in comparing the results obtained by observation and by calculation by this method, which is absent in the X-ray method. Also for all but the most simple molecules the accuracies claimed differ in favour of the X-ray method. As the X-ray method requires stable well formed crystals and electron diffraction a volatilizable substance, it is very rarely that one substance can be studied by both methods. Dimethyl ketene dimer is one of these. This compound is one of several cyclobutane compounds which have been studied in the past few years (2),(3),(4),(5),(6),(7). Of more particular interest in connection with this investigation is the work of Owen and Hoard (2) on C_4Cl_8 and that of Dunitz (7) on tetraphenylcyclobutane. The results obtained by X-ray and spectroscopic methods indicate that some workers have found the cyclobutane ring planar,

whereas others investigating different compounds have found the ring to be puckered. Lipscomb and Schomaker found dimethyl ketene dimer to be 2,2,4,4-tetramethylcyclobutadione-1,3. This has been confirmed by this investigation. The bond lengths and angles agree fairly closely, except for the carbon-methyl group bond which has been found shorter than the value obtained by Lipscomb and Schomaker, but within the stated experimental limits. This point is referred to again in the discussion.

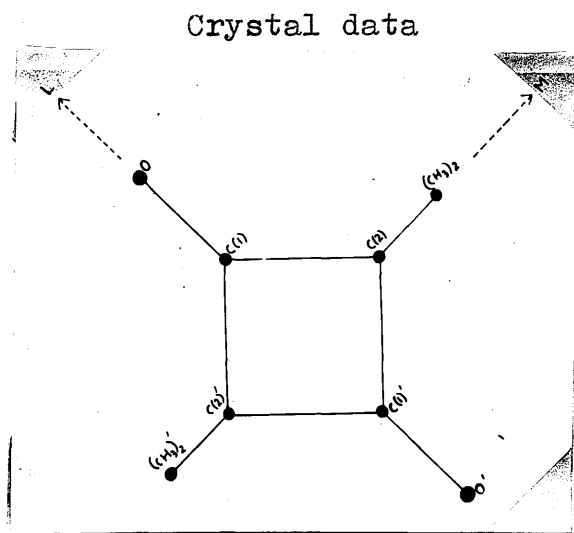


Figure 3

Dimethyl ketene dimer $C_8O_2H_{12}$ F.W. 140 m.p. $113^\circ C.$

d. calc. 1.114 d. obs. (by flotation) 1.10

Monoclinic $a = 6.55 \pm 0.01A.$, $b = 10.26 \pm 0.03A.$,

$c = 6.43 \pm 0.01A.$, $\beta = 104.0^\circ \pm 0.5^\circ$

Absent spectra: (hkl) absent when $h+k$ is odd

Possible space groups: $C_{2h}^3 - C 2/m$, $C_2^3 - C 2$, $C_s^3 - C m$

Two molecules per unit cell

Molecular symmetry required: plane of symmetry with two-fold axis at right angles to plane of symmetry (for $C 2/m$)
two-fold axis parallel to b (for $C 2$)

plane of symmetry parallel to (010) (for $C m$)

Volume of unit cell 417.4 \AA^3

Absorption coefficient for X-rays = $(1.54 \text{ \AA}) = 7.38 \text{ per cm.}$

Total number of electrons per unit cell = $F(000) = 152.$

Crystal structure

The observed spectral absences do not lead to a definite identification of the space group. Possible space groups are: $C_2^3 - C 2$, $C_s^3 - C m$, $C_{2h}^3 - C 2/m$. All these space groups are possible and X-rays cannot distinguish between them on the basis of 'halvings' or systematic absences in the spectra. The pyro-electric effect (8) would eliminate $C_{2h}^3 - C 2/m$ if it could be positively observed, as it would indicate the absence of a centre of symmetry in the molecule. When an experiment was carried out no definite effect could be observed.

Then as there are two molecules in the unit cell if the space group is C_2^3 molecule must have a two-fold axis of symmetry (2) parallel to b, if the space group is C_s^3 molecule must have a plane of symmetry (m) parallel to (010) and if it is C_{2h}^3 molecule must have a two-fold

axis perpendicular to plane of symmetry ($2/m$). Any of these possibilities are consistent with the postulated chemical structure.

As a basis for the evaluation of the structure factor it is convenient to construct a model with the maximum permitted symmetry, $2/m$ and place its origin in the special positions required by the space group C_{2h}^3 viz.

$$(0,0,0 ; 1/2, 1/2, 0)$$

Each ring carbon and ketonic oxygen then lies on a symmetry plane and has the co-ordinates,

$(0,0,0 ; 1/2, 1/2, 0)$ and $(x \ 0 \ z ; \bar{x} \ 0 \ \bar{z})$, while the methyl groups occupy the general positions,

$(0,0,0 ; 1/2, 1/2, 0)$ and $(xyz ; \bar{x}\bar{y}\bar{z} ; \bar{x}\bar{y}\bar{z} ; \overline{xyz})$.

The asymmetric crystal unit then consists of one quarter of the chemical molecule, made up of one methyl group, and one half of each of two ring carbons, and one half of one oxygen atom. The justification for the space group will depend on how well such a molecule can explain the observed intensities.

A simple model based on a square ring with $C-C=1.54$ A. and $C-O=1.20$ A. was now tested. It immediately led to excellent agreement with the observed structure factors. In particular the strong series of reflection (001) and $(0k0)$ were accounted for almost quantitatively to the seventh and tenth order respectively, and at this stage

the overall agreement for some 70 structure factors was about 26%. Refinement by the double Fourier series method was then applied, giving projections of the structure along the a and b axes. The final electron density maps obtained in this way are shown in Figures 4 and 5. The a axis projection gives quite good resolution of the methyl group and fixes its b and z co-ordinates. The b axis projection fixes the co-ordinates of carbon C(1), but the other atoms are obscured by heavy overlapping. In view of the excellent agreement of the (0k0) reflections the b co-ordinates are fairly certain, but the x and z co-ordinates of atoms C(2) and O(1) had to be found by trial and error using the discrepancy

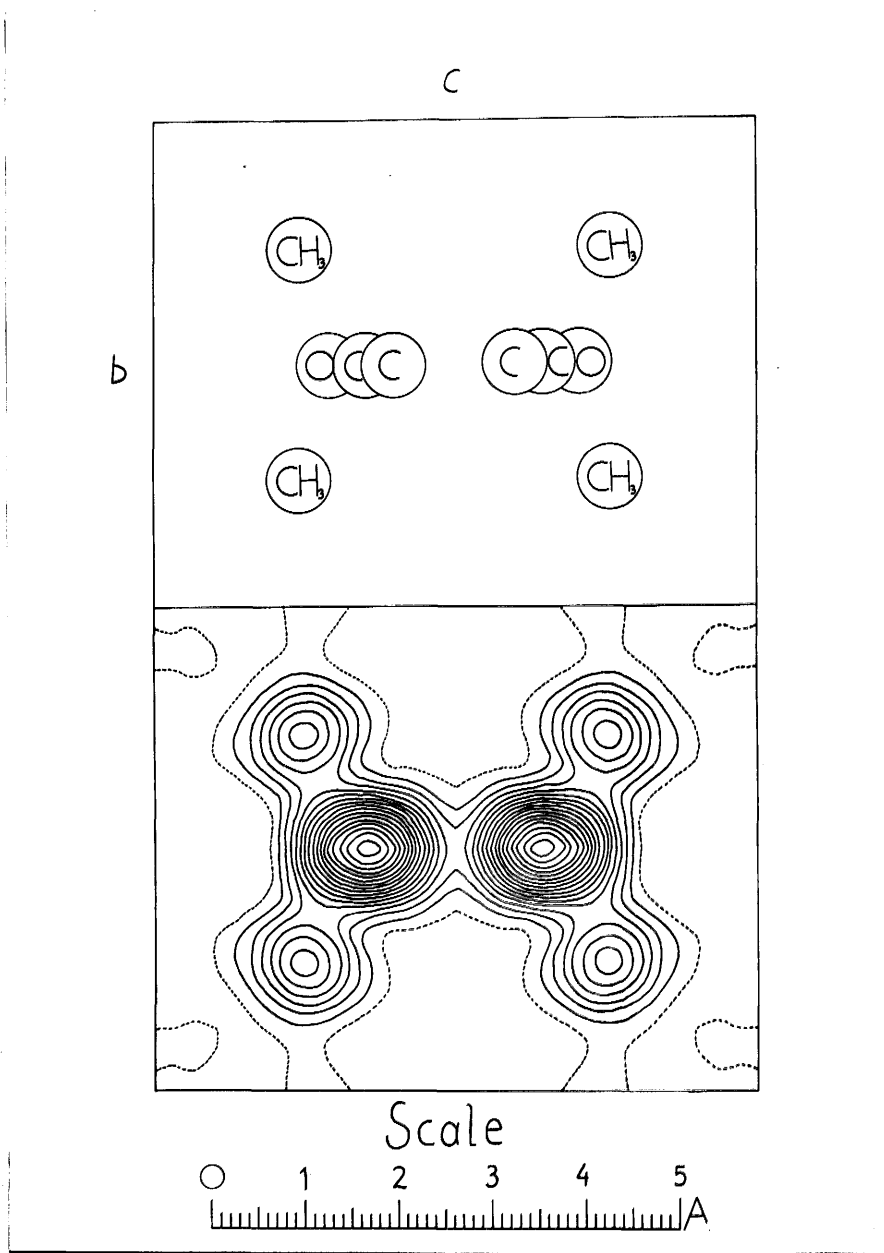
$$\Delta = \frac{\sum \{ |F \text{ calc.}| - |F \text{ obs.}| \}}{\sum |F \text{ obs.}|} \times 100$$

as an index of reliability. The set of co-ordinates finally chosen gave the following zonal discrepancies. 0k1 11.2%, hk0 12.8%, h0l 21.8%, the average discrepancy for the three zones being 17.9%.

Co-ordinates, Dimensions and Orientation

The set of co-ordinates giving above discrepancies are listed in table I. The origin is chosen at the centre of symmetry. Only half the atoms of the molecule

Figure 4



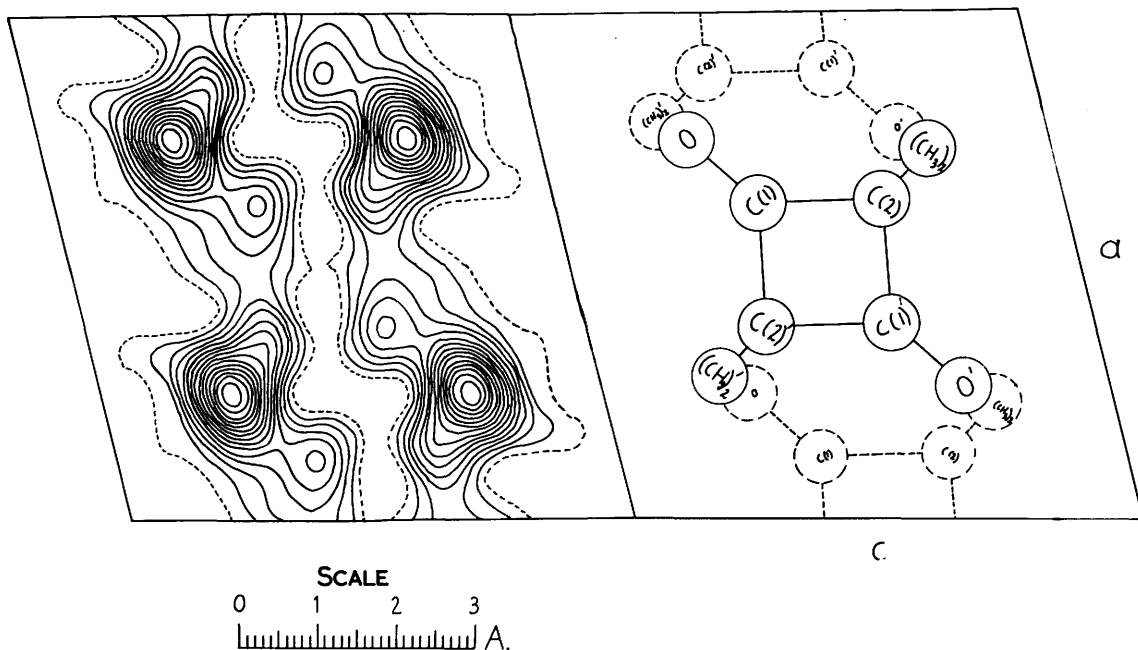
a axis projection of dimethyl ketene dimer

are listed (the asymmetric unit).

Table I. Co-ordinates referred to crystal axes
(origin at centre of symmetry).

