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The Crystal Structure of Indanthrone

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(*Received* 17 *July* 1954)

The crystal structure of the α form of indanthrone has been determined by two-dimensional Fourier projections on (010) and three-dimensional line syntheses parallel to [010]. The interatomic distances and inter-bond angles have been calculated, and a slight departure from planarity of the molecule has been established.

The crystals are monoclinic; $a = 30\cdot83$, $b = 3\cdot833$, $c = 7\cdot845$ Å, $\beta = 91°\ 55'$; space group $P2_1/a$; two molecules in the unit cell.

Introduction

The structure of indanthrone is of particular interest because of its commercial significance as a vat dyestuff. Many complex organic compounds whose structures have been determined are of industrial importance, but, with the exception of the phthalocyanines (Robertson, 1935), few crystal structures have been determined in the dyestuffs field. Indanthrone is known to exist in several polymorphic forms (B.I.O.S., 1945; F.I.A.T., 1948) and the present paper describes the crystal-structure determination of the stable α form.

Experimental

Dendritic clusters of single crystals were grown by vacuum sublimation of pure δ indanthrone, and were identified as the α form by X-ray powder photographs. The individual crystals were very elongated [*b*] laths, platy on {100}, with small {001}, and very poorly defined terminal faces. They have excellent fibrous cleavage along the lath. The unit-cell dimensions were measured from Weissenberg photographs and the angle β was determined goniometrically:

$$a = 30\cdot83,\ b = 3\cdot833,\ c = 7\cdot845\ \text{Å};\ \beta = 91°\ 55'.$$

Monoclinic, holosymmetric class; space-group $P2_1/a$. There are two centrosymmetrical molecules $C_{28}H_{14}O_4N_2$ in the unit cell. Density by flotation = 1·60 g.cm.$^{-3}$; calculated density = 1·58 g.cm.$^{-3}$.

Weissenberg photographs using Cu $K\alpha$ radiation were taken of the zero, first, second, and third layers of the *b* axis, and the zero layer of the *c* axis; and the intensities were estimated visually by comparison with a calibrated scale of time exposures of one reflection from the same crystal. The appropriate geometrical correction factors were applied and the relative structure amplitudes were calculated. The absolute scale and a temperature factor

$$\exp\,(-4\cdot0\,\sin^2\theta/\lambda^2)$$

were obtained graphically from a comparison of the observed and calculated structure factors.

Structure determination

Assuming the molecule to be approximately planar, its tilt from the (010) plane was limited to less than 30° by the short *b*-axis length of 3·833 Å. There were several possible ways of packing the molecules in this plane, and indication of the correct one was given by the unusually large structure factors of several high-order planes, which had spacings corresponding to the 1·20 and 2·08 Å spacings in the molecule formed by the regular repetition of hexagonal rings.

The initial ($h0l$) structure-factor calculations were made assuming a planar molecule, built of regular hexagons of side 1·39 Å; and the *x* and *z* coordinates were then refined by successive Fourier projections on (010). The final projection (Fig. 1) included 165 observed reflexions and was summed at intervals of 1/120 and 1/60 along the *a* and *c* axes respectively. All the atoms were resolved, and the *x* and *z* coordinates corresponding to the centres of the peaks were located analytically by least squares, assuming a Gaussian electron-density distribution of the form

$$\varrho(x, z) = \exp\,(r-sx^2-tz^2-ux-vz-wxz)\,.$$

Since the (311) and (410) planes gave the strongest (hkl) reflexions, trial *y* coordinates were calculated for the molecule in these and intermediate planes, and the

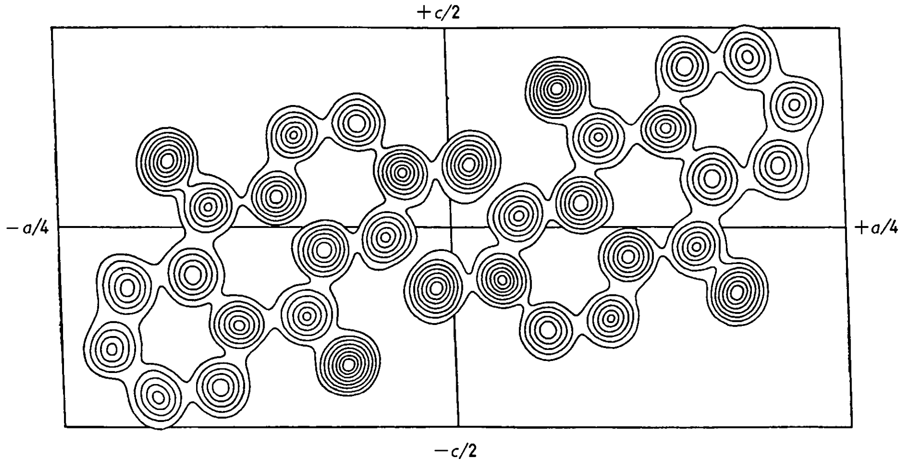

Fig. 1. Projection of the electron density on (010).

corresponding (*hk*0) structure factors were computed. Sufficient signs were determined to be included in a [*c*] Fourier projection of 37 terms, from which improved *y* coordinates were obtained, although the overlap was considerable. The *y* coordinates were further refined by successive three-dimensional syntheses along lines parallel to the *b* axis and having the *x* and *z* coordinates of each of the 17 atoms. The final line syntheses included 245 (*h*1*l*) terms, 160 (*h*2*l*), terms, and 87 (*h*3*l*) terms.

