

The Crystal and Molecular Structure
of
Pentacene and Hexacene (Part I)
and of
Some Derivatives of Tropolone (Part II)

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Doctor of Philosophy

at

The University of Glasgow

by

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Summary

Chapter I

Introduction

The Crystal

Preface

This thesis describes research in chemical crystallography which was carried out during a three year period in the Chemistry Department of the University of Glasgow. It is expected that the work will be published.

It is a pleasure to express my sincere thanks to Professor J. Monteath Robertson for suggesting the problems for study and for his continued interest and guidance.

To the Department of Scientific and Industrial Research I owe thanks for a Maintenance Allowance.

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Summary

The crystal structures of the polycyclic aromatic hydrocarbons pentacene and hexacene have been determined by X-ray analysis. Pentacene is triclinic, space-group $P_{\bar{1}}$, with two centro-symmetric molecules per unit cell. The molecular arrangement is similar to that in tetracene and to that in monoclinic anthracene. Although 19 carbon atoms out of 22 in the asymmetric unit are resolved in the (Okl) projection attempts to refine the structure by two-dimensional Fourier series methods have failed. Hexacene is also triclinic, space-group $P_{\bar{1}}$, with two molecules per unit cell. The crystal structures of the hydrocarbons are closely similar to each other and to those of the preceding members of the homologous series.

A two-dimensional analysis of α -monobromotropolone has been carried out. α -Monobromotropolone is orthorhombic, space-group $P2_12_12_1$, with four molecules per unit cell. A Patterson analysis determined the positions of the four bromine atoms in the (hk0) projection. This was followed by two-dimensional Fourier syntheses and in the final projection all the atoms are clearly resolved. Bond lengths have not been worked out because the tropolone ring appears to deviate slightly from a planar heptagon. This deviation may be due to a steric effect of the large

bromine atom or the deviation may be a spurious effect resulting from the effect of the heavy bromine atom on the measured intensities. An approach distance of length 3.05 Å. occurs between oxygen atoms of two different molecules and might provide a basis for identifying these oxygens as hydroxyl oxygens.

An analysis of cupric nootkatin has been accomplished, also in two dimensions only, by making use of the phase-determining power of the copper atom. Cupric nootkatin is monoclinic, space-group $P2_1/a$, with two centro-symmetric molecules of the co-ordination complex per unit cell. In the final projection, made by the usual Fourier series method, only 6 carbon atoms out of the 15 carbon atoms and 2 oxygen atoms in the asymmetric unit are resolved. It has proved possible, however, to elucidate the unknown aspects of the chemical structure of nootkatin viz. the points of attachment of the two side chains to the tropolone ring. Nootkatin would appear to be

β -isopropyl γ -(3-methyl but-2-enyl) tropolone.

Preliminary investigations of the crystal structures of tropolone, tropolone hydrobromide, and ferric tropolone have been made. Tropolone is monoclinic, space-group $P2_1/a$, with four molecules per unit cell. Tropolone hydrobromide is monoclinic, space-group $P2_1/a$, with eight molecules per unit cell. The positions of the bromine atoms in the

(hk0) projection have been determined, somewhat approximately because of overlap of the two bromine atoms in the asymmetric unit, by Patterson analysis. Ferric tropolone is monoclinic, space-group Cc, with four molecules of the co-ordination complex per unit cell.

For a number of years now, the X-ray diffraction method has been used for the determination of the structure of crystalline solids. The method is based on the fact that the atoms in a crystal are packed in a regular array and the diffraction pattern is governed by a large number of independent parameters these can be refined and accurately determined by the use of Fourier series methods. With the determination of reliable values for single, double, and triple carbon-carbon bond lengths it became clear that the links in aromatic molecules are of a length intermediate between the pure single and the pure double bond lengths.

Recent three-dimensional surveys, by the X-ray diffraction method, of naphthalene (1) and anthracene (2) have shown that the carbon-carbon bond lengths in these molecules are of a length intermediate between the pure single and the pure double bond lengths. This is in agreement with the results of the present survey.

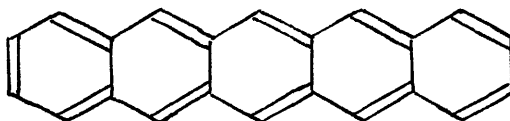
Part I

Introduction

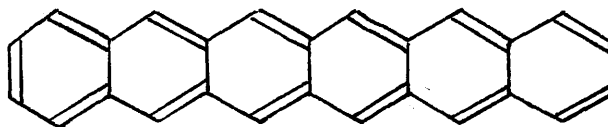
Many methods are now available for the precise measurement of bond lengths in molecules. Calculations based on spectroscopic data yield the most accurate results for simple types of molecule, but diffraction methods have a much greater range of application. For the more complex types of structure crystal diffraction methods are perhaps the most suitable, because even when the structure is governed by a large number of independent parameters these can be refined and accurately determined by successive applications of Fourier series methods. With the determination of reliable values for single, double, and triple carbon-carbon bond lengths it became clear that the links in aromatic molecules are of a length intermediate between the pure single and the pure double bond lengths.

Recent three-dimensional surveys, by the X-ray diffraction method, of naphthalene (1) and anthracene (2) indicated small variations in carbon-carbon bond lengths in different parts of the molecules. These variations are in qualitative agreement with calculations of the bond lengths from the non-excited valency bond structures alone. However, while it is interesting to study the measure of

agreement obtained by the comparison, it is not to be expected that the Kekule structures by themselves make a major contribution to the normal state of the larger aromatic molecules. Pentacene and hexacene, described in part I of this thesis, are of interest as members of the naphthalene-anthracene series of linear aromatic hydrocarbons (see Fig. 1).



pentacene



hexacene

Fig. 1.

Hexacene is the highest member of the series to have been isolated. The stability decreases and ease of oxidation increases as the number of benzene rings linearly condensed increases.

Although complete and accurate data can be obtained only from a full three-dimensional analysis, some interesting variations in carbon-carbon bond lengths in aromatic hydrocarbons have been observed as the result of two-dimensional investigations. Often there is obtained

for each structure only one really useful projection, which can be refined by Fourier series methods. The procedure then is to assume that the molecule has a strictly planar form and to deduce its orientation in the crystal. The most probable centres for all the atoms are then decided and the bond lengths worked out with due allowance for the orientation. If there should be any substantial departure from planarity the results will be in error, but the assumption of a planar form is tested by the agreements obtained between calculated and observed structure factors in other zones. It was hoped in this investigation of the hydrocarbons to detect bond-length variations by two-dimensional methods, or to refine the atomic parameters to a point where three-dimensional analysis might be undertaken. The progress of the investigation has been very much limited by the nature of the crystal specimens available.

The Crystal Structure of Pentacene

Crystal Data.

Pentacene, $C_{22}H_{14}$; M, 278.2; d, calc. 1.345, found 1.333.

Triclinic, a = 7.90 A. b = 6.06 A. c = 15.95 A.

$\alpha = 101.3^\circ$ $\beta = 111.8^\circ$ $\gamma = 94.4^\circ$

$a^* = 0.2128$ $b^* = 0.2625$ $c^* = 0.1072$

$\alpha^* = 76.0^\circ$ $\beta^* = 66.7^\circ$

Absent spectra, none. Space-group, $P\bar{1}$. Two molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell = 686.4 A.³. Absorption coefficient for X rays ($\lambda = 1.54$ A.) $\mu = 6.97$ per centimetre⁻¹. Total number of electrons per unit cell = $F(000) = 292$.

Experimental Measurements.

A plate-like crystal, on which the (001) face only is developed, was employed. The crystal was obtained, by Dr. E. Clar, by crystallisation from trichlorobenzene. Attempts to secure more suitable crystals by recrystallisation in an atmosphere of pure carbon dioxide from the solvent trichlorobenzene were unsuccessful. The density was determined by flotation in a solution of potassium iodide. The value obtained, 1.333, is in good agreement with the value, 1.345, calculated for a unit cell containing two molecules.

All the X-ray work was carried out with copper-K α

radiation ($\lambda = 1.54 \text{ \AA}$). Rotation and oscillation photographs were taken about the axes and diagonals. Moving-film photographs were taken of the a and b axis zero-layer lines. The absence of systematic absences led to the space-groups $P_{\bar{1}}$ or P_1 . In pentacene although (101) and (301) spectra are present, they are extremely weak in comparison with (201) planes. This pseudo-monoclinic symmetry suggests use of the centre of symmetry which the pentacene molecule possesses leading to the space-group $P_{\bar{1}}$, thus giving the greatest possible similarity to naphthalene and anthracene. Intensity measurements were carried out on the (Okl) zone and on the (h0l) zone, the integrated intensities being obtained by careful visual measurement. The multiple-film technique (3) was used to obtain correlation between very strong and very weak reflections. Eighteen-hour exposures produced an intensity range of 1000 to 1 in the (Okl) zone and of 3000 to 1 in the (h0l) zone. 62 reflections were recorded out of a possible 236 in the (Okl) zone (26.3%), and 71 reflections out of a possible 310 in the (h0l) zone (22.9%). The crystal employed had a cross-section normal to the a axis of 0.53 mm. by an immeasurable thickness, and normal to the b axis the crystal had a cross-section of 1.06 mm. by an immeasurable thickness. Due to the extreme thinness of the crystal the mean path through the specimen

was almost constant for all planes, and no relative-absorption corrections were applied. Measured values of F were calculated from the intensities using the usual formulae for mosaic-type crystals. The scale of the measured F values was obtained by correlation with the structure factors calculated from the atomic positions.

The Fourier summations were carried out by the 5-figure strip and stencil method (4). For the projection along the a axis on a plane normal to the a axis, the electron density was computed at 900 points on the asymmetric unit, the axial subdivisions being $b \sin \gamma / 30 = 0.201$ A. and $c \sin \beta / 60 = 0.247$ A.. The positions of the contour lines were obtained by graphical interpolation from the summation totals, by making sections of both the rows and the columns. In the structure factor calculations the atomic f -curve for carbon used in the three-dimensional investigation of anthracene (2) was used.

Analysis of the Structure.

A comparison of moving-film photographs of pentacene and tetracene showed a marked similarity in the intensities of corresponding reflections. Two of the strongest planes observed in tetracene were the (200) and the ($20\bar{1}$) and this was also the case in pentacene. Also the relative

values of the intensities along the c axis showed a close relation in the two compounds.

Another clue to the molecular arrangement is provided by the characteristic appearance of the c axis rotation photograph (see Fig. 2) and by comparison with naphthalene and anthracene and tetracene. In pentacene there is a tendency for the sixth and seventh layer line ($l = 6$ and $l = 7$) to be enhanced. In naphthalene the third and fourth layer line ($l = 3$ and $l = 4$), in anthracene the fourth and fifth layer line ($l = 4$ and $l = 5$), and in tetracene the fifth and sixth layer line ($l = 5$ and $l = 6$) are enhanced. It may be inferred that the arrangement of the benzene rings in these crystals is such that the periodicities indicated in Fig. 3 coincide at least approximately with the direction of the c axis in each case.

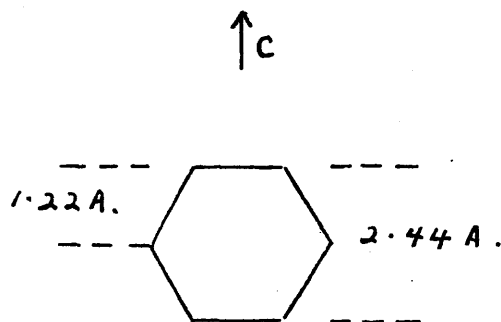


Fig. 3.