Atom	x(A)	2 x/a	y(A)	2 y/b	z(A)	2 z/c
C(1)	0.7641	42°	0.0	0°	- 0.6430	- 36°
C(2)	0.8187	45	0.0	0	0.9466	53
O(1)	1.5830	87	0.0	0	- 1.3390	- 75
CH ₃	1.4550	80	1.225	43	1.6700	93.5
CH ₃	1.4550	80	- 1.225	- 43	1.6700	93.5

Figure 5



b axis projection of dimethyl ketene dimer

The molecular axes chosen are shown in Figure 3, which also shows the naming of the atoms. The orientation of the molecule in the crystal is expressed by the angles χ_L, ψ_L, ω_L ; χ_M, ψ_M, ω_M ; χ_N, ψ_N, ω_N which the molecular axes L, M and N make with the crystal axes a, b and c' (c' being the axis at right angles to the a-b plane). As the molecule is planar and lies in the above specified way, the direction cosines of the L molecular axis completely specify its orientation. These are,

$$\chi_L = 34.1^\circ \quad \omega_L = 138.1^\circ$$

Table II. shows the bond lengths and bond angles obtained by calculating the distance between the set of atomic co-ordinates (Table I.) and the corresponding set of values obtained by Lipscomb and Schomaker.

Table II. Bond lengths and bond angles

	<u>X-ray</u>	<u>electron diffraction</u> (1)
C-C ring	1.56 A.	1.56 \pm 0.05 A.
C-CH ₃	1.49 A.	1.54 \pm 0.05 A.
C-O	1.20 A.	1.22 \pm 0.04 A.
C-CO-C	89°30'	93° \pm 6°
CH ₃ -C-CH ₃	111°8'	111° \pm 6°

The molecular axes chosen are shown in Fig. 3, which also shows the naming of the atoms. The orientation of the molecule in the crystal is expressed by the angles $\chi_L, \psi_L, \omega_L; \chi_M, \psi_M, \omega_M; \chi_N, \psi_N, \omega_N$ which the molecular axes L, M and N make with the crystal axes a, b and c' (c' being at right angles to the a-b plane). As the 4 carbons of the ring and the 2 oxygens are coplanar, it is possible to specify the orientation of the molecule by means of only two direction cosines χ_L and ω_L , when space group $C_{2h}^3 - C 2/m$ is assumed. These are,

$$\chi_L = 34.1^\circ \quad \omega_L = 138.1^\circ$$

Table II. shows the bond lengths and bond angles obtained by calculating the distance between the set of atomic co-ordinates (Table I.); the corresponding values obtained by Lipscomb and Schomaker are also shown.

Table II. Bond lengths and bond angles

	<u>X-ray</u>	<u>electron diffraction</u> (1)
C(1)-C(2)	1.576 A.	} 1.56 \pm 0.05 A.
C(1)-C(2)'	1.550 A.	
C-CH ₃	1.49 A.	1.54 \pm 0.05 A.
C-O	1.20 A.	1.22 \pm 0.04 A.
C- \hat{C} O-C	89°30'	93° \pm 6°
CH ₃ - \hat{C} -CH ₃	111°8'	111° \pm 6°
C(2)-C(1)-O	138°12'	----

Experimental

The crystals employed were prepared by Dr. Rydon to whom I extend my thanks. The substance is very volatile, but specimen mounted on a glass fibre and sealed into a soft glass capillary tube could be preserved for weeks at 16° C., but tend to volatilize and deposit on the walls of the tube at even slightly higher temperatures. The density was determined by flotation in a CCl_4 , C_6H_6 mixture. Copper- $\text{K}\alpha$ radiation Ni filtered was used to obtain rotation, oscillation, zero and first layer moving films about the three principal zones. The multiple film technique (Robertson 1943;(9)) was used to obtain visual estimates of the intensities and these were put on an absolute scale by correlation with the calculated intensities. No absorption corrections were made, as the crystals employed were of uniform cross section (8/33 x 10/33 mm) and because the linear absorption coefficient is very small. The F obs. values were derived by the usual formulae for mosaic type crystals. The Fourier syntheses were carried out by the three figure numerical method (Robertson 1948;(10)). The anthracene curve was employed to calculate F calc. (11).

Discussion

Apart from the interest that lies in comparing the results obtained by the two methods, two further points

Experimental

The crystals employed were prepared by Dr. Rydon to whom I extend my thanks. They are colourless, waxlike, irregular in shape and very volatile. When exposed to the atmosphere, the crystals volatilized in a matter of minutes. A crystal of approximately uniform cross-section (0.24 x 0.3 mm.) was selected, mounted on a glass fibre and sealed into a soft glass capillary tube. When so prepared the crystal could be preserved for weeks at 16° C., but other specimens used when the room temperature exceeded this temperature volatilized and deposited on the walls of the capillary tube. The density was determined by flotation in a CCl_4 , C_6H_6 mixture. Copper- $\text{K}\alpha$ radiation, Ni filtered was used to obtain rotation, oscillation, zero and first layer moving films about the three principal zones. The multiple film technique (Robertson 1943;(9)) was used to obtain visual estimates of the intensities and these were put on an absolute scale by correlation with the calculated intensities. The film used was Ilford fast film having an absorption factor of 3.3. This factor had been determined a short time previously by two independent observers, on the same delivery of film. The excellent agreement of the (OkO) spectra confirms the accuracy of the film to film factor. The linear absorption coefficient is small and the two crystals used had such dimensions that no absorption correction seemed necessary. This is confirmed by the good agreement of F obs. with F. calc. for low index planes. The F obs. values were

(100)

derived by the usual formulae for mosaic type crystals. Only 17 (hk0) spectra were recorded despite prolonged exposures (18 hours). The low melting and boiling points make for a high degree of thermal vibration. This coupled with the fact that most of the atoms are co-planar, creates conditions in which the intensities of spectra fall off rapidly. Several f curves were tried, the anthracene curve, which gave the best agreement, was finally adopted (11). The Fourier syntheses were carried out by the three figure numerical method (Robertson 1948; (10)).

In view of the relatively small number of spectra recorded the question of accuracy of the co-ordinates must be raised. The y co-ordinates can be considered reliable, because even a slight amount of puckering would diminish the good agreement of F obs. and F calc. for (Ok0) planes. It is also thought that puckering would show in Fig. 4. The y co-ordinates of all the atoms and the x and z co-ordinates of the methyl groups and of atom C(1) are fairly certain. Many attempts were made to shift the remaining two atoms. While the small number of observed planes was a disadvantage in fixing the parameters of the atoms, it also enabled a correspondingly greater number of trial and error shifts to be calculated. On approaching the final values, the discrepancy dropped considerably.

Discussion

Apart from the interest that lies in comparing the results obtained by the two methods, two further points

are mentioned briefly. As has been observed in several earlier investigations of cyclobutane systems (7),(12), (13), the carbon-carbon distance has again been found higher than the 'normal' 1.54 Å. This feature of cyclobutane systems has been investigated by Dunitz (7) in connection with his investigation of 1,2,3,4-tetraphenylcyclobutane. Dunitz postulates that because of the strain in the 4-membered ring caused by the bond angles being constrained to close to 90°, the usual sp^3 hybridization is modified. The orbitals involved in the formation of the cyclobutane ring tend to acquire extra p character at the expense of increased s character in orbitals directed towards the hydrogen atoms. Dunitz found that the bonds from the cyclobutane ring to the 4 benzene rings in tetraphenylcyclobutane had decreased in length from 1.54→1.50 Å. This interesting hypothesis gains confirmation from this investigation, where the central ring has been found to be 1.56 Å. and the carbon-methyl group bond 1.49 Å. It must be pointed out however, that the bond lengths of dimethyl ketene dimer obtained in this investigation, are likely to be much less accurate than those of Dunitz, whose investigation of tetraphenylcyclobutane was 3-dimensional. Otherwise a shortening of the carbon-methyl group bond of the same order as with a benzene system would be surprising.

There is considerable disagreement on whether the cyclobutane ring is planar or puckered. There are four investigations of C_4F_8 by spectroscopic and electron

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There is considerable disagreement on whether the cyclobutane ring is planar or puckered. There are four investigations of C_4F_8 by spectroscopic and electron

diffraction methods, two of which favour planar rings, two puckered rings (3),(4),(5),(6). Tetraphenylcyclobutane (7) has been found to have a planar ring. If the space group of dimethyl ketene dimer is in fact $C_{2h}^3 - C 2/m$, which cannot be proved absolutely, the cyclobutane ring would, in dimethyl ketene dimer, be planar. If $C_2^3 - C 2$ is the real space group and the atoms of the ring lie almost but not quite on a plane, the puckering cannot be much more than 0.05 A., as the agreement F' obs. with F' calc. (0k0) would preclude a greater degree of puckering.

Table of Structure Factors.

Dimethyl ketene dimer: measured and calculated values
of the structure factor.

<u>hkl.</u>	<u>2sin θ.</u>	<u>F obs.</u>	<u>F calc.</u>	<u>hkl.</u>	<u>2sin θ.</u>	<u>F obs.</u>	<u>F calc.</u>
001	.25	35.3	39.0	041	.65	27.8	24.4
002	.49	57.0	-50.0	042	.78	13.6	13.0
003	.74	31.3	-19.5	043	.95	22.7	-18.8
004	.99	6.2	6.1	044	1.15	17.6	-18.8
005	1.24	< 4.0	- 3.5	045	1.37	< 4.0	2.7
006	1.49	6.8	- 7.0	061	.94	17.6	14.8
007	1.74	< 4.0	1.6	062	1.03	< 4.0	- 3.0
020	.30	67.1	72.5	063	1.17	14.7	-12.1
040	.60	14.2	15.2	064	1.33	8.5	- 6.6
060	.90	23.9	23.5	081	1.23	8.5	8.4
080	1.20	26.7	28.4	082	1.30	11.3	-10.0
0,10,0	1.50	11.4	13.4	083	1.41	7.9	- 6.0
200	.49	43.8	-48.8	110	.29	40.9	40.7
400	.97	4.5	4.4	130	.51	23.3	22.1
600	1.46	8.0	- 8.2	150	.79	19.9	13.7
800	1.97	3.4	5.7	170	1.08	14.2	13.2
021	.38	40.9	32.8	220	.57	14.7	-16.1
022	.57	16.5	-15.1	240	.78	13.6	11.0
023	.79	23.3	-21.1	260	1.02	< 4.0	- 3.8
024	1.02	10.8	- 7.4	310	.75	17.0	-25.8
025	1.26	< 4.0	- 2.6	330	.86	13.6	- 8.3

Part II.The Crystal and Molecular Structure of
aceanthrono-(2'.1' : 1.2)-aceanthroneIntroduction

This compound was first prepared by Clar (14). Thanks are due to Messrs. I.C.I. Ltd., for donating the sample used. Aceanthrono-(2'.1' : 1.2)-aceanthrone or acedianthrone is usually obtained as a brown powder, but it has been possible to obtain crystals which were dark green opalescent in colour by crystallizing from nitrobenzene. Acedianthrone, whose structure was in some doubt, contains a very unusual five membered ring system. While cyclopentadiene exists, there is no corresponding compound pentalene. Figure 1 (p.6) shows the proposed chemical formula of pentalene. It appears to be too unstable to exist. Recent experiments by Blood and Linstead (1952;(15)) confirm this, but Craig and Maccoll (16) predict a rather high resonance energy and a reasonable stability for pentalene. In this connection the chemical properties of dibenzopentalene (Figure 2) are of interest. Dibenzopentalene behaves like a conjugated diene. Nevertheless Blood and Linstead find from the absorption spectrum of dibenzopentalene, that it differs significantly from linear

dienes with the same number of π electrons and indicates some degree of resonance interaction. Acedianthrone, which contains the dibenzopentalene system, appears to be fully aromatic, judging by its colour, stability and bond lengths. The presence of the two aromatic parts of this molecule stabilises the system.

Anthraquinone, which it resembles, has been studied several times lastly by Sen (17). Acedianthrone is one of several anthraquinone dyestuffs on which X-ray studies have been carried out (H.P. Stadler, private communication). Apart from the object of confirming the chemical structure of acedianthrone, it was desired to obtain information on the five membered ring system and, if it proved possible, to obtain accurate bond lengths. Earlier investigations showed that the central carbon bond (marked A-A' in Figure 6a) is always a single bond. A-H and A'-B could be bonds with a large amount of double bond character. It is even possible that there is a resonance transfer across the single bond. To obtain information on these points was the main aim of the investigation.