A [*b*] difference synthesis has been computed and gives peaks corresponding closely to hydrogen positions (Table 1) which have been calculated assuming that these atoms lie in the plane of the molecule at a distance of 1·08 Å from the carbon atoms.

Table 1. *Theoretical hydrogen coordinates*

Atom	*x*	*y*	*z*
C_3H	0·048	0·054	0·616
C_4H	0·119	0·772	0·664
C_5H	0·230	0·214	0·049
C_6H	0·251	0·973	0·327
C_7H	0·201	0·005	0·560
C_8H	0·128	0·263	0·511
$N_{17}H$	0·023	0·760	0·258

Table 2. *Fractional atomic coordinates*

Atom	*x*	*y*	*z*
C_1	0·0410	0·835	0·0300
C_2	0·0291	0·968	0·8635
C_3	0·0572	0·955	0·7415
C_4	0·0972	0·781	0·7662
C_5	0·2076	0·223	0·1518
C_6	0·2202	0·091	0·3090
C_7	0·1909	0·104	0·4346
C_8	0·1506	0·254	0·4086
C_9	0·1542	0·518	0·9466
C_{10}	0·0935	0·541	0·2278
C_{11}	0·1102	0·666	0·9266
C_{12}	0·1657	0·371	0·1189
C_{13}	0·1375	0·376	0·2470
C_{14}	0·0807	0·680	0·0553
O_{15}	0·1789	0·504	0·8303
O_{16}	0·0688	0·535	0·3480
N_{17}	0·0106	0·862	0·1555

The structure amplitudes have been calculated for all the (*hkl*) reflexions (over 1,400) from the final atomic coordinates listed in Table 2. The observed and calculated structure amplitudes for the (*h*0*l*), (*h*1*l*), (*h*2*l*), and (*h*3*l*) zones are compared in Tables 5, 6, 7 and 8,* the factor $R = \Sigma(|F_o|-|F_c|) \div \Sigma|F_o|$ having values 0·14, 0·13, 0·15 and 0·16 respectively. When the contributions from the hydrogen atoms are added to the (*h*0*l*) structure amplitudes the *R* factor for this zone is reduced to 0·11. The agreement would probably be further improved by applying higher temperature factors to the atoms at the ends of the molecule, since their peaks (Fig. 1) are appreciably flatter than those near the centre of the molecule.

An estimation of the accuracy has been made using Cruickshank's formula (1949) for the standard deviation of a peak position in terms of the central curvature of the peak and the structure-factor agreement. The central curvatures have been estimated from the final (*h*0*l*) projection for a selection of atoms from the oxygen peaks to the less sharp carbon peaks at the ends of the molecule (C_5, C_6, C_7 and C_8). They are listed with the corresponding standard deviations in Table 3. Since β is 91° 55′ the cell has been assumed orthogonal.

Table 3. *Standard deviation of peak positions*

Atom	$\partial^2\rho/\partial x^2$ (e.Å^{-4})	$\partial^2\rho/\partial z^2$ (e.Å^{-4})	$\sigma(x)$ (Å)	$\sigma(z)$ (Å)
O_{16}	−152	−147	0·003	0·004
C_{14}	−142	−112	0·004	0·005
C_1	− 75	− 90	0·006	0·007
C_6	− 47	− 48	0·010	0·012

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* *Editorial note.*—Tables 5–8 have been deposited with the Institute of Physics, 47 Belgrave Square, London S.W. 1, England. Application to inspect these tables should be made to the Secretary of the Institute.

Description of the structure

The molecular arrangement in the unit cell is illustrated in Fig. 2. There are no inter-molecular forces other than the van der Waals type, and an economical packing of the large organic molecules is obviously the predominant feature of the structure. The arrangement is such that there are 56 interatomic distances of less than 4·1 Å between the atoms of one molecule and the six adjacent molecules in the (010) plane, excluding the additional contacts with the two molecules 3·83 Å above and below along the b axis. It can be seen from Fig. 2 that the majority of the contacts are of the type in which an oxygen atom is approximately equidistant from two adjacent carbon atoms. The perpendicular distance between adjacent molecules along the b axis is 3·44 Å, which agrees well with other values listed by Stadler (1953) for various compounds of this type.

The molecule is centrosymmetrical, and the accuracy is sufficient to show small but quite definite deviations from planarity. The equation of the mean plane through the molecule was obtained by the method of least squares. The perpendicular distances of the atoms from this plane showed effective planarity of the two rings at each end of the molecule, but a slight staggering of the atoms of the three central rings. The plane through the twelve co-planar atoms C_5, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, O_{15}, and O_{16}, was calculated by least squares, and referred to the orthogonal axes a, b and c^* has the equation

$$0·3461x+0·8970y+0·2749z+0·1365 = 0\,. \qquad \text{(i)}$$

Likewise, the twelve corresponding centrosymmetrical atoms lie on a parallel plane

$$0·3461x+0·8970y+0·2749z-0·1365 = 0 \qquad \text{(ii)}$$

at a perpendicular distance of 0·273 Å through the origin from the first plane. The perpendicular displacements of the atoms from the plane (i) are listed in Table 4.