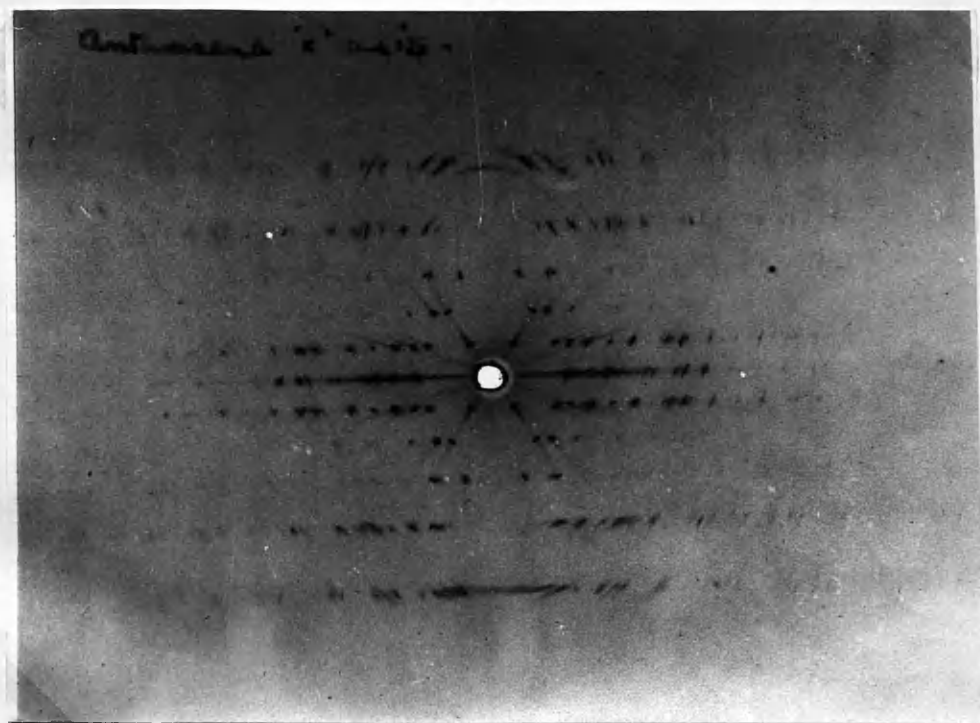
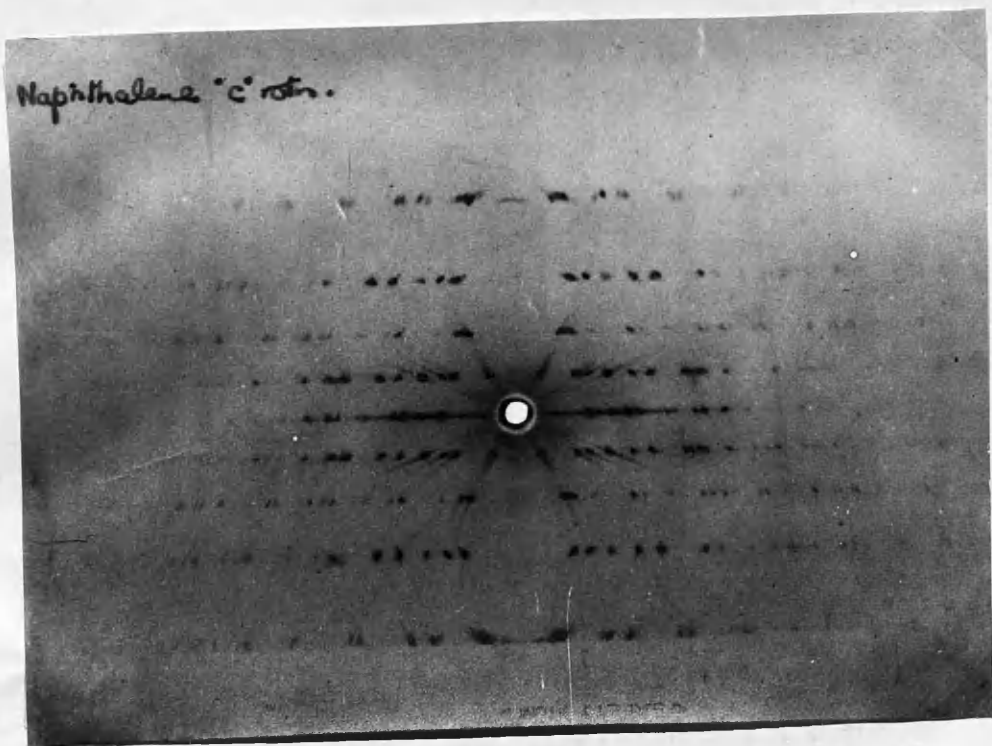


Fig. 2.

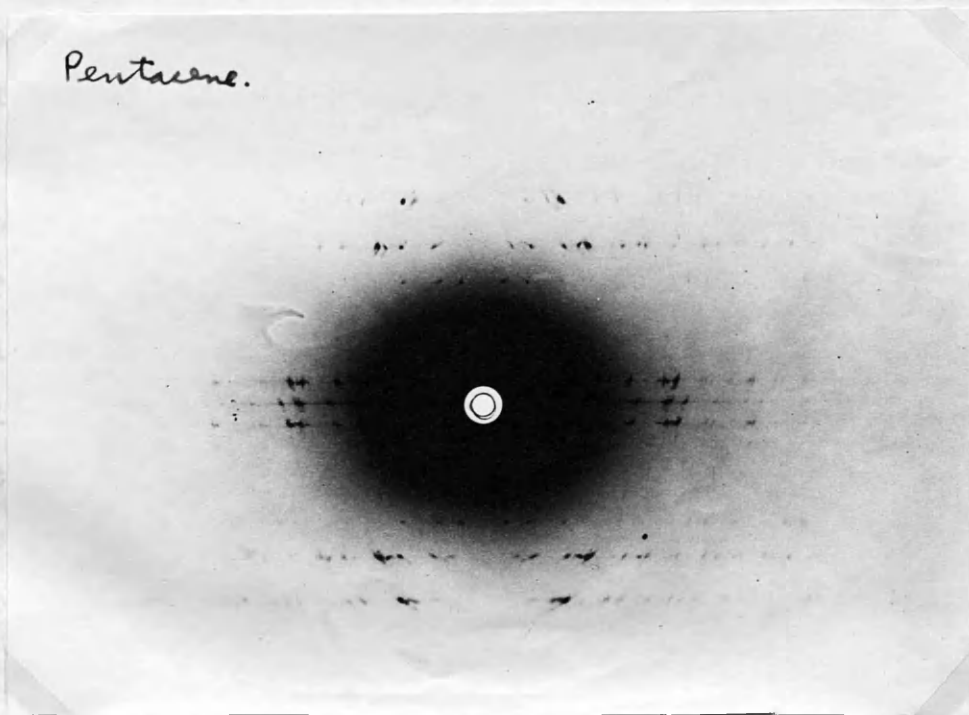
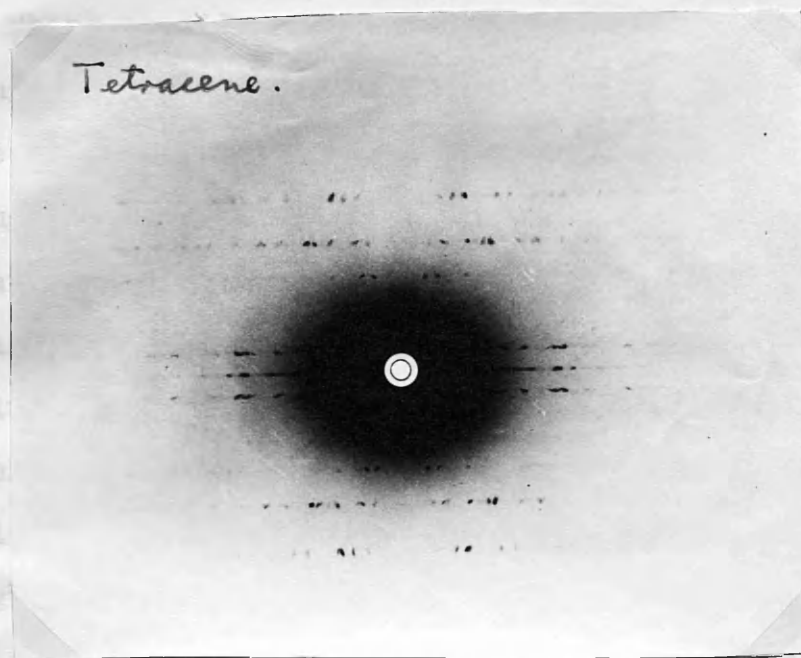


Fig. 2.

These considerations suggested that the structure given by the projection along the b axis would be similar to tetracene. A trial structure was therefore set up having the same molecular orientations as in tetracene (5). The average discrepancy, obtained by dividing the sum of the individual discrepancies by the total of the measured F values, was 28.4% and a Fourier synthesis was carried out, 51 terms being included representing measured values of the ($h0l$) structure factors. The resulting contour map did not give sharp definition of many atomic positions.

Attention was directed to the projection along the a axis, a projection which would be more sensitive to small variations in the tilt of the molecules from the (010) plane. An inspection of the moving-film photograph of the ($0kl$) zone of pentacene indicated that for the small-spacing planes (047), ($02\bar{6}$), and ($06\bar{5}$), the contributions of many of the atoms must be in phase. Two of the strong planes observed in tetracene were the (020) and (021) planes and this was also the case in pentacene. A trial structure was set up having the same molecular orientations as in tetracene. The average discrepancy was 30.0% and a Fourier synthesis was carried out, 56 terms being included representing measured values of the ($0kl$) structure factors. Fig. 4 shows the contour map obtained and an

explanatory diagram is shown in Fig. 5. The map extends over the whole unit cell, twice the asymmetric unit, and covers two molecules of pentacene. The molecules overlap slightly in projection but in space the second molecule is situated half a translation along the a axis from the first one. Of the 22 atoms comprising the asymmetric unit the 12 forming the inner pairs are fairly well resolved, but the exact positions of the others are obscured by the overlap. On recalculating the structure factors using atomic positions indicated by small crosses in Fig. 4 the average discrepancy from the measured value was found to be 31.3%.

Orientation and Co-ordinates.

The orientation of the molecules is most conveniently referred to an orthogonal system of axes. For this purpose arbitrary axes were chosen consisting of the b crystal axis, the projected a axis, asin γ , and another axis c perpendicular to b and to asin γ . The orientation of the molecules with respect to these three axes is given in Table 1. The long axis of the molecule is denoted by L, the short cross axis by M, and the axis at right-angles to both of these by N. The angles between these molecular axes and the orthogonal axes are shown as χ_L, ψ_L, ω_L , etc.. The angles which the triclinic crystal axes make

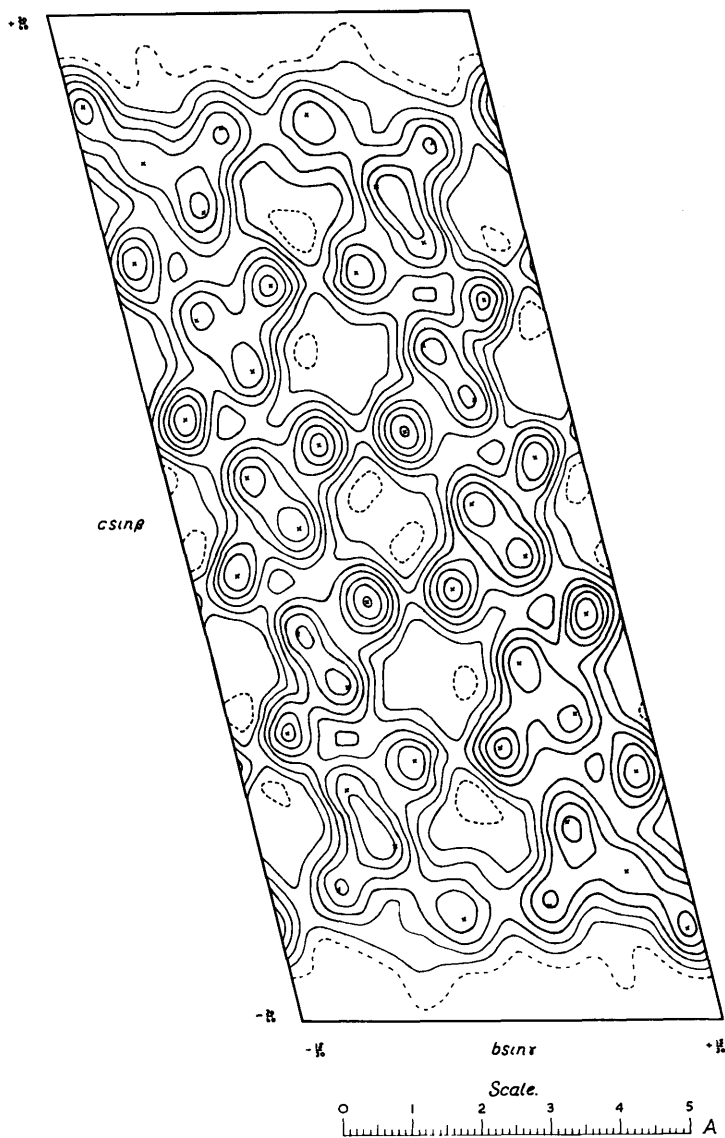


Fig. 4. Electron-density projection along the a axis on (100) covering two molecules of pentacene. Contour scale one electron per \AA^2 per line, the one-electron line being dotted.