Crystal Data

Acedianthrone

$C_{30}O_2H_{14}$

F.W. 406.1

d. calc. 1.490

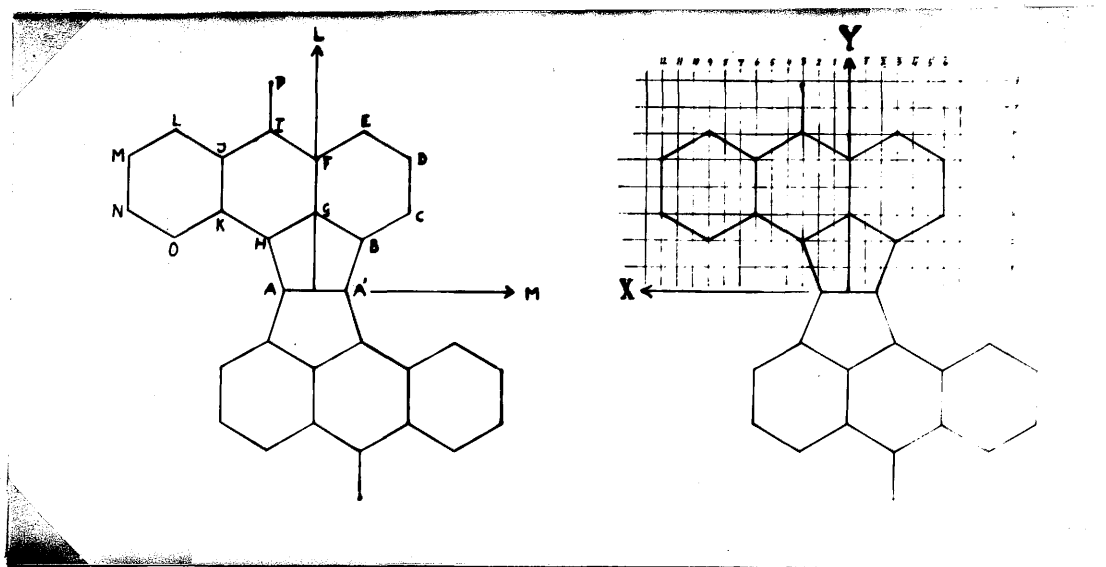
d. obs. (by flotation) 1.498

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Crystal Data

Acedianthrone $C_{30}O_2H_{14}$ F.W. 406.1 m.pt. $> 360^\circ C.$
 d. calc. 1.490 d. obs. (by flotation) 1.498



(a)

(b)

Figure 6

Monoclinic $\underline{a} = 5.64 \pm 0.01$ A., $\underline{b} = 10.96 \pm 0.02$ A.,
 $\underline{c} = 15.49 \pm 0.03$ A., $\beta = 108.2^\circ \pm 0.5^\circ$

Absent spectra: (h0l) when l is odd
 (0k0) when k is odd

Space group: $C_{2h}^5 - P 2_1/c$

Two molecules per unit cell.

Molecular symmetry: centre.

Absorption coefficient for X-rays $= (1.54\text{A.}) = 8.7$ per cm.

Total number of electrons per unit cell $= F(000) = 420$

The crystals are fine needles, well formed and elongated along the \underline{a} axis.

Crystal Structure

No conclusions could be drawn from the cell dimensions about the orientation of the molecule. As there are only two molecules per unit cell in a space group requiring four asymmetric units, the molecule must make use of its centre of symmetry. This fixed the position of the centre of symmetry of the molecule and determined that it was either planar, which seemed the more likely case, or bent in such a way as to maintain its centre of symmetry. It was therefore hoped that the orientation of the molecule would be a relatively simple task, provided a) the chemical structure assumed for trial and error methods of correlating calculated and observed structure factors was right and b) the molecule is, if not planar, then not too twisted. It was noted that the X-ray spectra when expressed in terms of the unitary structure factor,

$$U_0 = \hat{F}(000) = 1$$

were mainly weak reflections, but this was at this stage falsely attributed to the complexity of the structure and not, as it turned out later, to the effect that the atoms of one molecule lie almost exactly half-way between the atoms of the molecule above, when projected on the (010) plane. This halves the interatomic distances

from their usual value to 0.7 or 0.8 Å. and only a few planes inside the sphere of reflection for copper- $K\alpha$ are really strong. At first the method of tracing the prominent small spacing planes was tried. A successful use of this method is described by Robertson and White (18) in their investigation of coronene. The orientation could not be obtained in this way. This again was due to 'interlacing' which blurred the intersections of these small spacing planes. In the a axis projection, where there is no overlap of atoms, this method cannot be used, as the geometric structure factor is either a product of cosines or one of sines. The geometric structure factors vary from point to point in the pattern of a chess board, a white square say, being positive, a black square negative. If several prominent planes are superimposed, the resulting picture is confused and only Beevers-Lipson charts can be used for trial and error methods in such projections.

An attempt was made to find the approximate orientation by studying the indices of refraction. Acidianthron crystallises to give crystals which are opaque, but very thin crystals, less than about 0.01 mm. transmit light. Such excessively small crystals, particularly when they absorb light as strongly as these, are most unsuitable for the determination of refractive indices and after several unsuccessful attempts to obtain consistent results the attempts to find the orientation by this method was abandoned.

A Fourier transform was then made. This method first proposed by Ewald, Bragg and others, lately by Booth, Wrinch and Knott (19) determined the orientation. The F obs. of the three principal zones were listed and put on an absolute scale. This was done in two ways. (i) by summing the F calc. obtained in a large number of trial and error attempts and comparing this sum with $\sum F$ obs. over the same planes. (ii) by comparing $\sum F$ calc. of ovalene, a hydrocarbon with the same scattering properties as acedianthrone (ovalene has 16 carbon atoms per asymmetric unit, acedianthrone 15 carbon atoms and 1 oxygen atom. Both have the space group $P 2_1/c$) and summing $\sum F$ calc. (h0l) ovalene up to a ξ value of 1.00, similarly finding F obs. (h0l) acedianthrone up to ξ 1.00, a scaling factor was found. The second method is really only an adaptation of Wilson's method of finding absolute intensities from relative ones (20) but the adaptation was preferred. The scaling factor obtained by the first method was later found to be accurate to about 2%, the second method gave a scaling factor 4% in error. From this the geometric structure factor of every observed plane was found. Knott points out (19), that a molecule can be represented by weighted reciprocal space. The structure factor of any plane (hkl) in a crystal can be expressed as

$$F(hkl) = \sum f(hkl) e^{2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)}$$

A Fourier transform was then made. This method first proposed by Ewald, Bragg and others, lately by Booth, Wrinch and Knott (19) determined the orientation. The F obs. of the three principal zones were listed and put on an absolute scale. This was done in two ways. (i) by summing F calc. obtained in each of a large number of trial and error attempts and comparing this sum with $\sum F$ obs. over the same planes. (ii) by comparing $\sum F$ calc. of ovalene, a hydrocarbon with the same scattering properties as acedianthrone (ovalene has 16 carbon atoms per asymmetric unit, acedianthrone 15 carbons and 1 oxygen atom. Both have space group $P 2_1/c$) and summing $\sum F$ calc. (h0l) ovalene up to a ξ value of 1.00, similarly finding $\sum F$ obs. (h0l) acedianthrone up to $\xi = 1.00$, a scaling factor was found. [It has since been pointed out to the writer that such a procedure only has a theoretical justification if the summation is carried out to $\xi = 2$]. The second method is really only an adaptation of Wilson's method of finding absolute intensities from relative ones (20), but the adaptation was preferred. The scaling factor obtained by the first method was later found to be accurate to about 2%, the second method gave a scaling factor 4% in error. From these absolute F obs. values the geometric structure factor of every observed plane was found.

The structure factor of any plane (hkl) consists in general of a real and an imaginary part called A and B. In the case of a space group with a centre of symmetry (such as $P 2_1/c$), if the origin is taken at the centre of symmetry, $B = 0$.

where a, b and c are the translations and x, y and z the atomic co-ordinates, $f(hkl)$ being the atomic scattering factor for the particular plane. $F(hkl)$ may be written in terms of the reciprocal distances a^{*}, b^{*} and c^{*} where

$$\underline{a}^* = \frac{1}{a \sin \beta} \quad \underline{b}^* = \frac{1}{b} \quad \underline{c}^* = \frac{1}{c \sin \beta}$$

If $F(hkl)$ is calculated for every possible value of a^{*}, b^{*} and c^{*}, a continuous distribution of structure factors in space can be obtained. If the molecule is planar, then the transform is cylindrical and a projection on the X Y plane of the molecule (see Fig. 6b) can be used to calculate structure factors for all planes $F(hkl)$. As pointed out in Knott's paper, the atomic scattering factor was eliminated by assuming all the atoms to have equal scattering power (a permissible assumption in the case of acedanthrone $C_{15}O_1$). For the purpose of the Fourier transform all bond lengths including the C-O bond and those of the five membered ring were assumed to be 1.40 A. and the benzene rings perfectly regular hexagons. As with the direct cell, the reciprocal cell has four asymmetric units and only half the molecule needs to be considered. Two sets of planes were found which gave maximum reflections of every atom in the asymmetric unit of the X Y plane, the two sets being at right angles to each other and so chosen, that every atom lay an integral number of planes from the

Considering the real part of the structure factor,

$$A(hkl) = \sum f \cos 2\pi(hx + ky + lz)$$

where h , k and l are the Miller indices of the plane and x , y and z the atomic co-ordinates in fractions of the axial lengths. When all the atoms have the same or nearly the same number of electrons (C , N or O) it is possible to rewrite the structure factor thus,

$$\frac{A(hkl)}{f} = \sum \cos 2\pi(hx + ky + lz) \dots\dots(i)$$

A discontinuous function is obtained, as only integral values of h , k and l give rise to reflections.

It is possible to consider the structure factor of a molecule independent of the unit cell which it uses in the crystal. If we write,

$$T_{C1} = \sum \cos 2\pi(HX + KY + LZ) \dots\dots(ii)$$

where X , Y and Z are the co-ordinates in A . of atoms of the molecule with respect to any convenient origin.

Then H , K and L and T_{C1} , ^{we use A^{-1}} the real (or cosine) transform of the molecule may be evaluated over the whole of reciprocal space H , K , L . In the case of a molecule with a centre of symmetry the imaginary (or sine) part of the transform is zero i.e. $T_{S1} = 0$.

Thus the Fourier transform T_{C1} is continuous over the whole of reciprocal space. The similarity between (i) and (ii) is immediately obvious and (ii) is the molecular

origin (Figure 6b). Each atom in the asymmetric unit is thus assigned a plane, all of equal value and arbitrarily chosen as 100, and a double Fourier synthesis carried out. The indices of the planes are listed in table III.

Table III. acedianthrone, Fourier transform co-ordinates.

Atom	X	Y	Atom	X	Y
A	- 2	0	I	3	6
B	- 3	2	J	6	5
C	- 6	3	K	6	3
D	- 6	5	L	9	6
E	- 3	6	M	12	5
F	0	5	N	12	3
G	0	3	O	9	2
H	3	2	P	3	8

A continuous distribution in space of the molecular structure factor is thus obtained, giving the algebraic values of the geometric structure factors for every possible orientation of the molecule. As acedianthrone uses its centre of symmetry, the origin of the reciprocal lattice is also the origin of the Fourier transform. Further, because of the centre of symmetry, there is also no sine transform, which makes the determination of the orientation much easier. In practice the first transform that was drawn up could not be interpreted,

structure factor calculated as a continuously variable function throughout the reciprocal space HKL corresponding to the reciprocal space represented by Miller indices (hkl).

Evaluation

For the evaluation of the transform axes X, Y and Z have to be selected. Obvious axes are Z perpendicular to plane of molecule, X and Y as shown in Fig. 6b. Then let the atomic co-ordinates be expressed as integral multiples of convenient units. The values of the transform are invariant along the \bar{Z} axis (since $Z=0$ for all atoms). For the purpose of the Fourier transform all bond lengths including the C-O bond and those of the five membered ring were assumed to be 1.40 A. and the benzene rings perfectly regular hexagons. As the molecule of acedianthrone is not symmetrical about the Y axis, the two bonds A-H and A⁸-B will not have equal length, but at this stage it is convenient to assume that they *have*. Table III. lists the atomic co-ordinates X, Y of acedianthrone.

Table III. Atomic co-ordinates for Fourier transform of acedianthrone.

Atom	X	Y	Atom	X	Y
A	- 2	0	I	3	6
B	- 3	2	J	6	5
C	- 6	3	K	6	3
D	- 6	5	L	9	6
E	- 3	6	M	12	5
F	0	5	N	12	3
G	0	3	O	9	2
H	3	2	P	3	8

as the atoms had not lain truly on the planes chosen and the transform gave a distorted picture. This was discovered when the value as read off from the transform, was compared with the value obtained by ordinary calculation of a known orientation. For the second attempt greater care was taken in choosing planes, so that all atoms contribute maximum. From this it would appear, that a Fourier transform is only likely to be sufficiently accurate to lead to an orientation of the molecule, if the assumed atomic co-ordinates of the molecule are not more than approximately 0.15 A. out from their real values in the case of random errors and 0.1 A. if the error is systematic. These margins are, of course, very large.