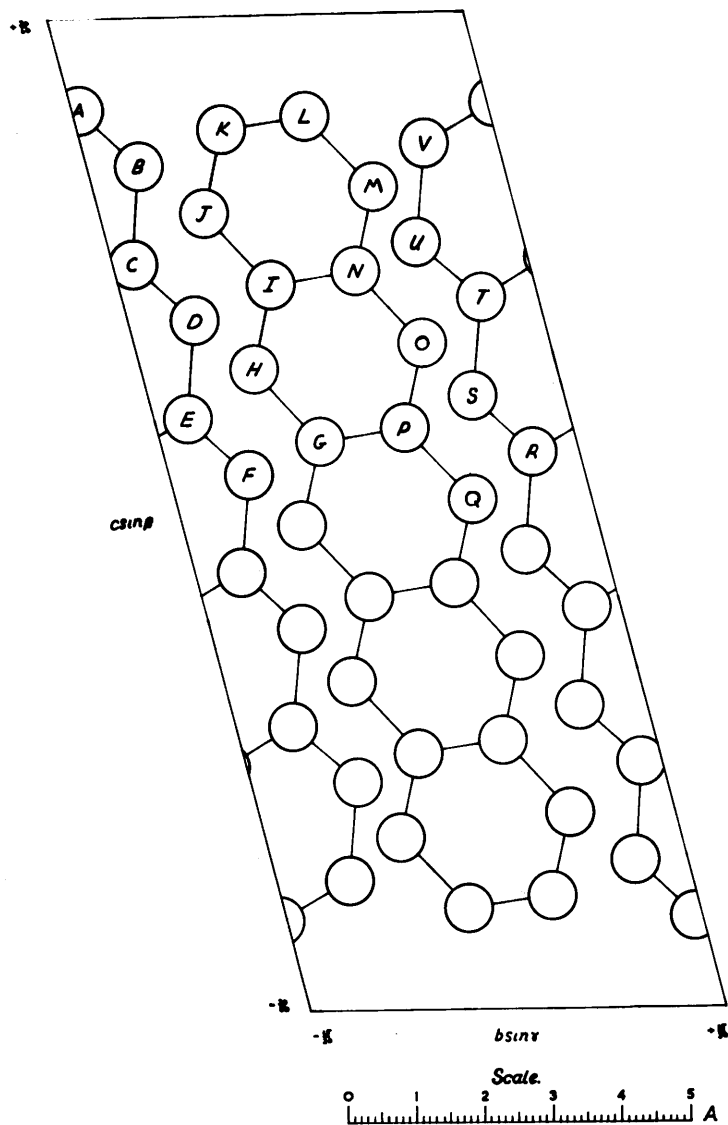


Fig. 5. Projection along the a axis on (100) covering two molecules of pentacene and showing the arrangement of the molecules.

with the orthogonal reference axes are shown in Table 2.

Co-ordinates in harmony with planar molecules composed of regular hexagons with a carbon-carbon distance of 1.40 A. and orientated as in tetracene are shown in Table 3. The origin is chosen at the centre of symmetry and the co-ordinates are expressed as fractions of the triclinic axial lengths in degrees. Only the atoms of the asymmetric crystal unit (halves of two chemical molecules) are listed, the co-ordinates of the other atoms in the unit cell being obtained from the relations applicable to the space-group $P_{\bar{1}}$.

Discussion.

The failure of attempts to refine the atomic positions in pentacene can be attributed to the unsuitable nature of the crystal specimen employed and to the consequent unreliability of the intensity measurements.

The most interesting feature of this investigation is the close similarity of pentacene to the preceding hydrocarbons of the homologous series, namely, tetracene, anthracene, and naphthalene. The general arrangement of the molecules in the unit cell is very like that of tetracene and anthracene. It is surprising that the crystal system should change from monoclinic to triclinic in passing from anthracene to tetracene. The crystal structure

Table 1. Orientation of the molecules in the crystal. Centre of symmetry as origin.

Orientation of the molecules in the crystal.

Molecule I.	Molecule II.
$\chi_L = 104.8^\circ$	$\chi_L = 105.3^\circ$
$\psi_L = 107.0$	$\psi_L = 99.3$
$\omega_L = 22.9$	$\omega_L = 18.0$
$\chi_M = 70.1$	$\chi_M = 116.3$
$\psi_M = 30.2$	$\psi_M = 27.0$
$\omega_M = 68.2$	$\omega_M = 84.6$
$\chi_N = 25.3$	$\chi_N = 30.2$
$\psi_N = 114.2$	$\psi_N = 66.6$
$\omega_N = 83.1$	$\omega_N = 72.1$

Table 2.

Orientation of the triclinic crystal axes.

$\chi_a = 4.4^\circ$	$\chi_b = 90.0^\circ$	$\chi_c = 67.2^\circ$
$\psi_a = 94.4$	$\psi_b = 0.0$	$\psi_c = 101.3$
$\omega_a = 90.0$	$\omega_b = 90.0$	$\omega_c = 25.7$

Table 3.

Co-ordinates referred to the crystal axes. Centre of symmetry as origin.

Atom (cf. Fig. 5)	$2\pi x/a$	$2\pi y/b$	$2\pi z/c$
G	21.5°	- 39.7°	27.3°
H	42.3	- 79.5	54.2
I	37.1	- 45.2	84.9
J	58.5	- 84.9	111.9
K	53.1	- 50.6	142.7
L	26.7	23.5	146.2
M	5.8	63.2	118.6
N	10.7	28.9	88.3
O	- 10.2	68.6	61.1
P	- 5.0	34.3	30.7
Q	- 27.0	74.0	3.4
R	172.0	139.3	21.3
S	163.2	98.6	43.0
T	-172.6	126.7	77.7
U	177.5	85.8	98.6
V	-157.6	114.0	133.4
A	-124.7	-177.3	146.4
B	-115.8	-136.6	124.9
C	-140.0	-164.6	90.6
D	-131.1	-123.9	69.1
E	-155.3	-151.9	34.6
F	-146.9	-111.2	13.3

of an aromatic hydrocarbon is determined by the shape of the molecules, and the arrangement which gives the closest packing will be the one normally adopted. A comparison of the closest approach distances between the molecules in pentacene and tetracene and anthracene should therefore provide an explanation of the change of symmetry.

A similar phenomenon was encountered in

hexamethylbenzene (7). In this compound the (001) plane approaches very closely to hexagonal symmetry, $a = 8.92 \text{ \AA.}$, $b = 8.85 \text{ \AA.}$, $\gamma = 119^{\circ}34'$, but it was shown that the slight deviation resulted in a very much closer packing of the molecules in the crystal lattice and an increase in density of 9%. The slight departure from monoclinic symmetry in pentacene and tetracene will probably have a similar explanation.

A noticeable feature of the contour map (Fig. 4) is that there is a slight falling off in the peak values of the electron density on the individual atoms as we pass outward from the centres of the molecules. This corresponds to the effect found in the three-dimensional investigation of anthracene (2). The effect was also detectable in anthracene by a two-dimensional structure determination (6). As has been suggested in the case of anthracene this feature may be due to thermal vibration. If the molecules are oscillating about their centres the effect would be most marked on the outlying atoms.

The Crystal Structure of Hexacene

Crystal Data.

Hexacene, $C_{26}H_{16}$; M, 328.4; d, calc. 1.332.

Triclinic,	a = 7.96 A.	b = 6.16 A.	c = 18.10 A.
	$\alpha = 97.8^\circ$	$\beta = 110.0^\circ$	$\gamma = 95.3^\circ$
	a* = 0.2028	b* = 0.2551	c* = 0.0918
	$\alpha^* = 79.6^\circ$	$\beta^* = 69.9^\circ$	$\gamma^* = 81.5^\circ$

Absent spectra, none. Space-group, $P\bar{1}$. Two molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell = 818.3 A.³. Total number of electrons per unit cell = $F(000) = 344$.

Experimental Measurements.

A plate-like crystal, on which the (001) face only is developed, was employed. The crystal was obtained, by Dr. E. Clar, by sublimation in a stream of pure carbon dioxide. Attempts to secure more suitable crystals by recrystallisation in an atmosphere of pure carbon dioxide from the solvent trichlorobenzene were unsuccessful.

Retention of air bubbles by the small, awkwardly-shaped crystals has made an accurate density determination, by the usual flotation method, difficult. A value of 1.29 obtained using potassium iodide solution, indicated that the unit cell contained two molecules, the calculated value for two molecules per unit cell being 1.332.

All the X-ray work was carried out with copper-K α radiation ($\lambda = 1.54 \text{ \AA}$). Rotation and oscillation photographs were taken about the a and b axes and about the ($1\bar{1}0$) diagonal. Moving-film photographs were taken of the a and b axis zero-layer lines. The absence of systematic absences led to the space-groups $P_{\bar{1}}$ or P_1 . The pseudo-monoclinic symmetry observed suggests, as in pentacene and tetracene, use of the centre of symmetry in the molecule and the space-group $P_{\bar{1}}$, thus giving the greatest possible similarity to naphthalene and anthracene.

The values for c, α and β , and V, quoted for hexacene were obtained by first evaluating parameters for the reciprocal cell from measurements made on the moving-film photographs of the a and b axis zero-layer lines. A rock-salt powder specimen was used to calibrate the photographs. Parameters for the direct cell were then calculated with the aid of the usual transformations. V calculated from the equation $V = abc \sin \gamma / c^*$ amounted to 819.3 \AA^3 . V calculated from the equation,

$$V = abc (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}$$

amounted to 817.2 \AA^3 . The unit cell dimensions tabulated for hexacene are probably accurate only to about one per cent., not because of the method of derivation but because of the unsuitable nature of the crystal specimen.

employed.

It was thought that hexacene and pentacene as long-spacing compounds, that is with c suitably greater in length than a or b , and as members of a homologous series, might lend themselves to deduction of their unit cells from powder photographs (8). A number of powder photographs were taken but were found to be quite unsuitable for the purpose intended. No lines were obtained in the most accurate region, $2\sin\theta > 1$, which could be identified, and the reflections given by planes of smaller $2\sin\theta$ value were rather diffuse due to thermal vibration which made precise measurement difficult. The powder photographs confirmed the similarity in structure between pentacene and hexacene, but were worthless as a means of obtaining accurate cell dimensions.

Analysis of the Structure.

A comparison of moving-film photographs of hexacene and pentacene showed a marked similarity in the intensities of corresponding reflections. Two of the strongest planes observed in pentacene were the (200) and the (20 $\bar{1}$) planes and this was also the case in hexacene. Also the relative values of the intensities along the c axis showed a close relation in the two compounds. An inspection of

the moving-film photograph of the (0k1) zone of hexacene indicated that for the small-spacing planes (048) and (02 $\bar{7}$) the contributions of many of the atoms must be in phase. Two of the strong planes observed in pentacene were the (020) and the (021) planes and this was also the case in hexacene. It may be inferred that the orientations of the molecules in hexacene are very similar to those in pentacene and tetracene.

Discussion and a comparison of hexacene, pentacene, tetracene, anthracene, and naphthalene.

The most interesting feature of this investigation is the close similarity of hexacene to the preceding hydrocarbons of the homologous series. The general arrangement of the molecules in the unit cell must be very like that in pentacene and tetracene. In Table 4 a comparison is made of unit-cell dimensions in naphthalene, anthracene, tetracene, pentacene, and hexacene.

Table 4.

	a	b	c	β
naphthalene	8.24 A.	6.00 A.	8.66 A.	122.9°
anthracene	8.56	6.04	11.16	124.7
tetracene	7.98	6.14	13.57	112.4
pentacene	7.90	6.06	15.95	111.8
hexacene	7.96	6.16	18.10	110.0

To make this comparison possible the usual convention in naming the axes of triclinic crystals has not been employed.

The a axis shows a slight variation in passing from anthracene to tetracene, due to a slightly different tilt of the molecules. The b axis remains practically constant in the five compounds. The c axis increases by 2.5 A. in going from naphthalene to anthracene, by 2.4 A. in going from anthracene to tetracene, by 2.4 A. in going from tetracene to pentacene, and by 2.2 A. in going from pentacene to hexacene. This indicates that the long axis of the molecules lies close to the c axis and the increase in length is due to the increase in longitudinal extension of the ring systems. The similarity is further revealed by the fact that in the higher members of the series the α and γ angles do not deviate greatly from right angles. It is apparent that the arrangement of the molecules in the crystal lattices of the higher members must be closely analogous to the arrangement in the anthracene lattice without, however, maintaining the monoclinic symmetry.

In anthracene the arrangement of the molecules in the projection along the c axis is as shown in Fig. 6. Molecule I is reproduced at the centre of the unit cell by virtue of the a glide plane. This symmetry gives rise to halvings in the (h0l) zone, (h0l) reflections

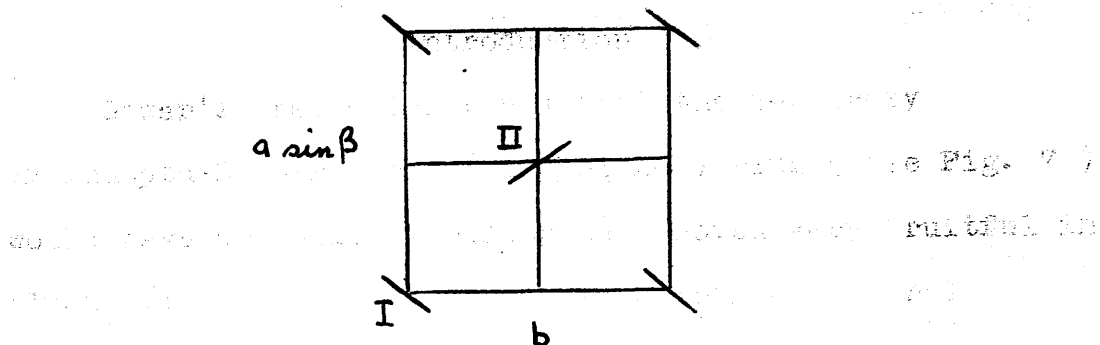


Fig. 6.

Arrangement of molecules in anthracene c axis projection.

absent when h is odd. In the higher members of the series although (101) and (301) spectra are present they are extremely weak in comparison with (201) planes. This suggests that although the central molecule in the case of the higher members is not related by any symmetry elements to molecule I, it lies very close to such a position. If we assume that the centre of symmetry in the molecule is used by the higher-member molecules and if we place it at the origin and centre in Fig. 6, we have an arrangement in the unit cell giving the greatest possible similarity to naphthalene and anthracene. This is the P_{-1} space-group with pseudo-monoclinic symmetry.

Part II

Introduction

Dewar's prediction (9) that the 2-hydroxy cyclohepta-2:4-trienone (tropolone) ring (see Fig. 7) would have aromatic stability has proved very fruitful in elucidating the structures of a variety of natural products (10).

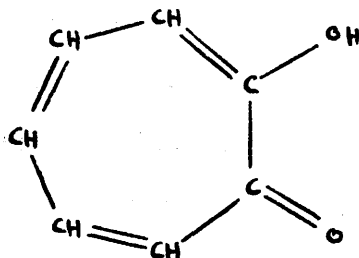


Fig. 7. Tropolone.

Stipitatic acid, puberulic acid, α -, β -, and γ -thujaplicin and purpurogallin have been shown to be derivatives of tropolone. The number of biochemically important compounds found to contain the tropolone ring is increasing, and the behaviour of these compounds appears to depend greatly on the behaviour of the tropolone ring. The chemistry of tropolone and of some of its derivatives has been described by Cook and his collaborators (11), and the aromatic stability of the tropolone ring has been fully confirmed.

A point of fundamental interest which cannot be completely solved by organic-chemical methods concerns the fine structure of the tropolone ring. The infra-red absorption of tropolone in dilute solution has been investigated by Koch (12). Inspection of the O-H region indicated strong intramolecular association of the hydroxyl group involving hydrogen bonding with the neighbouring carbonyl oxygen. An estimate of not more than 1.10 A. for the O-H bond precluded anything like a symmetrical equilibrium position of a proton between the two oxygen atoms in the structure. The possibility of electronic resonance degeneracy involving two equivalent bonds between a proton and the two oxygen atoms (see Fig. 8)

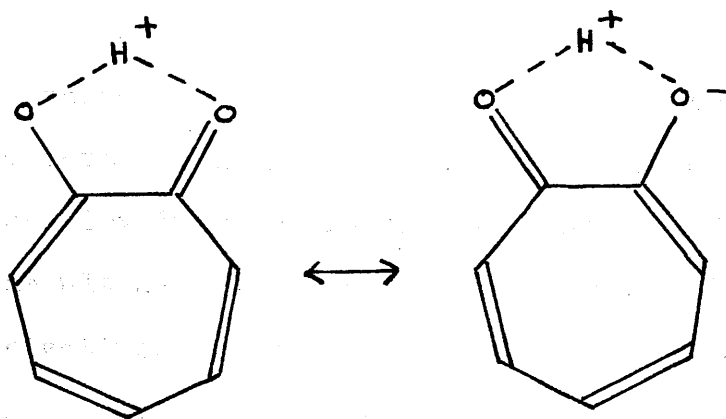


Fig. 8.

was therefore ruled out. The strength of the hydrogen

bonding was explained by postulating resonance involving a planar ring of smeared-out alternate single and double bonds (see Fig. 9).

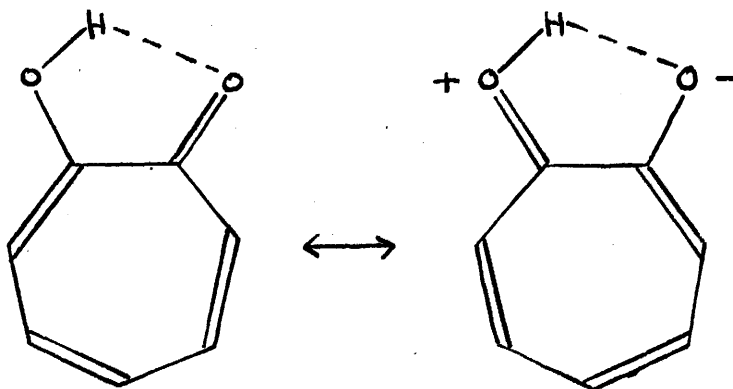


Fig. 9.

It was postulated also that the hydroxylic-hydrogen atom of tropolone might be expected to be symmetrically located on a time average basis between the two oxygens, which will thus become chemically equivalent. The final infra-red spectroscopic picture of the structure of tropolone may be formulated as in Fig. 10, I and II to be regarded as tautomers involving rapid interchange.

The ultra-violet absorption spectra of tropolone and its derivatives are consistent with the above concept of the fine structure (11). The close similarity between the ultra-violet absorption curves of tropolone and its methyl ether would appear to tell against any formulation

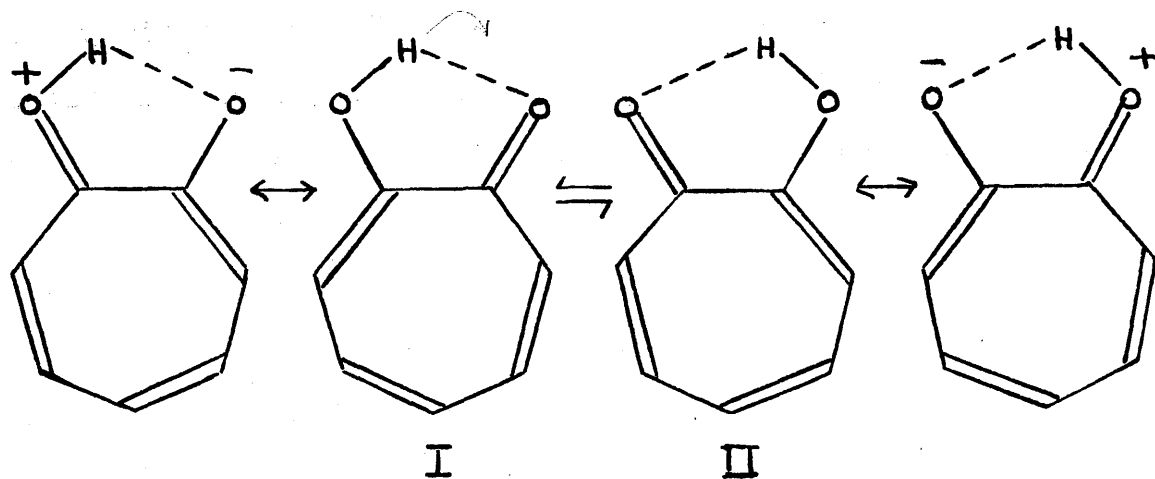


Fig. 10.

of tropolone as a true resonance hybrid. The ultra-violet absorption curve of the yellow tropolone anion, that is of tropolone in sodium hydroxide solution, indicates a radical change of structure in the ion, which may be attributed to its existence as a 'benzenoid' resonance hybrid. It has been suggested that the rather high latent heat of sublimation of tropolone may be due to intermolecular hydrogen bonding, giving rise to a structure analogous to the hydrogen-bond dimers of carboxylic acids.

It is obviously desirable to measure the spatial positions of the atoms in fundamental tropolones as precisely as possible. The most feasible way of doing this with certainty for structures of this degree of complexity is by means of the X-ray crystallographic method.

J. M. Robertson has carried out a two-dimensional analysis

of cupric tropolone, making use of the phase-determining power of the copper atom (13). The tropolone ring appears to be an almost regular planar heptagon with an average carbon-carbon distance of 1.40 A., indicating strong aromatic character. It is possible to differentiate the oxygen atoms as carbonyl and hydroxyl. Inspection of tropolone formulae will show that the bond between the oxygen-bearing carbons, the 1:2 bond, is not essential to the conjugation. It is always represented as a single bond. Robertson's work shows that the 1:2 bond is not a long bond devoid of double bond character as is implied in the chemical formulae for tropolone, but that it appears to be indistinguishable from the other bonds in the ring.

Part II of this thesis describes results obtained by the X-ray crystallographic method for α -monobromotropolone and for cupric nootkatin. Preliminary investigations of tropolone, tropolone hydrobromide, and ferric tropolone are also recorded. Nootkatin is not a fundamental tropolone. Characteristic ultra-violet absorption has been utilised to establish its tropolone structure (14). Its investigation has been undertaken to determine the orientation of an isopropyl and a 2-methyl but-2-enyl side chain attached to the tropolone ring. The copper derivative was chosen for study to make possible a direct approach to the structure, using the phase-determining power of the copper

atom. The actual crystals and the crystal structure of the copper derivative have not proved particularly favourable. The copper atoms are found to lie at symmetry centres in the structure, but the shortest axis is the monoclinic a axis (space-group $P2_1/a$) and the principal projection is compounded from the ($0kl$) structure factors. The copper atoms only contribute to those structure factors for which k is even. For the structure factors with k odd the contributions from the copper atoms cancel each other out, and consequently these reflections are not phase determined. The analysis has been limited by the size and shape of the crystals to two dimensions.