Figure 7 shows the Fourier transform with the (h0l) reciprocal lattice net superimposed. The \underline{b}^* axis is also shown. In $P 2_1/c$ all the molecules project parallel in the \underline{b} axis projection, so the reciprocal lattice picks out the algebraic value of the geometric structure factor of each (h0l) plane on the transform. This can be seen in Figure 7. Each full line indicates one positive unit of geometric structure factor, dashed lines indicate a negative unit. Zero values are shown by dotted lines. As there are 16 atoms in the asymmetric unit, the maximum value of the geometric structure factor is plus or minus 16. There are four such peaks corresponding to these maxima in figure 7. One at the origin, one along the \underline{x} axis and two negative peaks,

In order to calculate structure factors by the transform method it is necessary to combine the transforms of each of the asymmetric units and determine the mutual orientation of the transform axes and the cell axes or, more usefully, the transform axes and the axes \underline{a}^* , \underline{b}^* and \underline{c}^* of the reciprocal unit cell.

The directions of \underline{a}^* , \underline{b}^* and \underline{c}^* were determined as shown in Figure 7. The origin of the transform and of the reciprocal unit cell coincide. The planes (100), (200), (300), (500) and (600) all had fairly large geometric structure factors and the direction of \underline{a}^* was soon found. The (00 l) planes were all weak and \underline{c}^* was found next. The direction of \underline{b}^* was found by the absence of (020) and (060). Fig. 7 shows the Fourier transform (with the (h0 l) reciprocal lattice net superimposed). In $P 2_1/c$ all the molecules project parallel in the \underline{b} axis projection, so the reciprocal lattice picks out the algebraic value of the geometric structure factor of each (h0 l) plane on the transform. This can be seen in Fig. 7. Each full line indicates one positive unit of geometric structure factor, dashed lines indicate a negative unit. Zero values are shown by dotted lines. As there are 16 atoms in the asymmetric unit, the maximum value of the geometric structure factor is plus or minus 16. There are 4 such peaks corresponding to these maxima in Fig. 7, one at the origin, one along the X axis and two negative peaks,

one near plane 1,0,10 the other near $\bar{6}08$. The rest of the transform is a relatively flat plateau.

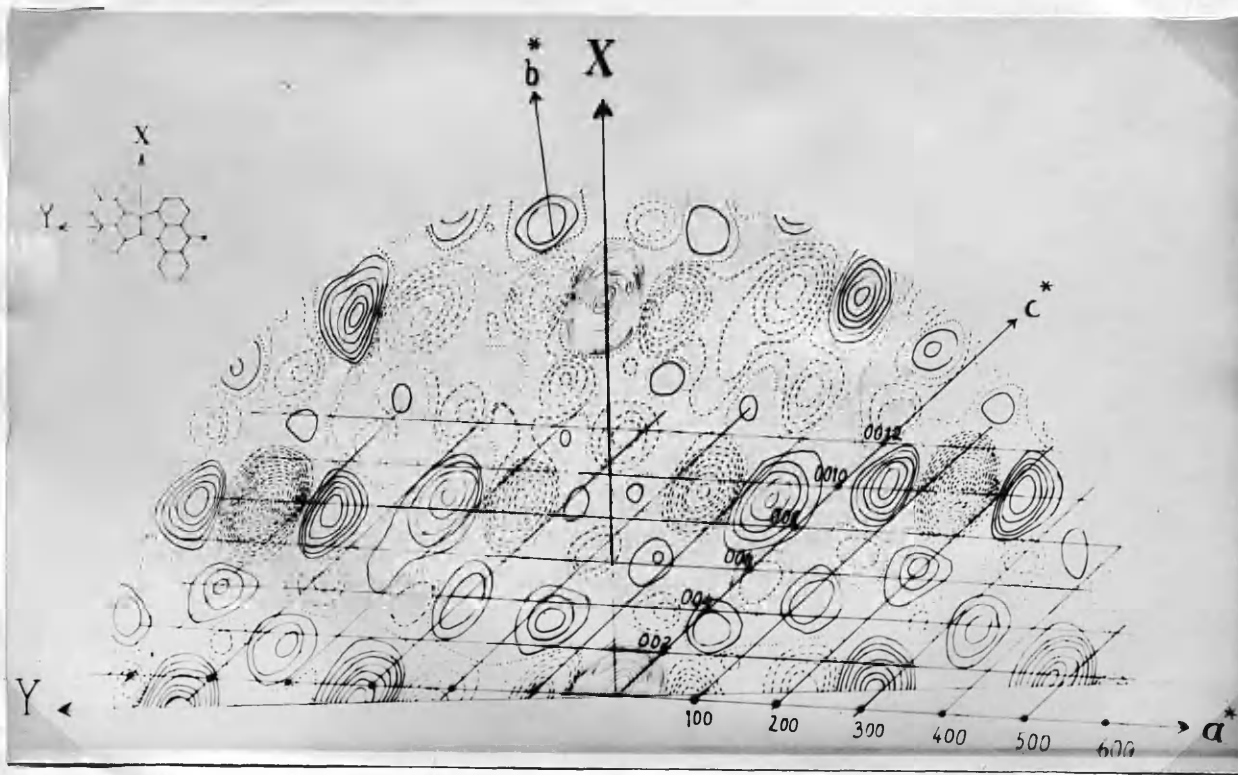


Figure 7 Fourier transform of acedianthrone with (h0l) reciprocal lattice net superimposed.

In the c and a axial projections, the two molecules of the unit cell are not parallel, but are related to each other by the set of equivalent points;

$$(\underline{x}, \underline{y}, \underline{z}) ; (\bar{x}, 1/2+y, 1/2-z)$$

from which the projections of the reciprocal points can be calculated thus;

Transform relations

$$T(hkl) = 2 \sum \cos 2\pi(hx + ky + lz)$$

Equivalent points; (x, y, z) ; $(\bar{x}, 1/2 + y, 1/2 - z)$

for hk0;

$$T_1 = 2 \sum \cos 2\pi(hx + ky)$$

$$T_2 = 2 \sum \cos 2\pi(\bar{h}\bar{x} + k \overline{1/2 + y})$$

$$T_2 = 2 \sum \cos 2\pi hx \cdot \cos 2\pi k \overline{1/2 + y} - 2 \sum \sin 2\pi hx \cdot \sin 2\pi k \overline{1/2 + y}$$

$$= 2 \sum \cos 2\pi hx \left[\cos 2\pi \frac{k}{2} \cdot \cos 2\pi ky - \sin 2\pi \frac{k}{2} \cdot \sin 2\pi ky \right]$$

$$+ 2 \sum \sin 2\pi hx \left[\sin 2\pi \frac{k}{2} \cdot \cos 2\pi ky - \cos 2\pi \frac{k}{2} \cdot \sin 2\pi ky \right]$$

$$\left\{ (\bar{h}\bar{x}) = -hx; -\cos x = \cos x \right\}$$

$$= 2 \sum \cos 2\pi hx \cdot \cos \pi k \cdot \cos 2\pi ky$$

$$- 2 \sum \cos 2\pi hx \cdot \sin \pi k \cdot \sin 2\pi ky$$

$$+ 2 \sum \sin 2\pi hx \cdot \sin \pi k \cdot \cos 2\pi ky$$

$$+ 2 \sum \sin 2\pi hx \cdot \cos \pi k \cdot \sin 2\pi ky$$

now $\cos \pi k = (-1)^k$; $\sin \pi k = 0$

$$\therefore T_2 = (-1)^k \cdot 2 \sum \cos 2\pi hx \cdot \cos 2\pi ky \\ + (-1)^k \cdot 2 \sum \sin 2\pi hx \cdot \sin 2\pi ky$$

$$\therefore T_2 = (-1)^k \cdot 2 \sum \cos 2\pi(hx + k\bar{y})$$

\therefore for planes with $k = 2n$

$$T_2 = 2 \sum \cos 2\pi(hx + k\bar{y})$$

\therefore for planes with $k = 2n + 1$

$$T_2 = -2 \sum \cos 2\pi(hx + k\bar{y})$$

$$\therefore \text{for planes with } k \text{ even: } F \text{ calc.} = 1/2 \left\{ T(hk) + T(h\bar{k}) \right\}$$

$$\text{for planes with } k \text{ odd: } F \text{ calc.} = 1/2 \left\{ T(hk) - T(h\bar{k}) \right\}$$

and for $0kl$

$$T_1 = 2 \sum \cos 2\pi(ky + lz)$$

$$T_2 = 2 \sum \cos 2\pi(k \overline{1/2 + y} + l \cdot \overline{1/2 - z})$$

$$= (-1)^k (-1)^l \cdot 2 \cos 2\pi(ky + l\bar{z})$$

∴ for planes with $k+l$ even: $T_2 = 2 \sum \cos 2\pi(ky + l\bar{z})$

for planes with $k+l$ odd: $T_2 = -2 \sum \cos 2\pi(ky + l\bar{z})$

and for planes with $k+l$ even:

$$F \text{ calc.} = 1/2 \left\{ T(Ok1) + T(Ok\bar{1}) \right\}$$

for planes with $k+l$ odd:

$$F \text{ calc.} = 1/2 \left\{ T(Ok1) - T(Ok\bar{1}) \right\}$$

special case $k=0$

$$\begin{aligned} F \text{ calc.}(001) &= 1/2 \left\{ T(001) + T(00\bar{1}) \right\} \\ &= T(001) \end{aligned}$$

In this particular investigation it was noticed that the transform was much less accurate in the (Ok1) and (hk0) zones. There is a doubling of errors, because the transform has to be read on two places and the \underline{b} axis was probably more sensitive to errors because of the high tilt of the \underline{b}^* axis. Thus only the (h01) zone could be used to find the orientation, but in the case of a planar molecule one zone defines the orientation unambiguously. Sufficient signs could be assigned from the transform for the (hk0) and (Ok1) zones, to obtain Fourier projections which were useful, but in practice another method was adopted.

The algebraic values of the geometric structure factor were assigned to about 60% of the observed (h0l) planes. The discrepancy (defined on page 12) was found to be about 40%. A double Fourier synthesis was carried out and although heavy overlapping obscured most of the atoms of the molecule, the oxygen atom was well resolved, also two carbon atoms A and B of the five membered ring. This established a relationship between the real orientation and the orientation assigned to the molecule from the Fourier transform. This real orientation was then used to calculate the corresponding orientation on the Fourier transform. Using vector notation,

let x' Molecular model atomic co-ordinates in A.
 x (h0l) Fourier map atomic co-ordinates in A.
 h' Transform co-ordinates in reciprocal A.
 h Miller indices of plane.

$$x'_i = a_k^i x^k$$

$$x^s = a_t^s x'^t$$

$$h'_i = a_i^k h_k$$

$$h_s = a_s^t h'_t$$

$$a_k^i a_t^k = \delta_t^i$$

$$a_t^i a_i^s = \delta_t^s$$

then for $h_1 = 1, h_2 = 0$ (i.e. 100 plane)

$$h = (1, 0)$$

$$h'_1 = a_1^i \cdot 1$$

$$k'_2 = a_2^i \cdot 1$$

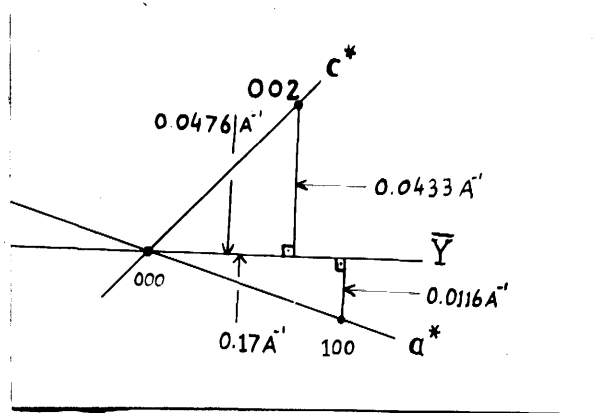
and for $h_1 = 0$, $h_2 = 1$ (i.e. 001 plane)

$$h = (0, 1) \quad h_1' = \alpha_1^2 \cdot 1 \quad k_2' = \alpha_2^2 \cdot 1$$

$$\therefore \alpha_1^1 = -0.0116 \quad \alpha_1^2 = 0.0433$$

$$\alpha_2^1 = -0.17 \quad \alpha_2^2 = 0.0476$$

these values are obtained as indicated in the enlargement of the (h0l) reciprocal lattice net, as in Figure 7.



Enlargement of (h0l) reciprocal lattice net

Finally the Fourier map atomic co-ordinates are obtained by substituting the above coefficients in the transformation equation,

$$x = -0.0116 x' - 0.17 y'$$

$$y = 0.0433 x' - 0.0476 y'$$

By using the (h0l) Fourier map atomic co-ordinates of atoms P and I and substituting in above equations, the reciprocal lattice dimensions in projection could

be calculated. A few signs changed and the agreement between G obs. and G . Fourier transform showed some improvement. A second Fourier projection incorporating these changes was carried out. An electron density map of this Fourier projection is shown in Figure 8.