Of the other compounds described in part II, α -monobromotropolone, tropolone, and tropolone hydrobromide are more-fundamental tropolones. These compounds have been examined principally with the idea of learning something about the fine structure of the tropolone ring. The heavy-atom derivatives are not well suited to this purpose for two reasons. First a large part of the structure amplitude is on the average due to the heavy-atom contribution. Therefore a much higher accuracy in intensity measurements would be necessary to fix the positions of the light atoms with the same precision as might be obtained if the whole structure amplitude were due to the

light atoms alone. In the second place, the accuracy realisable in making intensity measurements is actually less when heavy atoms are present owing to the high absorption coefficient for X rays and consequent errors due to the details of shape and size of the crystal specimens. However, α -monobromotropolone has been studied in most detail and most progress has been made with it for the following reasons. One crystal axis is as short as 4.2 A. It has therefore been possible to obtain a clear projection of the whole structure in this direction. Interleaving of the molecules within this periodicity is clearly not possible. Also the phase-determining power of the bromine atom opened up the possibility of a perfectly direct approach to the structure. The analysis has been limited by the size, shape, and nature of the crystals to two dimensions.

The Crystal Structure of Cupric Nootkatin

Crystal Data.

Cupric nootkatin, $(C_{15}H_{19}O_2)_2Cu$; M, 526.2;

d, calc. 1.256, found 1.27.

Monoclinic, $a = 8.40 \text{ \AA}$ $b = 11.96 \text{ \AA}$ $c = 15.21 \text{ \AA}$.

$\beta = 115.5^\circ$

$b^* = 0.1287$ $c^* = 0.1113$

Absent spectra, $(h0l)$ when h is odd, $(0k0)$ when k is odd. Space-group, $C_{2h}^5-P2_1/a$. Two molecules per unit cell.

Molecular symmetry, centre. Volume of the unit cell =

1391 \AA^3 . Absorption coefficient for X rays ($\lambda = 1.54 \text{ \AA}$)

$\mu = 14.7$ per centimetre⁻¹. Total number of electrons per unit cell = $F(000) = 558$.

Experimental Measurements.

Small needle-like crystals, elongated in the direction of the a axis, were obtained by crystallisation from a mixture of chloroform and methyl alcohol. The density was determined by flotation in a solution of potassium iodide. The value obtained, 1.27, is in good agreement with the value, 1.256, calculated for a unit cell containing two molecules of the co-ordination complex.

All the X-ray work was carried out with copper-K radiation ($\lambda = 1.54 \text{ \AA}$). Rotation and oscillation

photographs were taken about the axes and about the (101) diagonal. Moving-film photographs were taken of the a and b axis zero-layer lines. The systematic absences observed led to the space-group $P2_1/a$ without ambiguity. Intensity measurements were carried out on the (0kl) zone and on the (h0l) zone, the integrated intensities being obtained by careful visual measurement. The multiple-film technique (3) was used to obtain correlation between very strong and very weak reflections. A thirty-hour exposure produced an intensity range of 3000 to 1 in the (0kl) zone. 92 reflections were recorded out of a possible 224 (41.1%). For the (0kl) zone the crystal employed had a cross-section normal to the a axis of 0.15 mm. by 0.02 mm. For the (h0l) zone the crystal employed had a cross-section normal to the b axis of 0.45 mm. by 0.02 mm. No absorption corrections were attempted and the investigation has been confined to the (0kl) zone. Measured values of F, calculated from the intensities using the usual formulae for mosaic-type crystals, are listed under 'Fmeas.' in Table 6. The measured F values were placed on an approximately absolute scale by correlation with the structure factors calculated from the atomic positions. The Fourier summations were carried out by the 3-figure strip and stencil method (4). For the projection along

the a axis the electron density was computed at 900 points on the asymmetric unit, the axial subdivisions being $b/60 = 0.1993 \text{ \AA}$. and $c \sin \beta / 60 = 0.2306 \text{ \AA}$. The positions of the contour lines were obtained by graphical interpolation from the summation totals.

In the structure factor calculations an averaged atomic f-curve for carbon and oxygen was used (15), the atoms being weighted in the ratio of 6 to 9. For copper an empirical scattering curve was used, of similar shape to the f-curve found for nickel in the nickel phthalocyanine structure (16).

Analysis of the Structure.

As the unit cell contains only two copper atoms, these must lie on symmetry centres whose (Okl) zone co-ordinates will be (000) and ($0\frac{1}{2}0$). When k is even the contributions of the copper atoms will be in phase, and it was hoped that these contributions would determine the sign of the total structure amplitude for at least the great majority of these planes. It was therefore assumed that the (Okl) structure factors were of positive sign when k was even. When k is odd the contributions of the copper atoms cancel out. The structure factors observed in this case are due to the contributions of the lighter atoms in the molecule

and the signs of these structure factors may be either positive or negative. It is significant that the (0kl) reflections are generally much stronger when k is even: 70 of these even-index reflections were observed out of a possible 120 lying within the range of copper radiation, but only 22 odd-index reflections were observed out of a possible 104. Overall, 92 reflections were observed out of a possible 224 (41.1%).

A double Fourier synthesis was set up with the k-even structure factors as coefficients with all signs positive, the odd-index structure factors being entirely omitted. This process introduces a false plane of symmetry into the resulting projection. In the projection each atom will be accompanied by its mirror image. To obtain the real structure one atom must be selected from each of the resulting pairs and the other rejected. Use is then made of the co-ordinates of the selected atoms to calculate the phase constants of the odd-index reflections, and if necessary to modify the signs of some even-index reflections, and so complete the synthesis. Interpretation of the initial projection proved rather difficult for the following reasons, clearly revealed subsequently. In the first place the tropolone ring is not very favourably orientated with respect to the plane of projection. Secondly, as was not unexpected,

slight interleaving of the molecules takes place within the a axis periodicity of 8.40 Å. However, after a few trials fair agreement was obtained between the measured and the calculated values of the structure factors, and it was possible to proceed to refinement of the atomic positions by double Fourier series methods utilising even-index and odd-index reflections. It was found after the first calculation of structure factors that only a few of the k-even structure factors had changed to doubtfully positive, thus justifying the earlier assumption about the phase-determining power of the copper atom. The contour map shown in Fig. 11 is the result of a final Fourier synthesis containing 90 terms representing measured values of the (0kl) structure factors. The map extends over half the unit cell, twice the asymmetric unit, and covers one molecule of the co-ordination complex. An explanatory diagram is shown in Fig. 12.

Atomic positions indicated by dots in Fig. 11 are listed in Table 5. These were used to calculate all the structure factors with the results given in Table 6. The average discrepancy, obtained by dividing the sum of the individual discrepancies by the total of the measured F values, is 22.2%.

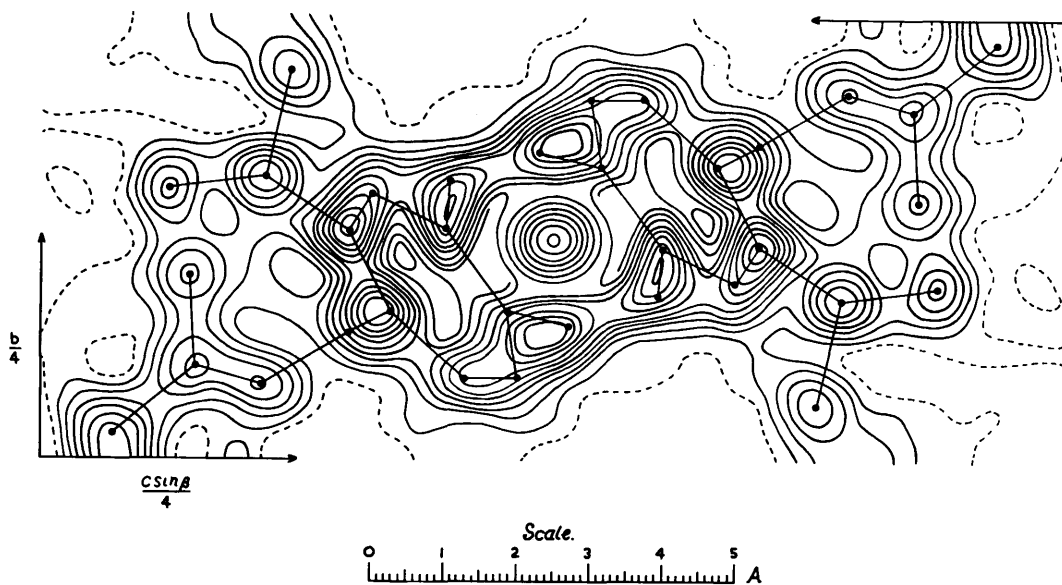


Fig. 11. Electron-density projection along the *a* axis on (100) covering one molecule of cupric nootkatin. Contour scale one electron per Å.² per line, the one-electron line being dotted. The scale is reduced by a factor of 5 on the copper atom.

Table 4.

Coordinates derived from the final projection,
Origin of symmetry as origin.

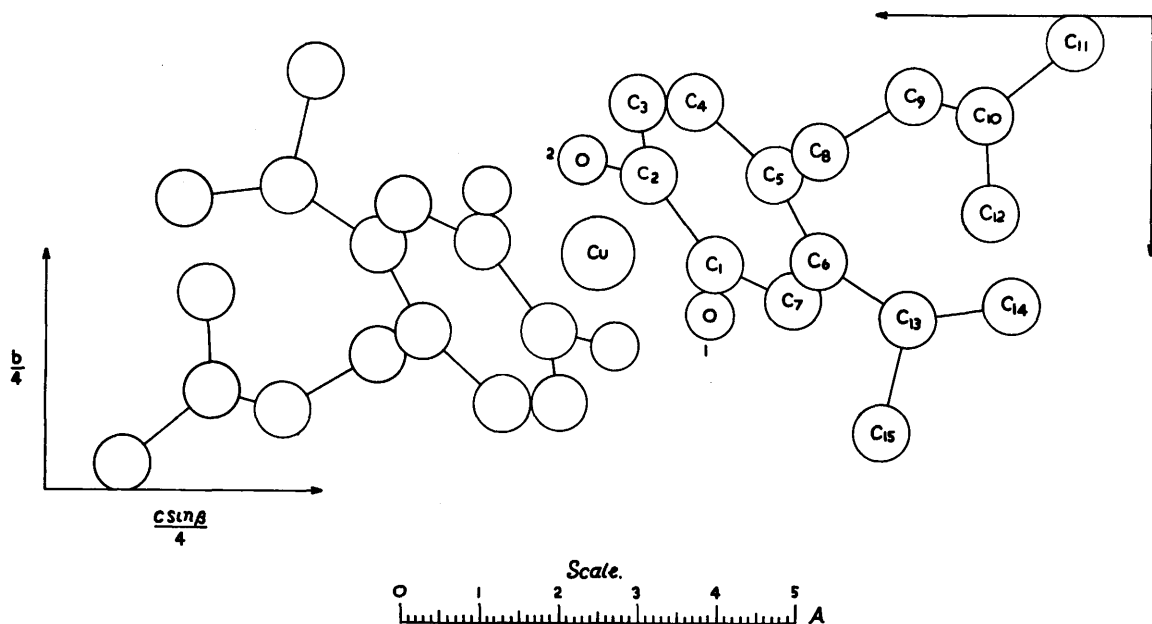


Fig. 12. Projection along the a axis on (100) covering one molecule of cupric nootkatin, and showing the arrangement of the atoms.

Table 5.

Co-ordinates derived from the final projection, Fig. 11.
Centre of symmetry as origin.

Atom (cf. Fig. 12)	$2 y/b^\circ$	$2 z/c^\circ$	Y(A.)	Z(A.)
Cu	0.0	0.0	0.0	0.0
O(1)	-23.0	36.8	-0.76	1.42
O(2)	35.2	- 5.2	1.17	-0.20
C(1)	- 4.3	38.5	-0.14	1.48
C(2)	29.3	16.3	0.97	0.63
C(3)	56.5	12.4	1.88	0.48
C(4)	57.0	31.3	1.89	1.20
C(5)	29.8	57.4	0.99	2.21
C(6)	- 2.4	72.4	-0.08	2.78
C(7)	-17.5	64.3	-0.58	2.47
C(8)	38.5	72.4	1.28	2.78
C(9)	59.7	102.9	1.98	3.96
C(10)	52.3	126.1	1.74	4.85
C(11)	79.8	155.0	2.65	5.96
C(12)	15.8	128.2	0.52	4.93
C(13)	-24.6	101.7	-0.82	3.91
C(14)	-19.3	135.5	-0.64	5.21
C(15)	-67.4	93.4	-2.24	3.59

Co-ordinates

The co-ordinates obtained from the final projection are listed in Table 5. The origin is chosen at a centre of symmetry and the co-ordinates, y and z , are expressed as fractions of the monoclinic axial lengths, b and c , in degrees. Co-ordinates also referred to the **rectangular** crystal axes b and $c \sin \beta$ but expressed in Angstrom units are given under Y and Z . Only the atoms of the asymmetric crystal unit (half the chemical complex) are listed, the co-ordinates of the other atoms in the unit cell being obtainable from

the relations applicable to the space-group $P2_1/a$.