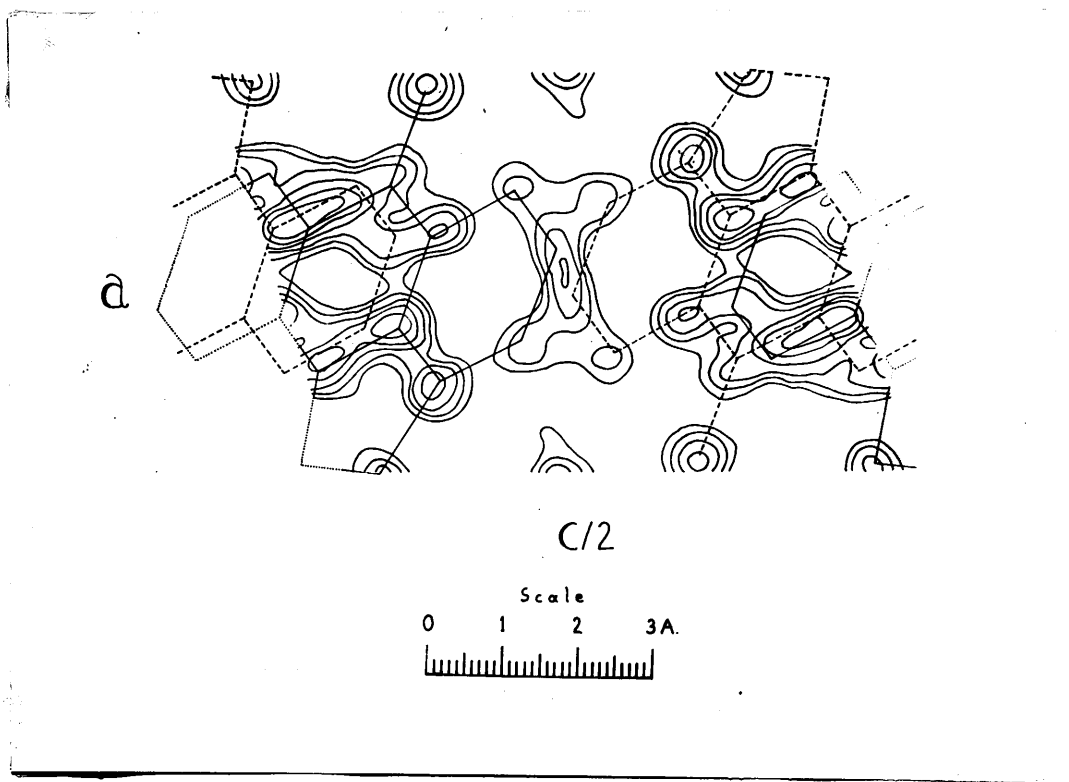


Figure 8 b axis projection of acedianthrone

As the resolution in this zone is so bad, that no further refinement can be expected, attention was now turned to the $(0kl)$ zone. Using the trigonometric relationships;

$$\cos^2 \chi_L + \cos^2 \psi_L + \cos^2 \omega_L = 1$$

$$\cos^2 \chi_M + \cos^2 \psi_M + \cos^2 \omega_M = 1$$

$$\cos^2 \chi_N + \cos^2 \psi_N + \cos^2 \omega_N = 1$$

$$\cos \chi_L \cos \chi_M + \cos \psi_L \cos \psi_M + \cos \omega_L \cos \omega_M = 0$$

$$\cos \chi_L \cos \chi_N + \cos \psi_L \cos \psi_N + \cos \omega_L \cos \omega_N = 0$$

$$\cos \chi_M \cos \chi_N + \cos \psi_M \cos \psi_N + \cos \omega_M \cos \omega_N = 0$$

$$\cos \omega_L = \cos \chi_L \tan \eta_L$$

$$\cos \omega_M = \cos \chi_M \tan \eta_M$$

$$x' = L \cos \chi_L + M \cos \chi_M$$

$$y = L \cos \psi_L + M \cos \psi_M$$

$$z' = L \cos \omega_L + M \cos \omega_M$$

$$x = x' - z' \cot \beta$$

$$z = z' \operatorname{cosec} \beta$$

where (x', y, z') are the rectangular co-ordinates referred to the a and b crystal axes and c' their perpendicular. (x, y, z) are the monoclinic crystal co-ordinates.

$$\begin{aligned} \cos \chi_L, \cos \psi_L, \cos \omega_L; \cos \chi_M, \cos \psi_M, \cos \omega_M; \\ \cos \chi_N, \cos \psi_N, \cos \omega_N, \end{aligned}$$

are the direction cosines of the molecular axes L, M and N.

$$\text{now, } \sin \psi_M = \frac{J\text{---}F \text{ in projection}}{J\text{---}F \text{ in space}} = 42^\circ 30'$$

$$\eta_L = \angle L \text{ makes with } \underline{a} \text{ in projection}$$

$$\eta_M = \angle M \text{ makes with } \underline{a} \text{ in projection}$$

$$\underline{y} = \pm 0.1949 L + 0.7373 M$$

a set of y co-ordinates was obtained.

Using these y co-ordinates and the x co-ordinates obtained from the last (h0l) zone Fourier synthesis, a set of (hko) structure factors was calculated in the usual way. A double Fourier synthesis of this zone only yielded information on the co-ordinates of the oxygen atom. The discrepancy was about 40%. The same procedure was followed for the (0kl) zone. The resolution in this zone is quite good, as there is no overlapping of atoms, but the molecule is so highly inclined to the plane of projection, as to make the projected bond lengths equal to 0.8 Å. in one direction, which is insufficient for complete resolution. The discrepancy at this stage was 29%. A second double Fourier synthesis reduced the discrepancy to 25%. An electron density map of this Fourier projection is shown in Figure 9. A difference synthesis (F obs. - F calc.) reduced the discrepancy of this zone to 22.6%.

A similar difference synthesis was carried out in the (h0l) zone. The interpretation of this difference synthesis proved difficult, because of the large number

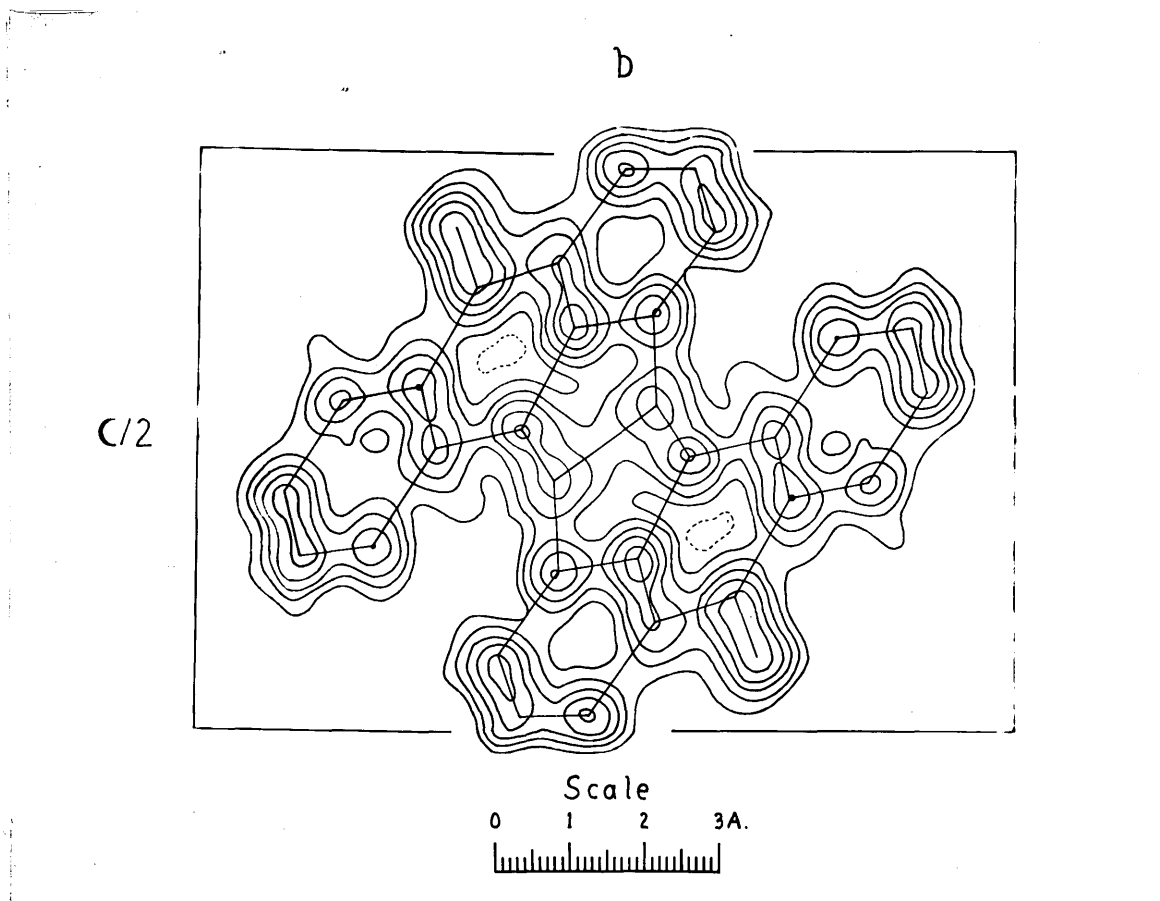
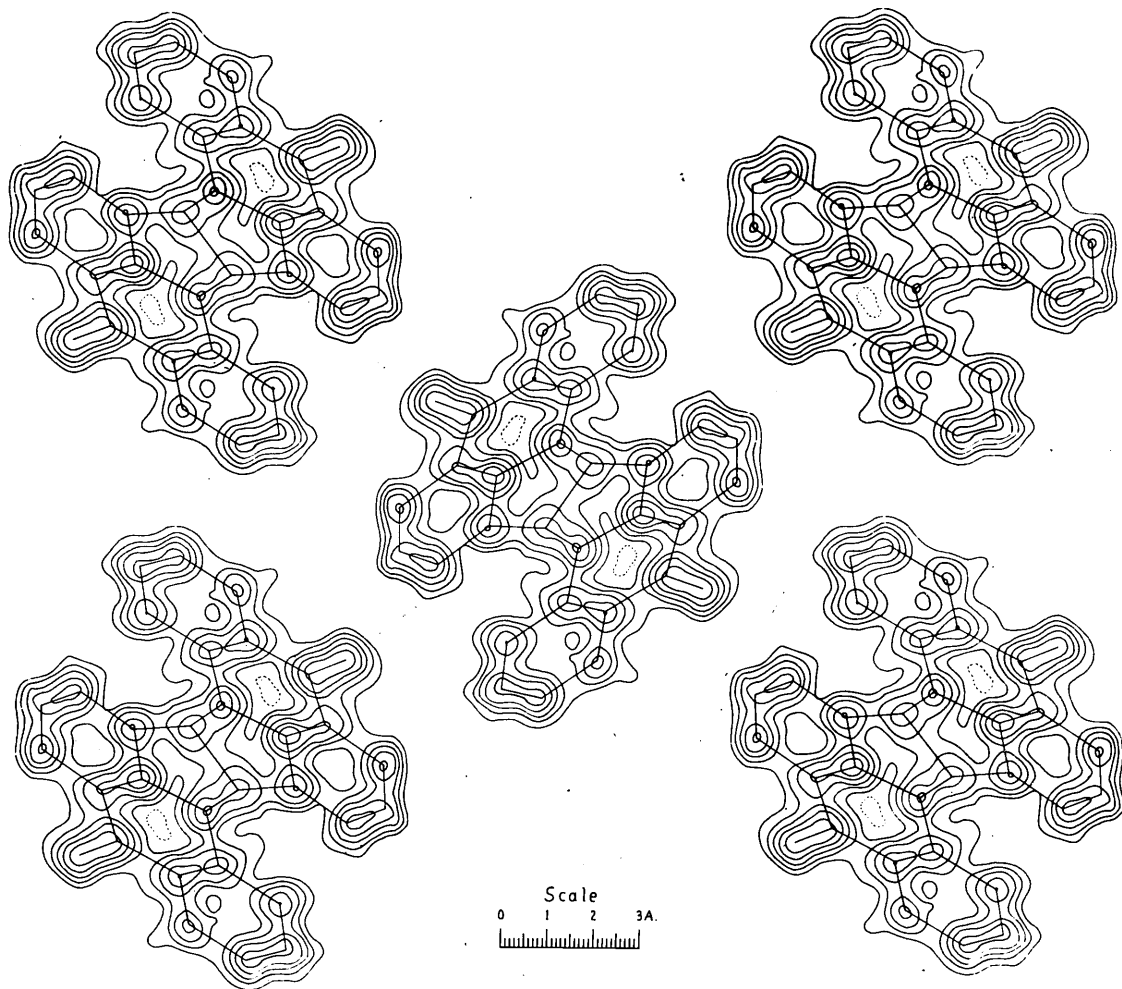


Figure 9. a axis projection of acedianthrone of peaks caused by the overlapping of atoms, but after several attempts the discrepancy was brought down in the three zones to:

hk0 20.0%, Okl 18.8%, h0l 27.8%,
 the average discrepancy for the three zones being 21.9%.

An attempt was made to improve this by including hydrogen atoms, but the improvement was negligible.

Figure 9a. A group of 5 molecules of acedianthrone in the a axis projection.



Co-ordinates, Dimensions and Orientation

The set of co-ordinates giving above discrepancies is listed in table IV. The atoms are numbered A.....P Only the atoms of the asymmetric unit are listed. Assuming the molecule to be planar, the orientation angles of the molecular axes L, M and N (L and M are shown in figure 6a, N is at right angles to the L and M molecular axes and passes through the centre of symmetry) are listed in table V.

Table V.

cos χ_L =	0.7743	χ_L =	39°16'
cos χ_M =	- 0.2183	χ_M =	102°36'
cos χ_N =	- 0.5906	χ_N =	126°12'
cos ψ_L =	0.1442	ψ_L =	81°42'
cos ψ_M =	- 0.8531	ψ_M =	148°34'
cos ψ_N =	0.5058	ψ_N =	59°36'
cos ω_L =	0.6163	ω_L =	51°57'
cos ω_M =	0.4746	ω_M =	61°40'
cos ω_N =	0.6288	ω_N =	51° 3'

Table VI shows the bond lengths obtained by calculating the distances between the set of co-ordinates listed in table IV.

Co-ordinates, Dimensions and Orientation

The set of co-ordinates giving above discrepancies is listed in Table IV. The atoms are numbered A....P Only the atoms of the asymmetric unit are listed. Assuming the molecule to be planar, the orientation angles of the molecular axes L, M and N (L and M are shown in Fig. 6a, N is at right angles to the L and M molecular axes and passes through the centre of symmetry) are listed in Table V. The molecules lie in planes 3.4 Å apart.

Table V.

cos χ_L	=	0.7743	χ_L	=	39°16'
cos χ_M	=	- 0.2183	χ_M	=	102°36'
cos χ_N	=	- 0.5906	χ_N	=	126°12'
cos ψ_L	=	0.1442	ψ_L	=	81°42'
cos ψ_M	=	- 0.8531	ψ_M	=	148°34'
cos ψ_N	=	0.5058	ψ_N	=	59°36'
cos ω_L	=	0.6163	ω_L	=	51°57'
cos ω_M	=	0.4746	ω_M	=	61°40'
cos ω_N	=	0.6288	ω_N	=	51° 3'

Tables VI. and VI.a show the bond lengths and bond angles obtained by calculating the distances between the set of co-ordinates listed in Table IV.

Table VI.a Bond angles

Δ	A'-A -H	104.0°
Δ	A -A'-B	107.7
Δ	A'-B -G	110.1
Δ	B -G -H	110.8
Δ	G -H -A	109.6

Table IV. CO-ordinates referred to crystal axes
(origin at centre of symmetry)

Atom	x(A)	2 x/a	y(A)	2 y/b	z(A)	2 z/c
A	0.06	3.8°	0.62	20.4°	- 0.47	- 11.0°
B	1.27	81.0	- 0.68	- 22.3	1.66	38.6
C	1.85	118.0	- 1.44	- 47.2	2.90	67.4
D	3.14	200.3	- 1.14	- 37.4	3.87	90.0
E	3.96	252.6	- 0.14	- 4.6	3.68	85.5
F	3.36	214.6	0.70	23.0	2.52	58.5
G	2.10	134.0	0.38	12.5	1.51	35.0
H	1.46	93.0	1.06	34.8	0.14	3.2
I	4.20	268.0	1.76	57.8	2.12	49.3
J	3.57	228.0	2.46	80.8	0.86	20.0
K	2.21	141.0	2.28	74.9	- 0.10	- 2.3
L	4.34	276.9	3.52	115.6	0.54	12.5
M	3.86	246.3	4.30	141.2	- 0.58	- 13.4
N	2.52	160.7	4.10	134.6	- 1.63	- 38.0
O	1.84	117.4	3.12	102.5	- 1.29	- 30.0
P	5.42	345.8	1.98	65.0	2.74	63.7

Table VI.

Bond	Distance in A.	Bond	Distance in A.
A - A'	1.59	H - K	1.49
A' - B	1.49	K - J	1.41
B - C	1.41	J - I	1.41
C - D	1.38	I - F	1.48
D - E	1.34	I - P	1.20
E - F	1.41	J - L	1.40
F - G	1.39	L - M	1.32
G - B	1.39	M - N	1.42
A - H	1.41	N - O	1.30
H - G	1.49	O - K	1.41

Experimental

Copper-K α radiation was used throughout to take rotation, oscillation and moving films about the three principal zones, the radiation being Ni filtered as before. The intensities were recorded photographically and were estimated by the multiple film method (9). For the calculation of the structure factor F calc. the benzoquinone curve (21) was found to give the best agreement. Lorentz and the usual polarisation corrections were made. Three planes 100, 002 and 011 calculate about 40% higher than they observe. Since absorption does not appear to have affected the remaining 180

observed planes, these three were omitted from the calculation of the discrepancy.

Discussion

It can be claimed that the chemical structure of acedianthrone postulated by Clar (14) has been confirmed. The molecule is planar within experimental limits. As it has not been possible to obtain clear resolution of the atoms of this molecule using the double Fourier technique, no great accuracy can be claimed for the bond lengths listed in table VI. These were mainly arrived at by using the technique of difference Fourier synthesis. Assuming however, a maximum error of 0.08 Å. and an average error of 0.05 Å., which is probably a conservative estimate, the following may be deduced.

The central bond marked A-A' (on figure 6a) is, as was expected, a single bond. All other bonds share to a greater or lesser extent in the resonance of the whole molecule. The benzene ring to which the oxygen atom is attached is larger than the two side benzene rings. A similar situation is reported by Sen (17) in the case of anthraquinone. The two bonds of the five membered ring, A-H and A'-B differ considerably in length.

Table of Structure Factors

Acedianthrone; measured and calculated values of the
structure factor.

<u>hkl.</u>	<u>2 sin θ.</u>	<u>F obs.</u>	<u>F calc.</u>
002*	0.21	36.8	58.6
004	0.42	18.4	18.5
006	0.63	5.2	3.0
008	0.84	8.4	15.3
00,10	1.05	7.8	1.6
00,12	1.26	7.3	11.3
00,14	1.47	16.7	-19.0
020*	0.28	< 2.4	6.4
040	0.56	21.5	-23.0
060	0.84	< 4.8	-1.7
080	1.13	6.8	-8.4
0,10,0	1.41	< 6.8	4.9
0,12,0	1.68	7.3	-5.9
100*	0.29	41.3	-75.8
200	0.58	30.6	-31.8
300	0.86	43.0	47.6
400	1.15	9.0	8.0
500	1.44	10.8	7.4
600	1.73	5.4	-2.8
011*	0.18	46.0	62.8
012*	0.25	2.4	-5.2

<u>hkl.</u>	<u>2 sin θ.</u>	<u>F obs.</u>	<u>F calc.</u>
013	0.35	34.9	- 35.6
014	0.44	18.9	15.8
015	0.55	26.2	19.4
016	0.64	14.7	- 5.2
017	0.75	15.2	13.0
018	0.86	19.9	- 25.8
019	0.96	13.6	9.7
01,10	1.05	< 5.7	0.8
01,11	1.16	10.4	10.4
01,12	1.27	6.8	12.3
021	0.30	15.2	- 11.8
022	0.35	24.6	- 34.8
023	0.42	50.2	- 54.3
024	0.51	< 3.6	3.1
025	0.60	28.8	28.8
026	0.69	17.2	- 15.9
027	0.78	< 4.7	- 2.9
028	0.89	20.9	21.0
031	0.43	23.6	21.6
032	0.47	22.0	18.6
033	0.53	23.6	19.2
034	0.60	13.6	18.7
035	0.68	39.2	- 31.3
036	0.76	22.6	20.7
037	0.85	12.0	- 18.8
039	1.04	9.8	11.8

<u>hkl.</u>	<u>2 sin θ.</u>	<u>F obs.</u>	<u>F calc.</u>
0,3,14	1.53	12.5	- 13.1
0,3,15	1.64	16.7	- 17.6
0,3,16	1.73	8.8	- 10.4
041	0.57	24.6	24.0
042	0.60	6.3	7.8
043	0.64	6.3	8.1
044	0.71	< 4.1	1.0
045	0.77	< 4.7	6.7
046	0.85	17.8	- 20.6
047	0.93	13.1	- 16.0
051	0.72	11.0	7.4
052	0.74	6.2	- 0.8
053	0.77	8.8	- 2.9
054	0.82	8.5	5.8
05,10	1.25	15.7	16.0
061	0.85	16.2	- 14.5
062	0.87	20.4	- 19.2
063	0.90	8.4	7.3
064	0.96	< 5.5	- 7.7
065	1.00	10.5	8.9
069	1.28	21.6	20.6
071	0.99	16.2	- 20.8
072	1.00	22.6	- 24.0
073	1.03	11.0	- 15.1
081	1.15	< 6.2	- 1.9
082	1.15	6.8	- 13.1

<u>hkl.</u>	<u>2 sin θ.</u>	<u>F obs.</u>	<u>F calc.</u>
083	1.17	9.3	7.6
084	1.20	9.9	6.3
085	1.24	15.7	15.9
086	1.29	12.5	14.3
087	1.35	13.1	13.4
091	1.27	9.8	11.0
092	1.31	< 6.7	5.3
093	1.30	16.2	15.1
094	1.33	11.0	10.8
095	1.37	18.4	13.7
0,10,1	1.45	< 6.7	3.4
0,10,2	1.46	< 6.7	2.3
0,10,3	1.44	20.3	19.1
0,10,4	1.47	11.0	17.2
110	0.32	22.6	29.9
120	0.40	4.6	1.8
130	0.51	12.0	12.0
140	0.63	6.8	7.6
150	0.76	16.5	19.6
160	0.89	17.4	13.3
170	1.02	6.4	5.8
180	1.16	14.5	16.7
190	1.33	< 6.7	1.1
1,10,0	1.47	< 6.7	6.3
1,11,0	1.57	11.2	12.4
210	0.58	16.8	13.3

<u>hkl.</u>	<u>2 sin θ.</u>	<u>F obs.</u>	<u>F calc.</u>
220	0.63	< 4.1	1.4
230	0.71	< 4.5	- 6.7
240	0.81	< 5.0	0.0
250	0.92	< 5.2	1.7
260	1.03	< 5.7	- 6.7
270	1.13	10.1	12.3
2,11,0	1.64	6.4	8.1
310	0.87	13.2	- 16.2
320	0.90	< 5.2	- 1.7
330	0.96	15.0	- 8.1
340	1.03	9.7	10.6
350	1.11	15.7	10.7
360	1.21	< 5.3	0.4
370	1.30	6.8	- 4.3
410	1.16	7.0	9.8
420	1.18	< 6.3	- 0.8
430	1.22	6.5	6.7
440	1.28	18.2	- 13.3
450	1.35	19.6	- 16.3
460	1.42	8.8	4.6
470	1.50	13.0	- 10.3
4,11,0	1.91	3.4	5.2
510	1.43	< 6.7	0.6
520	1.44	< 6.6	0.4
530	1.49	6.2	- 8.4
540	1.53	< 6.6	3.8

<u>hkl.</u>	<u>2 sin θ.</u>	<u>F obs.</u>	<u>F calc.</u>
550	1.59	< 6.4	1.3
560	1.66	< 6.2	- 3.3
570	1.74	14.3	15.9
580	1.82	11.9	- 11.0
610	1.72	6.4	5.8
620	1.72	< 6.0	- 0.5
630	1.75	< 5.8	- 3.5
640	1.81	5.6	3.5
102	0.40	13.1	17.7
202	0.67	28.4	- 28.9
302	0.95	18.9	22.8
402	1.22	< 6.0	- 0.5
502	1.52	15.3	15.0
$\bar{1}02$	0.30	22.6	- 18.6
$\bar{2}02$	0.55	15.8	- 11.5
$\bar{3}02$	0.81	< 4.8	- 1.0
$\bar{4}02$	1.09	< 6.0	3.8
104	0.57	5.8	10.7
204	0.78	< 4.7	- 10.5
304	1.04	< 5.7	2.6
$\bar{1}04$	0.43	< 3.2	- 3.1
$\bar{2}04$	0.60	13.5	10.6
$\bar{3}04$	0.84	17.1	12.2
$\bar{4}04$	1.10	6.8	7.8
$\bar{5}04$	1.36	< 6.8	4.0
$\bar{6}04$	1.65	8.1	2.7