Discussion.

Nootkatin has been shown to be β -isopropyl

γ -(3-methyl but-2-enyl) tropolone (see Fig. 13).

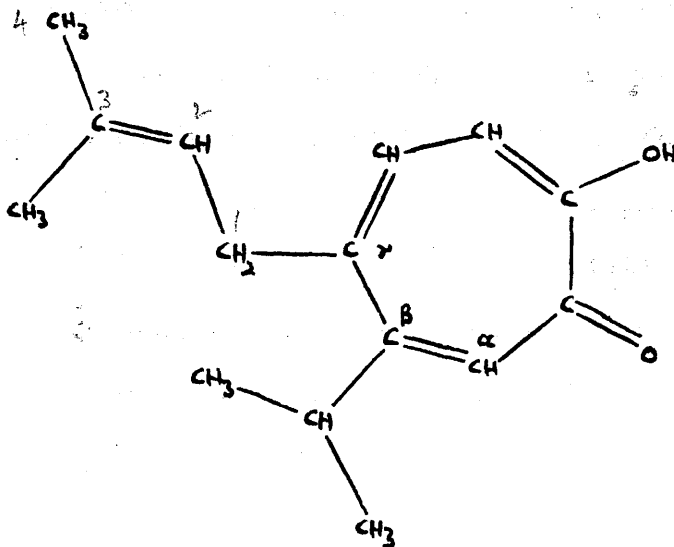


Fig. 13. β -isopropyl γ -(3-methyl but-2-enyl) tropolone.
The bonds in the ring are only conventionally
single and double bonds.

The assignment of the isopropyl group to the β position closer to the carbonyl oxygen is rather tentative. The positions of the tropolone ring and the attached oxygens in the (0kl) projection were obtained by fitting to the contours a projection of the regular planar structure found by Robertson in his investigation of copper tropolone (13).

A much better fit to the contours was obtained when the carbonyl oxygen was placed closer to the isopropyl group than when the hydroxyl oxygen was placed closer. Inspection of the (Okl) projection (Fig. 11) will make clear that this arrangement can only be tentative.

The ultra-violet spectrum of nootkatin has been recorded as more closely resembling that of γ -thujaplicin (γ -isopropyl tropolone) than those of the α - and β -thujaplicins (14). However, it is interesting to note in connection with our formulation of nootkatin as a derivative of β -thujaplicin that β -thujaplicin is the most common of the three naturally occurring thujaplicins.

031	0.876	181
032	0.859	80
033	0.419	19
034	0.518	17
035	0.511	82
036	0.718	82
038	0.977	87
039	1.070	
040	1.141	
041	1.251	
042	0.240	
043	0.241	
044	0.111	

Table 6.

Measured and calculated values of the structure factor
for cupric nootkatin.

hkl	$2\sin\theta$ ($\lambda = 1.54 \text{ \AA.}$)	F _{meas.}	F _{calc.}
001	0.111	132*	147
002	0.223	27	35
003	0.334	93	80
004	0.445	30	32
005	0.557	61	57
006	0.668	44	40
007	0.779	34	31
008	0.890	20	32
009	1.002	17	26
00,10	1.113	29	33
00,11	1.224	44	50
020	0.257	165	132
040	0.515	13	18
060	0.772	20	27
080	1.030	12	3
0,10,0	1.287	17	11
0,12,0	1.544	20	21
0,14,0	1.802	11	11
011	0.170	26	- 41
013	0.358	59	- 25
017	0.788	23	- 22
021	0.279	111	90
022	0.339	20	34
023	0.419	19	29
024	0.512	17	9
025	0.611	52	48
026	0.715	58	59
028	0.927	27	36
029	1.036	24	24
02,10	1.145	38	38
02,11	1.251	28	30
032	0.446	19	- 6
033	0.511	26	20
035	0.677	23	8 +
036	0.771	23	- 22
037	0.869	22	- 18

Table 6.

hkl	$2\sin\theta$ ($\lambda = 1.54 \text{ \AA.}$)	F _{meas.}	F _{calc.}
039	1.074	9	- 10
03,11	1.284	14	14
042	0.561	6	30
043	0.614	13	8
044	0.680	11	15
045	0.759	28	35
046	0.843	6	18
047	0.933	23	27
048	1.029	14	24
049	1.128	30	30
04,10	1.229	27	24
04,11	1.329	9	16
051	0.654	52	44
052	0.682	23	19
053	0.729	12	11
054	0.786	42	24
057	1.011	7	- 7
05,10	1.289	9	- 10
05,11	1.384	9	17
061	0.781	27	27
062	0.803	15	18
063	0.842	26	35
064	0.891	32	35
065	0.952	9	12
068	1.180	25	23
069	1.267	27	22
06,10	1.358	17	17
06,11	1.449	10	14
071	0.908	15	17
072	0.929	21	13
074	1.006	19	- 23
081	1.032	33	25
082	1.051	36	33
083	1.081	22	19
084	1.120	23	27
085	1.170	30	34
086	1.229	23	26

Table 6.

hkl	$2\sin\theta$ ($\lambda = 1.54 \text{ \AA.}$)	F _{meas.}	F _{calc.}
087	1.291	8	11
088	1.362	10	10
089	1.439	25	27
08,10	1.520	16	16
092	1.178	14	14
094	1.240	22	- 15
0,10,1	1.290	20	26
0,10,2	1.304	17	18
0,10,3	1.330	10	7
0,10,4	1.362	28	32
0,10,5	1.403	27	24
0,10,6	1.449	15	13
0,10,7	1.504	14	18
0,10,8	1.565	10	9
0,10,9	1.632	12	15
0,12,1	1.547	17	24
0,12,3	1.580	8	11
0,12,4	1.606	9	16
0,14,1	1.801	8	7

* Intensity estimated on an oscillation photograph.

The Crystal Structure of α -Monobromotropolone

Crystal Data.

α -Monobromotropolone, $C_7H_5O_2Br$; M, 201.0; m.p. 105° - 107° C.;
d, calc. 1.898, found 1.89.

Orthorhombic,

a = 25.64 ± 0.05 A. b = 6.485 ± 0.02 A. c = 4.23 ± 0.01 A.

a* = 0.0601 b* = 0.2374

Absent spectra, (h00) when h is odd, (0k0) when k is odd, (00l) when l is odd. Space-group, $D_2^4-P2_12_12_1$. Four molecules per unit cell. Molecular symmetry, none. Volume of the unit cell = 703.3 A.^3 . Absorption coefficient for X rays ($\lambda = 1.54 \text{ A.}$) $\mu = 76.5$ per centimetre⁻¹. Total number of electrons per unit cell = $F(000) = 392$.

Experimental Measurements.

Needle-like crystals, elongated in the direction of the c axis, were obtained by allowing solvent to evaporate slowly from a solution of α -monobromotropolone in a mixture of benzene and 80-100 pet. ether. The density was determined by flotation in a solution of zinc bromide. The value obtained, 1.89, is in good agreement with the value, 1.898, calculated for a unit cell containing four molecules.

All the X-ray work was carried out with copper-K α

radiation ($\lambda = 1.54 \text{ \AA}$). Rotation and oscillation photographs were taken about the axes. Moving-film photographs were taken of the b and c axis zero-layer lines. The systematic absences observed led to the space-group $P2_12_12_1$ without ambiguity. Intensity measurements were carried out on the (hk0) zone, the integrated intensities being obtained by careful visual estimation. The multiple-film technique (3) was used to obtain correlation between very strong and very weak reflections. A sixteen-hour exposure produced an intensity range of 1200 to 1 in the (hk0) zone. 141 reflections were recorded out of a possible 221 lying within the range of copper radiation (65.8%). The crystal employed had a cross section normal to the c axis of 0.2 mm. by 0.07 mm. No absorption corrections were employed. Attempts to cut crystals to more-uniform dimensions were unsuccessful because internal fractures spread from the cut surfaces throughout the specimens. Within a short time after cutting the specimens gave only powder patterns. Intensity measurements have been confined to the (hk0) zone. Measured F values were calculated from the intensities using the usual formulae applicable to mosaic-type crystals and are listed under F_{meas} in Table 8. The measured F values were placed on an approximately absolute scale by

correlation with the structure factors calculated from the atomic positions.

The Fourier summations were carried out by the 3-figure strip and stencil method (4). For the projection along the c axis the electron density was computed at 900 points on the asymmetric unit, the axial subdivisions being $a/120 = 0.2137$ A. and $b/30 = 0.2162$ A. The positions of the contour lines were obtained by graphical interpolation from the summation totals. In the structure factor calculations an averaged atomic f-curve for carbon and oxygen was used (15), the atoms being weighted in the ratio of 6 to 9. For bromine an empirical scattering curve was used.

Analysis of the Structure.

The bromine atoms occupy general positions in the unit cell and were located by Patterson methods. The structure amplitudes of the (hk0) reflections were evaluated (Table 8) and with the squares of these quantities a double Fourier series was set up summation of which would yield a projection of the interatomic vectors on the (001) plane. In the c axis projection the equivalent points for the space-group $P2_12_12_1$ are

$$x \ y, \quad \frac{1}{2}-x \ \bar{y}, \quad \frac{1}{2}+x \ \frac{1}{2}-y, \quad \bar{x} \ \frac{1}{2}+y,$$

and the following special vectors arise

$$\pm 2x \frac{1}{2}, \quad \frac{1}{2} \frac{1}{2} \pm 2y.$$

These special positions arise from vectors between atoms related by the symmetry operations of the space-group as has been pointed out by Harker (17). It is clear that Br-Br vectors will give rise to large peaks at

$$\pm 2x' \frac{1}{2}, \quad \frac{1}{2} \frac{1}{2} \pm 2y',$$

where x' and y' are the co-ordinates of the bromine atom in an asymmetric unit. Summation of the Patterson series along $y = \frac{1}{2}$ and along $x = \frac{1}{2}$ yielded

$$2\pi x'/a = +16.8^\circ, \quad 2\pi y'/b = +28.2^\circ.$$

The three other possible combinations of these angles and their supplements give the co-ordinates of the other three bromine atoms in the unit cell.

With the co-ordinates of the bromine atoms determined the structure analysis can proceed by successive approximations. The origin was transferred to $(\frac{1}{4}00)$, in which position it coincides with a centre of symmetry in the $(hk0)$ projection. The co-ordinates of the bromine atom in the chosen asymmetric unit become

$$2\pi x'/a = -73.2^\circ, \quad 2\pi y'/b = +28.2^\circ,$$

and the atomic structure factor referred to the new origin is

$$F(hk0) = 4\cos 2\pi hx \cos 2\pi ky \quad \text{when } (h+k) = 2n$$

$$F(hk0) = -4\sin 2\pi hx \sin 2\pi ky \quad \text{when } (h+k) = 2n+1.$$

The structure factors were calculated for the bromine contributions alone, and a double Fourier synthesis was performed giving a projection on the (001) plane. The electron-density map so obtained gave good resolution for all but one of the atoms expected from the chemical structure but with some distortion. The co-ordinates of the carbon and oxygen atoms were now estimated from this map and included in structure factor calculations. The co-ordinates were refined by successive Fourier syntheses and the final synthesis contained 133 terms representing measured values of the (hk0) structure factors. The contour map shown in Fig. 14 is derived from the final summation and extends over quarter of the unit cell, one asymmetric unit. An explanatory diagram extending over one unit cell is shown in Fig. 15.