<u>hkl.</u>	<u>2 sin θ.</u>	<u>F obs.</u>	<u>F calc.</u>
106	0.76	21.7	25.4
206	0.97	8.1	8.5
306	1.22	10.4	7.1
406	1.44	< 6.8	1.1
506	1.74	6.3	3.9
$\bar{1}$ 06	0.60	26.6	23.4
$\bar{2}$ 06	0.71	5.1	- 5.4
$\bar{3}$ 06	0.90	< 5.1	1.2
$\bar{4}$ 06	1.13	5.8	10.3
$\bar{5}$ 06	1.38	7.7	7.2
$\bar{6}$ 06	1.64	13.1	- 16.8
108	0.97	5.8	- 0.8
208	1.15	7.2	- 2.8
$\bar{1}$ 08	0.80	32.1	- 22.0
$\bar{2}$ 08	0.86	7.7	- 14.1
$\bar{3}$ 08	1.00	29.4	- 23.6
$\bar{4}$ 08	1.20	14.0	24.8
$\bar{5}$ 08	1.42	7.7	- 4.5
$\bar{6}$ 08	1.67	20.8	- 27.3
$\bar{7}$ 08	1.91	3.9	10.1
1,0,10	1.17	9.9	- 1.3
2,0,10	1.30	< 6.5	- 0.7
1,0,12	1.37	23.5	- 27.6
2,0,12	1.53	8.6	11.4
3,0,12	1.73	8.1	9.1

<u>hkl.</u>	<u>2 sin θ.</u>	<u>F obs.</u>	<u>F calc.</u>
$\bar{1},0,12$	1.20	5.8	8.8
$\bar{2},0,12$	1.21	7.2	- 5.7
$\bar{3},0,12$	1.29	9.0	- 7.8
1,0,14	1.54	< 6.3	3.3
2,0,14	1.73	8.6	- 6.6
$\bar{1},0,14$	1.39	< 6.8	- 2.6
$\bar{1},0,16$	1.82	4.4	- 3.2
$\bar{2},0,16$	1.68	< 6.5	- 0.5
$\bar{3},0,16$	1.73	< 6.3	4.3
$\bar{4},0,16$	1.88	5.7	- 4.4

* omitted from calculation of discrepancy

Appendix 1

A further analysis of the data obtained from the three dimensional Fourier synthesis of naphthalene.

Introduction

The three dimensional analysis of naphthalene by Abrahams, Robertson and White (22) has led to an accurate determination of bond lengths in the naphthalene molecule. Cruikshank (1952, private communication), using electronic computers and correcting for finite termination of series errors, finds, that the bond lengths given in above paper are accurate to within 0.005 A. This analysis gave electron densities at 54.000 points and if the symmetry properties are taken into account, it covers the unit cell. From these comprehensive data only the values of electron density in the molecular plane had been extracted, for which purpose use had to be made of the centre of symmetry in the naphthalene molecule. Only one half of the molecule is thus obtained on the Fourier section, the other half being assumed identical.

The location of hydrogen atoms is of great interest. If the experimental work is sufficiently accurate to give co-ordinates for hydrogen atoms, then the results may be accurate enough to give information that would be useful in the molecular orbital theory.

There are at present several methods of setting up electron formulae and calculating bond lengths and electron densities by means of these. The three principal methods are, the directed valence bond method developed by Pauling (1931) and J.C. Slater (1931), the molecular orbital method (Lennard-Jones, Hund, Mulliken, 1928) and the Heitler-Rumer method (1931).

In the valence bond method, which has not been displaced by the more recent molecular orbital method, it is supposed that when two atoms are joined by a covalent bond, the direction of the bond will correspond to one in which the orbital wave functions of the two electrons overlap as much as possible. In the molecular orbital method the idea of definite bonding pairs of electrons and directed valence bonds is discarded. The bond is the arrangement of atomic nuclei with the minimum potential energy. Thirdly, the Heitler-Rumer method is an application of Heitler and London's method of representing a diatomic molecule, to polyatomic molecules.

Naphthalene has been investigated by the three methods. Unlike benzene, it has bonds of unequal length, as one would expect from the different reactivities of the α , β and meso carbon atoms. This has been confirmed by the work of Abrahams, Robertson and White (22). Naphthalene is sufficiently non-simple to provide an important test-case of the three theories, yet simple enough to be tackled by the very complex mathematics used in these three methods, provided a

number of reasonable assumptions are made.

Klement (23), using the Heitler-Rumer technique and comparing this method with the other two above mentioned methods, claims that the Heitler-Rumer technique gives the best agreement with X-ray measurements.

C.A. Coulson (private communication), on the basis of the molecular orbital theory, has calculated that the electron cloud should be of a kidney shape, due to the effect of the π electrons. If the electron density around the carbon atoms is kidney shaped, this should be observable when sections are drawn parallel and perpendicular to the molecular plane. The further away from the molecular plane these sections are drawn, the greater will be the foreshortening effect, whereas if the electron distribution is spherical there will be no foreshortening. This is illustrated diagrammatically in figures 10 and 11.

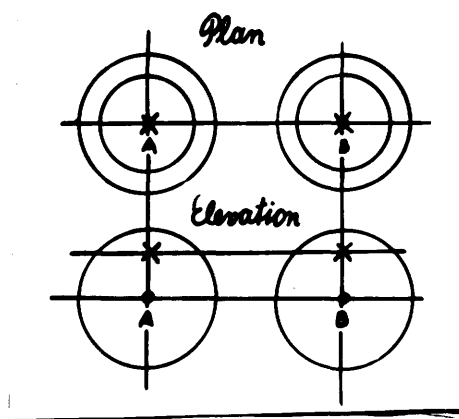


Figure 10

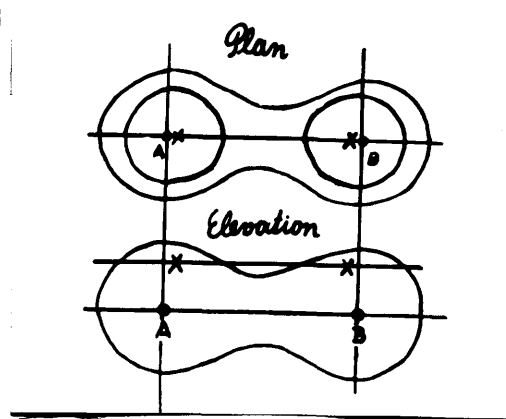


Figure 11

The Fourier series method of representing the

electron density of a molecule, gives an accurate picture of the shape of the atom. However, as has already been pointed out in the general introduction, there is at least one severe limitation to the method namely thermal motion. It is not precisely known what the bond shortening is quantitatively, but it may well be of the order an atom moves in the crystal due to thermal motion of the whole molecule.

From this investigation it would appear, that more valuable information on this point would be obtained, if the work on naphthalene were repeated as near the absolute temperature as can be achieved in practice.

Experimental

It had been decided earlier to draw a section through the molecule, of the electron density on a plane parallel to the molecular plane and $1/4$ A. distant from it. The results of the three dimensional analysis of naphthalene (22) were available in the form of the electron density values over $1/4$ of the unit cell, at 54.000 points. The average equation of the molecular plane with respect to rectangular axes (in A.) had been found to be

$$x' - 0.5265 y + 0.3689 z' = 0$$

The length of the desired normal is 0.25 Å.

Hence the equation of the plane parallel to the molecular plane and 1/4 Å. distant from it is,

$$x' - 0.5265 y + 0.3689 z' \pm \alpha = 0$$

$$0.25 = \frac{\pm \alpha}{\sqrt{(1 + 0.5265^2 + 0.3689^2)}}$$

$$\therefore \alpha = \pm 0.297$$

considering α to be positive, equation is,

$$x' - 0.5265 y + 0.3689 z' + 0.297 = 0.$$

Using the relations,

$$x' = x + z \cos \beta$$

$$z' = z \sin \beta$$

the equation with reference to monoclinic axes is,

$$x - 0.5265 y - 0.2336 z + 0.297 = 0.$$

Electron density values in this plane, which was divided into 60 equal parts along d and e, the intersections of this plane with the unit cell, were found by interpolating the values given in the three dimensional data and plotted in the usual way. Figure 12 shows the result obtained. The calculated position of the naphthalene molecule has been superimposed to indicate

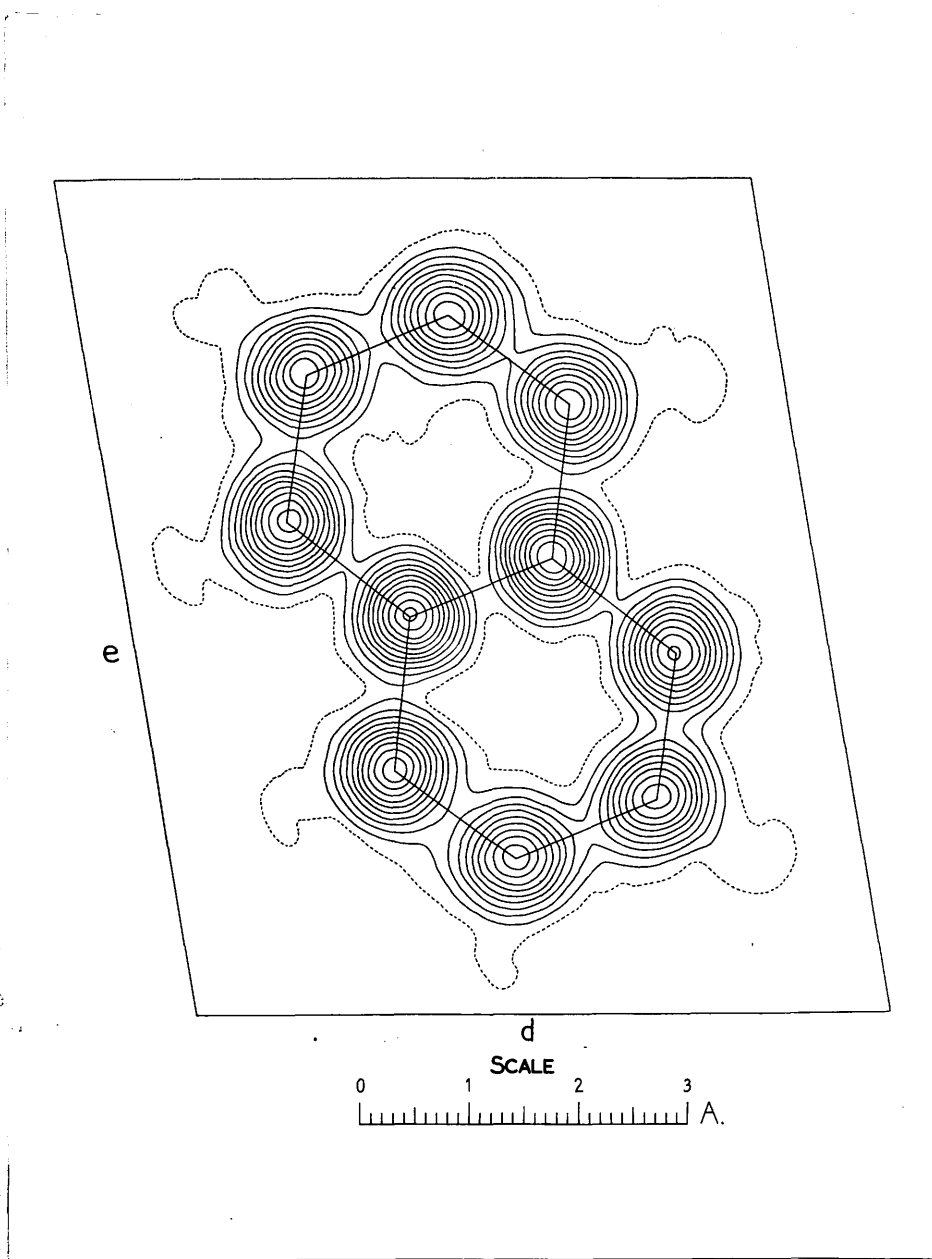


Figure 12

Electron density map of naphthalene on a plane parallel to the molecular plane and $1/4$ A. distant from it. Each contour line represents a density increment of $1/2 eA^{-3}$, the half electron line being dotted.

the positions of the carbon atoms when projected from the molecular plane on to this plane.

As the $1/4$ A. plane did not answer the question of bond shortening, it was decided to draw another parallel section at $1/2$ A. from the molecular plane. The procedure followed is identical α being this time 0.594 . At a distance of 0.5 A. away from the molecular plane the electron density at the carbon peaks is two to three electrons per A^3 . A section here might therefore be expected to be more sensitive to variations in the electron density. Figure 13 shows the result obtained. As before, a projection of the calculated positions of the carbon atoms in projection is shown superimposed. A third section through the molecule was also drawn. This section is at right angles to the molecular plane and through the two central carbon atoms (marked C-C' on figure 5, page 242 (22)). By reason of symmetry this plane also passes through the origin of the unit cell. The co-ordinates of the carbon atom C are,

$$(0.229, 0.611, 0.249)$$

these figures representing; x' A., y A., z' A.

The equation of the molecular plane is,

$$x' - 0.5265 y + 0.3689 z' = 0$$

with respect to rectangular axes.

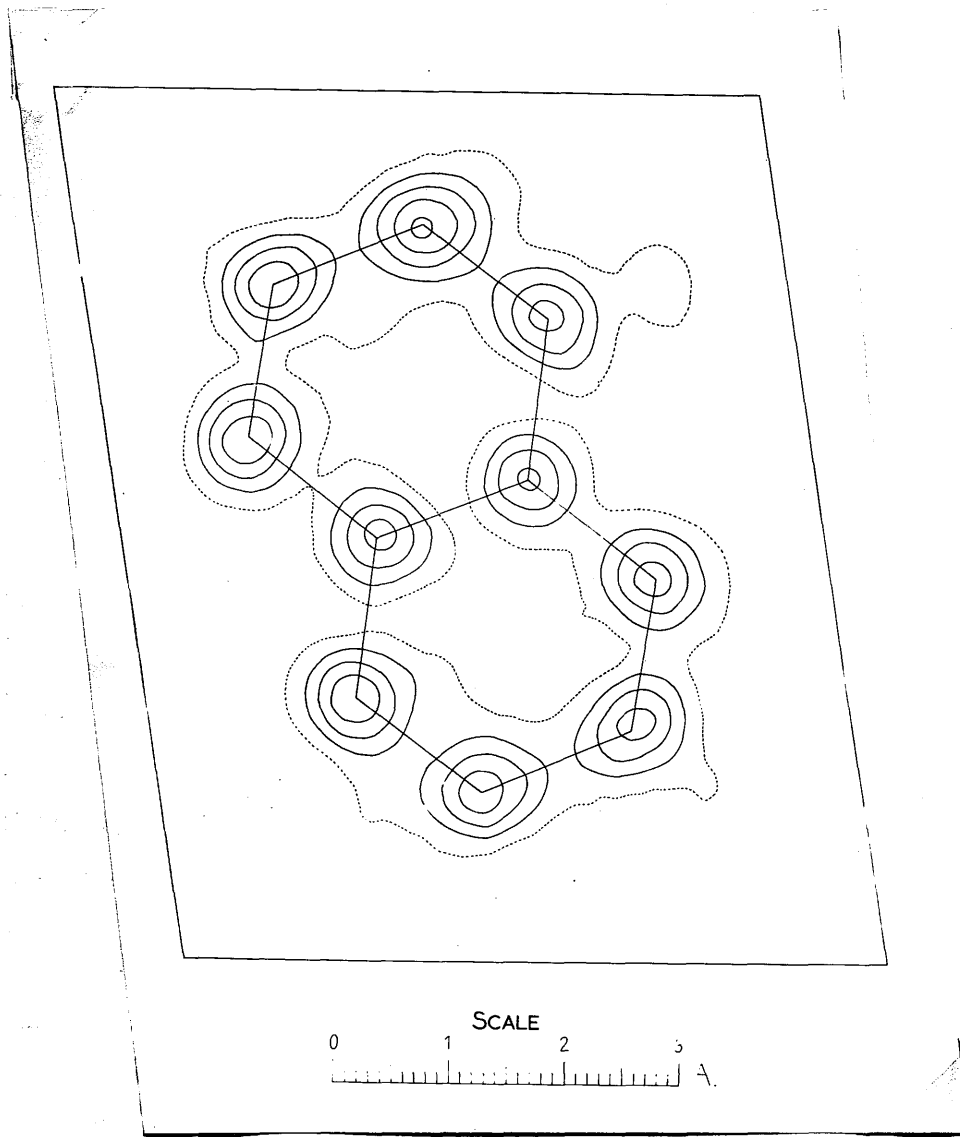


Figure 13

Electron density map of naphthalene on a plane parallel to the molecular plane and $1/2$ Å. distant from it. Each contour line represents a density increment of $1/2 eA^{-3}$, the half electron line being dotted.

To be at right angles the direction cosines of the two planes must fulfill the condition,

$$1 a' + (-0.527) b' + (0.369) c' = 0.$$

Therefore by solving the determinant,

$$\begin{vmatrix} x' & y & z' & 1 \\ 0 & 0 & 0 & 1 \\ 1 & (-0.527) & (0.369) & 1 \\ (0.229) & (0.611) & (0.249) & 1 \end{vmatrix} = 0$$

the required equation,

$$-0.3567 x' - 0.1645 y + 0.7317 z' = 0$$

is obtained. With respect to monoclinic axes and in terms of z it is,

$$\underline{z = 0.4415 x + 0.2035 y}$$

But the equation is required in terms of 60th of the axial lengths for interpolation,

$$\underline{z = 0.4200 x + 0.1410 y}$$

The required values were then obtained. In order to plot these, the intersection of this plane with the

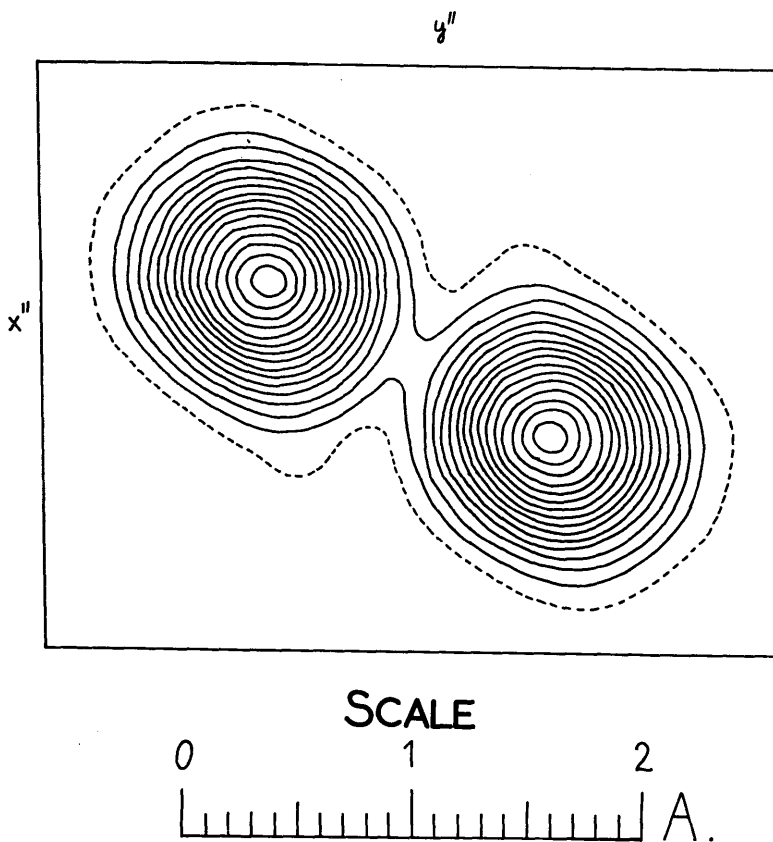


Figure 14

Electron density map of naphthalene on a plane perpendicular to the molecular plane and through the two central carbon atoms. Each contour line represents a density increment of $1/2 eA^{-3}$, the half electron line being dotted.

unit cell must first be calculated.

Let y'' be the line corresponding to \underline{d} , (figure 12)

Let x'' be the line corresponding to \underline{e} , "

Then, the equation of the plane is,

$$- 0.3567 x' - 0.1645 y + 0.7317 z' = 0$$

and y'' , the intersection of this plane with the
plane $\underline{y = 0}$ (rectangular axes)

$$y'' \hat{\circ} x = \tan^{-1} \frac{0.3567}{0.7317} = 26^\circ 0'$$

$$\begin{aligned} \text{The length of } y'' &= \frac{a \sin (180^\circ - \beta \text{ unit cell})}{\sin (\beta \text{ unit cell} - 26^\circ)} \\ &= \underline{6.96 \text{ \AA.}} \end{aligned}$$

Let x'' be the intersection of the plane with the
plane $\underline{x = 0}$

$$z = 0.4415 + 0.2035 y \text{ (monoclinic axes)}$$

$$\hat{x''_0 y} = \tan^{-1} 0.2035$$

$$= 11^\circ 30'$$

$$\begin{aligned} \text{the length of } x'' &= \frac{b}{\cos 11^\circ 30'} \\ &= \underline{\underline{6.126 \text{ A}}} \end{aligned}$$

Let θ be the angle between y'' and x'' .

direction cosines of y'' are;

$$\begin{aligned} \cos \alpha &= 90^\circ - \left\{ (180^\circ - \beta \text{ unit cell}) + 26^\circ \right\} \\ &= 6^\circ 55' \end{aligned}$$

$$\cos \beta = 90^\circ$$

$$\cos \gamma = 90^\circ + 6^\circ 55'$$

direction cosines of x'' are;

$$\cos \alpha = 90^\circ$$

$$\cos \beta = 11^\circ 30'$$

$$\cos \gamma = 90^\circ - 11^\circ 30'$$

$$\begin{aligned} \cos \theta &= \cos \gamma^{y''} \cdot \cos \beta^{x''} \\ &= -\sin 6^\circ 55' \cdot \sin 11^\circ 30' \end{aligned}$$

$$\underline{\underline{\theta = 91^\circ 24'}}$$

The values obtained by interpolation were then plotted in the usual way. Figure 14 shows the result obtained.

Discussion

In the section showing the molecular plane, figure 3 p. 241 (22) there are bumps in the half-electron line contour on the four carbon atoms of the asymmetric unit to which hydrogen atoms are attached. The approximate centres of these bumps are 1.1 A. from the centre of the carbon atom to which they are attached and therefore the bumps can be attributed to hydrogen atoms. In the section 1/4 A. from the molecular plane (figure 12) the bumps have changed considerably. Firstly, the symmetry has disappeared. Secondly, one of the bumps has disappeared and another one has made an appearance inside a benzene ring. This irregularity is maintained in the 1/2 A. section (figure 13). It may be concluded, that the half-electron contour line is very easily affected by irregularities.

The second result looked for is the foreshortening of certain carbon-carbon bonds. This cannot be observed in the case of the 1/4 A. plane, although the scale chosen was such that two points 0.02 A. apart can be readily distinguished. Figure 13 shows the 1/2 A. plane. As with the 1/4 A. plane each contour line represents an

increment of $1/2 eA^{-3}$, the half-electron line being dotted. The height of the peaks at a distance of 0.5 A. from their maximum is $2 eA^{-3}$, except atom A' (figure 5 p.242, (22)) which is $2.5 eA^{-3}$. On this plane also, foreshortening cannot be detected unambiguously. Figure 14 shows a section at right angles to the molecular plane and through the two central carbon atoms. The only noteworthy feature is the 'squashed' effect, the atomic radius at right angles to the molecular plane being 0.87 of the radius in the molecular plane.

Appendix 2A note on the crystal structure of fluoranthene.

Fluoranthene C₁₆H₁₀, a naturally occurring compound has been investigated by Daudel, Buu-Hoi et Mlle. Martin (24). These workers studied the resonance and activity of the molecule and concluded from their calculations based on the method of molecular mesomeric diagrams, that the positions 4 and 5 are the most reactive. Experimental evidence confirms this conclusion. It was decided to investigate this compound by X-ray analysis to see what further information can be obtained.

The crystals employed were isolated from coal tar by Dr. Schönthal of this department. The crystals which are of a pale yellow colour, crystallise in needles and plates from alcohol. Most of the crystals obtained were twinned. Fittig (1878) found fluoranthene to be monoclinic with the following axial ratios.

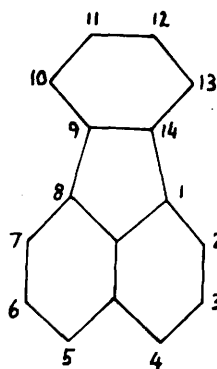
$$a : b : c = 1.495 : 1 : 1.025, \beta = 82^{\circ}50'$$

These are not the axial ratios of the primitive unit cell.

Crystal data

Fluoranthene $C_{16}H_{10}$

F.W. 202 m.p. 109° C.



Monoclinic: $\underline{a} = 18.48 \pm 0.02$ A., $\underline{b} = 6.27 \pm 0.01$ A.,
 $\underline{c} = 20.03 \pm 0.03$ A., $\beta = 110.2^\circ \pm 0.5^\circ$

Absent spectra: (0k0) when k is odd
 (h0l) when h + l is odd
 (hkl) present in all orders.

Space group: $P 2_1/n$

d. calc. 1.233 d. obs. (by flotation) 1.252

Eight molecules per unit cell

Molecular symmetry required: none

Volume of unit cell 2176.7 \AA^3

Total number of electrons per unit cell = $F(000) = 848$.

The most striking feature is the presence of two molecules per asymmetric unit, indicating the presence of two crystallographically non-equivalent types of molecule (Bunn (25)).

Experimental

All the X-ray work was carried out using copper-K α Ni filtered radiation and using photographic methods. Rotation, oscillation and moving films were taken about the three principal zones and the intensities determined in two zones, using the multiple film technique (9).

No features were observed, which could have assisted in the solving of the crystal structure.

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