The atomic positions indicated by dots in Fig. 14 are listed in Table 7. These were used to calculate all the structure factors with the results given in Table 8. The average discrepancy, obtained by dividing the sum of the individual discrepancies by the total of the measured F values, is 18.3%.

Co-ordinates and Dimensions.

The co-ordinates obtained from the final projection are listed in Table 7. The origin is chosen at a centre of

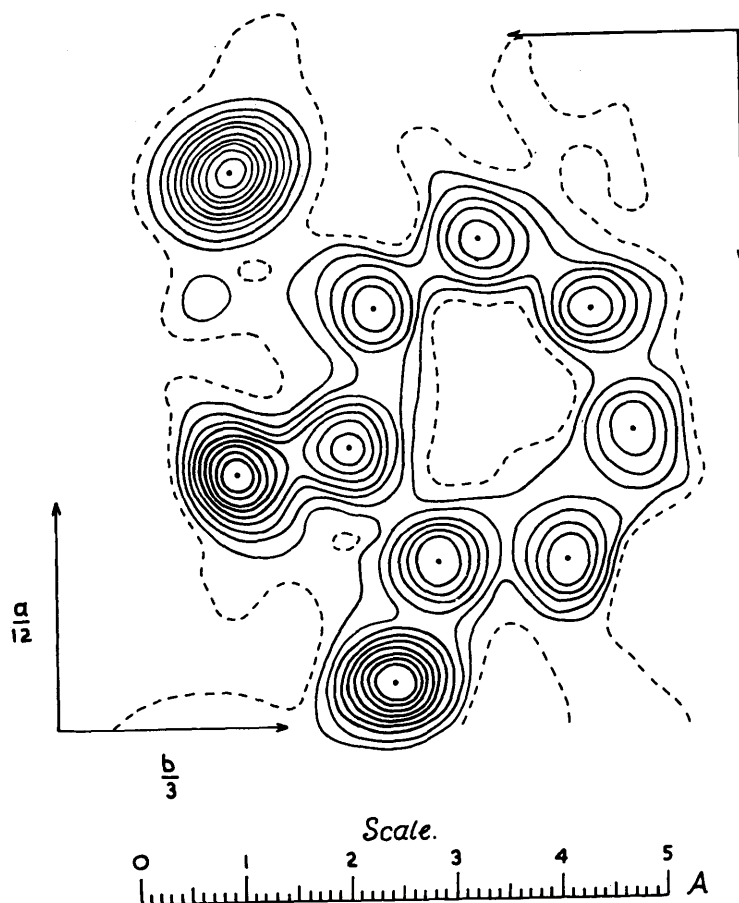


Fig. 14. Electron-density projection along the c axis on (001) covering one molecule of α -monobromotropolone. Contour scale one electron per \AA^2 per line, the one-electron line being dotted. The scale is reduced by a factor of 5 on the bromine atom.

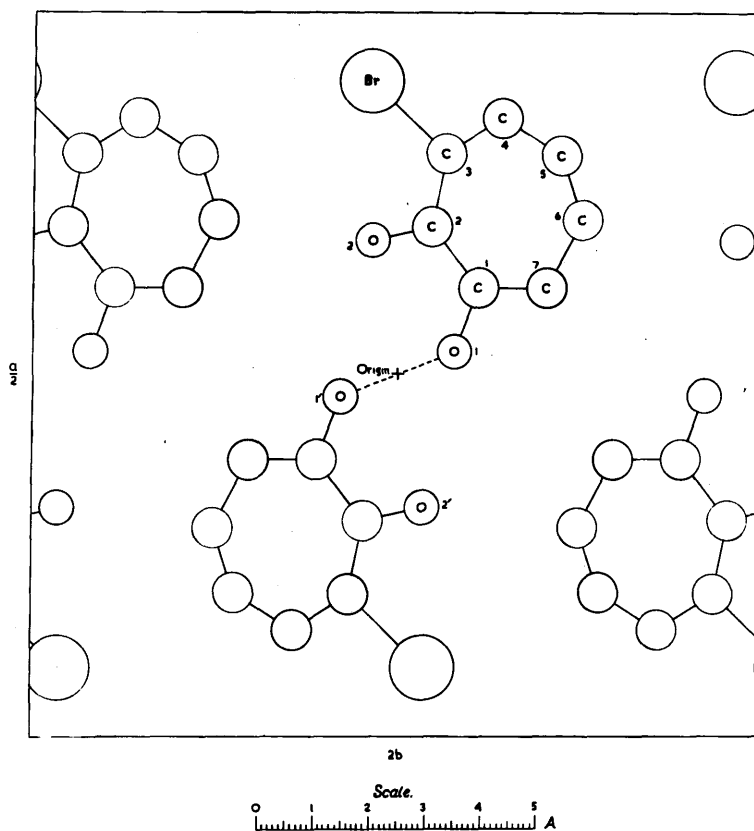


Fig. 15. Projection along the c axis on (001) covering four molecules of α -monobromotropolone, and showing the arrangement of the molecules.

Table 7.

Co-ordinates derived from the final projection, Fig. 14.
Centre of symmetry as origin.

Atom (cf. Fig. 15)	$2\pi x/a^\circ$	$2\pi y/b^\circ$	X(A.)	Z(A.)
Br	73.1	- 26.6	5.21	-0.48
O(1)	5.7	56.8	0.41	1.02
O(2)	33.2	- 24.6	2.37	-0.44
C(1)	21.6	80.1	1.54	1.44
C(2)	36.7	34.0	2.62	0.61
C(3)	55.0	47.6	3.92	0.86
C(4)	63.9	102.8	4.55	1.85
C(5)	54.8	161.3	3.90	2.91
C(6)	38.6	-177.5	2.75	3.29
C(7)	21.6	147.6	1.54	2.66

symmetry and the co-ordinates x and y are expressed as fractions of the orthorhombic axial lengths, a and b, in degrees. Absolute co-ordinates expressed in \AA units are also given under X and Y. Only the atoms of the asymmetric crystal unit are listed, the co-ordinates of the other atoms in the unit cell being obtainable from the relations applicable to the space-group $P2_12_12_1$.

Bond lengths have not been worked out because the tropolone ring appears to deviate slightly from a planar heptagon. Without entering into details of dimensions and orientation it is possible to apply a simple direct test of the shape of the ring. If the ring is a regular planar heptagon then lines like C(1)-C(7), C(2)-C(6), and

C(3)-C(5) in Fig. 15 will be parallel, and these lines will remain parallel in any projection. A lack of parallelism can be detected.

An intermolecular approach distance of 3.05 Å. occurs between oxygen atoms O(1) and O(1') in Fig. 15. These oxygen atoms are related by a centre of symmetry in the (hk0) projection and calculation of the approach distance requires only the two co-ordinates available for each atom.

Discussion.

The deviation from planarity in the tropolone ring may result from steric interaction between the bromine atom and the adjacent oxygen atom. Tropolone itself is likely to be planar, but it does seem possible that the steric effect of substituents may affect the degree of planarity attained by a tropolone ring. The average discrepancy, obtained by dividing the sum of the individual discrepancies by the total of the measured F values and by using the centres indicated by dots on the final Fourier projection (Fig. 14), is 18.3%. The ring centres were adjusted so as to conform to the projection of an almost regular planar heptagon with an average carbon-carbon distance of 1.40 Å. This involved a maximum shift in projection of 0.2 Å. in the case of atom C(6). The average discrepancy was recalculated using these centres and rose to 20.8%.

However, as has been pointed out in the introduction to part II of this thesis, in the investigation of a heavy-atom derivative the accuracy is reduced for two reasons. First a large part of the structure amplitude is on the average due to the heavy-atom contribution. Therefore a much higher accuracy in intensity measurements would be necessary to fix the positions of the light atoms with the same precision as might be obtained if the whole structure amplitude were due to the light atoms alone. In the second place, the accuracy realisable in making intensity measurements is actually less when heavy atoms are present owing to the high absorption coefficient for X rays and to consequent errors due to the details of shape and size of the crystal specimens. In the present case an attempt to correct for absorption by determining the path length for the mean ray through the crystal for each reflection was abandoned as being misleading. Therefore, in spite of the excellent resolution achieved in the electron-density map, the atomic co-ordinates are likely to be correct only to within about 0.1 A. and the deviation from planarity in the tropolone ring may be a spurious effect resulting from the effect of the heavy bromine atom on the measured intensities. It seems worthy of note, however, that the atoms are generally circular

in outline in the contour map and that excessive distortion which might be expected as the result of adverse absorption effects is absent.

An approach distance of length 3.05 Å. occurs between oxygen atoms of two α -monobromotropolone molecules. The two oxygen atoms, O(1) and O(1') in Fig. 15, are related by a centre of symmetry in the (hk0) projection and are chemically identical. This approach distance might be interpreted as involving weak intermolecular hydrogen bonding and as providing a basis for identifying these oxygens as hydroxyl oxygens. In theory the 3.05 Å. approach distance could be a van der Waals contact between carbonyl oxygens (19). In practice van der Waals contacts of under 3.4 Å. are not usual. For instance in benzoquinone the closest oxygen-oxygen van der Waals approach distance is 3.62 Å. (15).

An intermolecular approach distance of 3.05 Å. between hydroxyl oxygens does not indicate very strong hydrogen bonding. In the resorcinol structures hydrogen bonding results in intermolecular approach distances between oxygens of about 3.70 Å. (21). However in α -monobromo- tropolone the hydroxyl-hydrogen atom is likely to be involved in intramolecular hydrogen bonding with the adjacent carbonyl oxygen, resulting in a weakening of any

intermolecular hydrogen bonding.

If the approach distance of 3.05 Å. is accepted as evidence for weak intermolecular hydrogen bonding and for identifying the oxygens involved as hydroxyl oxygens, then α -monobromotropolone m.p. 105°-107° C. contains hydroxyl and carbonyl oxygens and is the geometrical isomer indicated in Fig. 16.

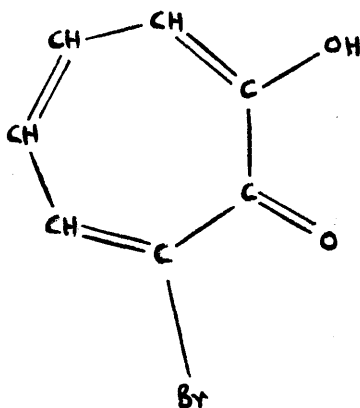


Fig. 16. α -Monobromotropolone m.p. 105°-107° C. The bonds in the ring are only conventionally single and double bonds.

The intermolecular approach distance of 3.05 Å. also occurs between atom O(1) and an oxygen atom equivalent to O(1') located a translation of c below O(1'). It also occurs between atom O(1') and an oxygen atom equivalent to O(1) located a translation of c above O(1). As a consequence the crystal structure consists of zig-zags

of linked α -monobromotropolone molecules with the axis of the zig-zag parallel to the c crystal axis. The intermolecular distances $O(1)\cdots O(2')$ and $O(2)\cdots O(1')$ have been estimated roughly by assuming that the oxygen atoms lie in the plane of a regular planar tropolone ring. Both distances are in excess of 5.4 A.

The bromine atom is elliptical in projection in Fig. 14 indicating that there is preferred vibration. The peak heights on the carbon atoms decrease from 8 on atom C(2) to 5 on atom C(6). This effect of preferred vibration on peak heights has been noted in anthracene (2).

Table 8.

Measured and calculated values of the structure factor
for α -monobromotropolone.

hkl	($\lambda = 1.54 \text{ \AA}$)	$F_{\text{meas.}}$	$F_{\text{calc.}}$
200	0.120	*	- 62
400	0.240	11	- 1
600	0.361	25	22
800	0.481	98	- 93
10,00	0.601	123	113
12,00	0.721	43	- 62
14,00	0.841	41	39
16,00	0.962	16	- 12
18,00	1.082	19	- 21
20,00	1.202	60	59
22,00	1.322	42	- 45
24,00	1.442	< 7	3
26,00	1.563	13	- 12
28,00	1.683	9	- 10
020	0.475	112	86
040	0.950	18	- 26
060	1.424	26	- 32
110	0.245	71	52
210	0.264	34	- 16
310	0.294	85	- 79
410	0.336	75	- 75
510	0.381	103	+110
610	0.430	16	35
710	0.479	95	- 96
810	0.534	69	- 68
910	0.586	73	68
10,10	0.643	7	17
11,10	0.698	25	29
12,10	0.756	23	20
13,10	0.818	44	- 46
14,10	0.870	39	- 36
15,10	0.931	51	55
16,10	0.992	29	27
17,10	1.051	60	- 75
18,10	1.108	31	- 30
19,10	1.166	32	25

Table 8.

hkl	$2\sin\theta$ ($\lambda = 1.54 \text{ \AA.}$)	F _{meas.}	F _{calc.}
20,10	1.224	16	- 6
21,10	1.286	<7	2
22,10	1.342	<7	- 8
23,10	1.401	8	- 9
24,10	1.461	14	- 12
25,10	1.520	14	17
26,10	1.579	7	13
27,10	1.638	17	- 23
28,10	1.700	<6	- 3
29,10	1.758	7	8
120	0.478	98	96
220	0.490	63	- 59
320	0.509	67	- 58
420	0.533	20	- 7
520	0.563	15	13
620	0.597	33	- 12
720	0.633	42	38
820	0.677	17	- 28
920	0.717	97	- 87
10,20	0.766	65	66
11,20	0.813	44	53
12,20	0.862	42	- 44
13,20	0.916	51	- 55
14,20	0.966	28	19
15,20	1.022	5	7
16,20	1.074	30	- 16
17,20	1.131	15	10
18,20	1.182	14	- 18
19,20	1.240	37	- 32
20,20	1.294	34	34
21,20	1.351	17	19
22,20	1.407	16	- 19
23,20	1.460	19	- 20
24,20	1.521	14	9
29,20	1.808	7	- 10
130	0.712	34	- 21
230	0.721	46	50
330	0.733	14	- 15
430	0.750	78	- 81
530	0.773	11	13

Table 8.

hkl	$2\sin\theta$ ($\lambda = 1.54 \text{ \AA.}$)	F _{meas.}	F _{calc.}
630	0.797	89	92
730	0.828	49	- 29
830	0.859	71	- 77
930	0.893	9	- 1
10,30	0.932	< 5	5
11,30	0.973	8	5
12,30	1.013	32	35
13,30	1.059	6	1
14,30	1.101	44	- 47
15,30	1.150	6	10
16,30	1.199	36	44
17,30	1.248	7	- 8
18,30	1.297	19	- 26
19,30	1.345	8	- 5
20,30	1.398	< 7	4
21,30	1.450	9	1
22,30	1.502	< 7	- 1
23,30	1.553	15	9
24,30	1.610	6	- 8
25,30	1.660	< 6	5
26,30	1.718	17	18
27,30	1.770	< 5	4
28,30	1.828	7	- 7
29,30	1.880	6	5
140	0.948	71	74
240	0.953	5	10
340	0.960	15	- 26
440	0.977	< 5	- 11
540	0.993	25	16
640	1.012	20	- 8
740	1.037	31	33
840	1.061	7	6
940	1.091	37	- 47
10,40	1.123	11	- 14
11,40	1.154	34	43
12,40	1.192	< 6	9
13,40	1.230	35	- 36
14,40	1.268	< 7	- 10
15,40	1.311	24	22
16,40	1.350	7	1
17,40	1.394	12	11

Table 8.

hkl	$2\sin\theta$ ($\lambda = 1.54 \text{ \AA.}$)	F _{meas.}	F _{calc.}
18,40	1.439	9	8
19,40	1.483	14	- 20
20,40	1.530	8	- 9
21,40	1.578	23	28
22,40	1.625	< 6	7
23,40	1.672	9	- 11
24,40	1.727	< 5	- 2
25,40	1.771	5	9
26,40	1.826	7	1
27,40	1.878	< 4	5
28,40	1.931	5	5
150	1.188	15	- 15
250	1.192	17	22
350	1.202	40	40
450	1.211	15	- 28
550	1.223	13	- 23
650	1.241	18	30
750	1.258	11	18
850	1.281	23	- 24
950	1.306	13	- 22
10,50	1.333	13	11
11,50	1.359	21	- 14
12,50	1.390	12	18
13,50	1.422	20	17
14,50	1.453	< 7	- 7
15,50	1.492	< 7	- 5
16,50	1.531	19	19
17,50	1.569	13	18
18,50	1.608	15	- 13
19,50	1.648	< 6	- 10
20,50	1.689	< 6	4
21,50	1.734	6	- 2
22,50	1.774	< 5	4
23,50	1.821	6	3
24,50	1.868	< 4	- 3
25,50	1.912	7	- 7
26,50	1.961	6	12
860	1.504	21	24
960	1.523	< 7	- 5
10,60	1.548	13	- 19

Table 8.

hkl	$2\sin\theta$ ($\lambda = 1.54 \text{ \AA.}$)	F _{meas.}	F _{calc.}
11,60	1.571	< 7	6
12,60	1.598	13	16
13,60	1.626	< 6	2
14,60	1.652	< 6	- 10
15,60	1.684	9	8
20,60	1.861	9	- 15
570	1.690	7	- 6
670	1.701	< 6	- 3
770	1.713	12	22
870	1.730	< 5	- 3
970	1.748	10	- 14

* F_{calc.} included in the Fourier syntheses, plane omitted from the discrepancy calculations.

determination by the usual flotation method, difficult. However, an approximate determination, using a mixture of methylene bromide and carbon tetrachloride, indicates that the unit cell contains eight molecules.

All the X-ray work was carried out with copper- K_{α} radiation ($\lambda = 1.54 \text{ \AA}$). Rotation and oscillation photographs were taken about the axes and about the (101) diagonal. A moving-film photograph was taken of the c axis zero-layer line. The observed systematic absences led to the space-group $P2_1/a$, but the (h0l) halving has been observed only as a halving of (h00). Intensity measurements have been carried out in the (hk0) zone, the integrated intensities being obtained by careful visual measurement. The multiple-film technique (5) was used to obtain correlation between very strong and very weak reflections. A fifteen-hour exposure produced an intensity range of 3000 to 1. 156 reflections were recorded out of a possible 271 lying within the range of copper radiation (57.6%). The crystal employed had a cross-section normal to the c axis of 0.52 mm. by 0.15 mm. No absorption corrections were attempted. The short time in which a small crystal volatilises has confined intensity measurements to the (hk0) zone. Measured values of F were calculated from the intensities using the usual formulae for mosaic-type

crystals.

The Patterson summation was carried out by the 3-figure strip and stencil method (4).

Analysis of the Structure.

The bromine atoms occupy general positions in the unit cell and were located approximately by Patterson methods. The structure amplitudes of the (hk0) reflections were evaluated and with the squares of these quantities a double Fourier series was set up summation of which would yield a projection of the interatomic vectors on the (001) plane. In the c axis projection the equivalent points for the space-group $P2_1/a$ are

$$x \ y, \quad \frac{1}{2}+x \ \frac{1}{2}-y, \quad \frac{1}{2}-x \ \frac{1}{2}+y, \quad \bar{x} \ \bar{y},$$

and the following special vectors arise

$$\frac{1}{2}\pm 2x, \quad \frac{1}{2}\pm 2y.$$

These special positions arise from vectors between atoms related by the symmetry operations of the space-group as has been pointed out by Harker (17). With two bromine atoms in the asymmetric unit it is clear that Br-Br vectors will give rise to large peaks at

$$\frac{1}{2}\pm 2x_1, \quad \frac{1}{2}\pm 2y_1, \quad \frac{1}{2}\pm 2x_2, \quad \frac{1}{2}\pm 2y_2,$$

where x_1, y_1 and x_2, y_2 are the co-ordinates of the bromine atoms in an asymmetric unit. The correct grouping of co-ordinates might be found by an examination of the

vectors given by a possible grouping and comparison with the Patterson map. The final choice might be verified by construction of a theoretical vector map (18).

However, summation of the Patterson series along $y = \frac{1}{2}$ and $x = \frac{1}{2}$ yielded

$$2\pi x_1/a = 33.1^\circ, \quad 2\pi x_2/a = 41.4^\circ, \quad 2\pi y_1/b = 2\pi y_2/b = 41.7^\circ.$$

This result corresponds with the fact that in the summation of the Patterson series along $x = \frac{1}{2}$ only one large peak of height h on an arbitrary scale occurred between 0 and π . In the summation along $y = \frac{1}{2}$ two peaks of height $h/2$ on the same arbitrary scale occurred, and overlapped to a great extent. It is clear that the two bromine positions in the asymmetric unit only differ appreciably in their z co-ordinates. An arrangement of this kind is permissible since twice the bromine ionic radius of ³⁻⁴1.95 A. (19) is just a little greater than half the length of the c axis ($c/2 = 3.79$ A.).

With the co-ordinates of the bromine atoms determined the structure analysis can proceed by successive approximations.

The Crystal Structure of Tropolone

Crystal Data.

Tropolone, $C_7H_6O_2$; M, 122.1; m.p. $49^\circ-50^\circ$ C.;

d, calc. 1.329.

Monoclinic, $a = 7.10$ A. $b = 12.19$ A. $c = 7.14$ A.

$$\beta = 99.3^\circ$$

Absent spectra, (h0l) when h is odd, (0k0) when k is odd. Space-group, $C_{2h}^5-P2_1/a$. Four molecules per unit cell.

Molecular symmetry, none. Volume of the unit cell = 609.8 A.³.

Experimental Measurements.

Needle-like crystals, elongated in the direction of the a axis, were obtained by allowing solvent to evaporate slowly from a solution of tropolone in a mixture of benzene and 80-100 pet. ether. Considerable difficulty was encountered in mounting the crystals for X-ray work. Tropolone volatilises at an appreciable rate at room temperature. It is soluble in organic solvents and waxes, and this solubility rendered various attempts to coat crystals unsuccessful. The fragile nature of the crystals limited the success attained by sealing them in formvar envelopes (20) . The crystals were preserved but strain set up by the envelope invariably distorted the crystal.

A successful mounting was obtained by sealing the crystals into thin-walled ordinary soft glass tubes.

The solubility of tropolone in water and in organic liquids has made a density determination by the usual flotation method difficult. However, the fact that the crystals were only slightly denser than a saturated solution of sodium chloride (density approximately 1.2 at 15° C.) indicates that the unit cell contains four molecules. Attempts to show that the density of tropolone is less than that of a saturated solution of calcium chloride (density approximately 1.4 at 15° C.) failed because in this solution tropolone dissolves immediately, presumably because of interaction between the tropolone hydroxyl grouping and the calcium.

All the X-ray work was carried out with copper-K α radiation ($\lambda = 1.54 \text{ \AA}$). Rotation and oscillation photographs were taken about the axes and about the (101) diagonal. Moving-film photographs were taken of the axial zero-layer lines. The observed halvings led to the space-group $P2_1/a$ without any ambiguity. Intensity measurements were carried out on the (hk0), (h0l), and (Okl) zones. The multiple-film technique (3) was used to obtain correlation between very strong and very weak reflections. For the (hk0) zone the crystal employed

had a cross section normal to the c axis of 1.36 mm. by 0.18 mm. For the (h0l) zone the crystal employed had a cross section normal to the b axis of 1.21 mm. by 1.30 mm. For the (0kl) zone the crystal employed had a cross section normal to the a axis of 0.51 mm. by 0.15 mm.

ADAPTATION OF THE X-RAY METHOD TO THE STUDY OF THE
 STRUCTURE OF THE CRYSTALS OF THE
 SYSTEM $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ - SrSO_4 - BaSO_4
 BY THE METHOD OF THE DIFFRACTION OF X-RAYS

EXPERIMENTAL PROCEDURE

Single uniformly developed crystals were prepared by
 allowing solvent to evaporate slowly from a solution
 of the substance in chloroform. The density was determined
 by flotation in a solution of calcium iodate. The
 refractive index was determined with the value,
 determined for a unit cell, determined from x-ray
 measurements.

All the measurements were made at room temperature.

(h00) absent when h is odd, (00l) absent when l is odd, and halving of the length of the (110) diagonal when measured on a rotation photograph, led to the space-group Cc.

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