Of the five non-coplanar atoms N_{17}, C_1, C_2 and C_3 lie between the two planes (i) and (ii), and C_4 lies beyond plane (i). The centrosymmetrical atoms N'_{17},

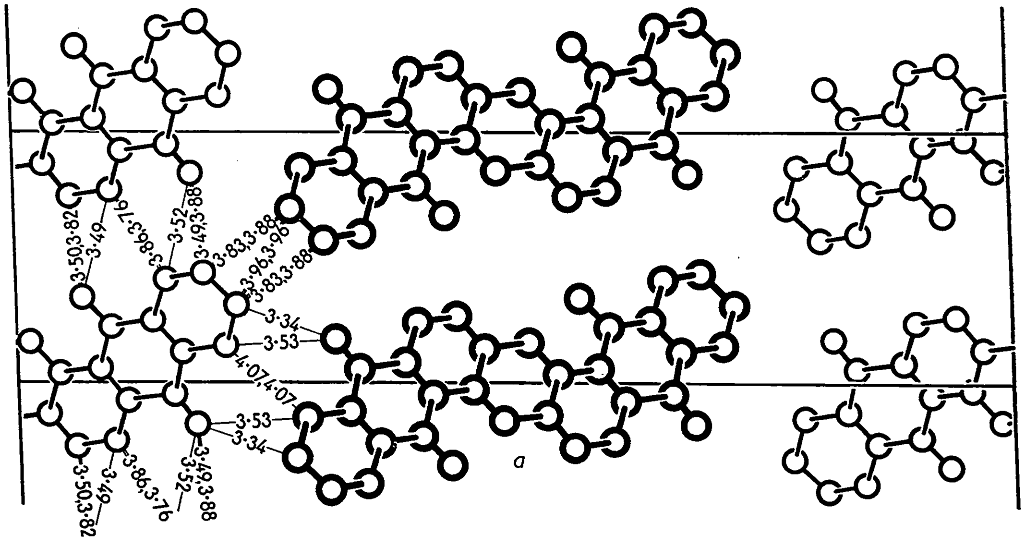

Fig. 2. Molecular arrangement in the unit cell showing intermolecular approaches of less than 4·1 Å.

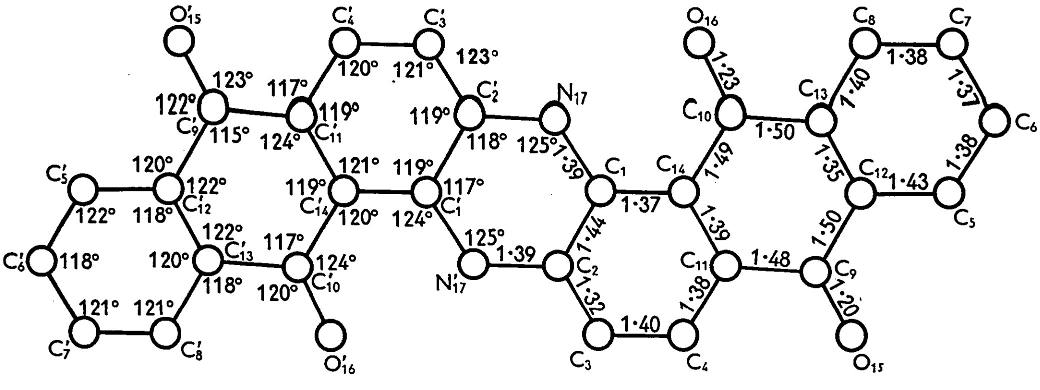

Fig. 3. Dimensions of the molecule.

Table 4. *Deviations from planarity*

C_5	$= -0{\cdot}006$ Å	C_{11}	$= +0{\cdot}014$ Å	C_1	$= +0{\cdot}069$ Å
C_6	$= -0{\cdot}001$	C_{12}	$= -0{\cdot}012$	C_2	$= +0{\cdot}055$
C_7	$= -0{\cdot}005$	C_{13}	$= -0{\cdot}031$	C_3	$= +0{\cdot}062$
C_8	$= +0{\cdot}023$	C_{14}	$= +0{\cdot}012$	C_4	$= -0{\cdot}062$
C_9	$= +0{\cdot}014$	O_{15}	$= -0{\cdot}007$	N_{17}	$= +0{\cdot}096$
C_{10}	$= +0{\cdot}027$	O_{16}	$= -0{\cdot}009$		

C'_1, C'_2, C'_3, and C'_4 are similarly displaced from plane (ii).

The dimensions of the molecule (Fig. 3) are generally consistent with the normally accepted values. The two C–N bonds have both the same length of 1·39 Å. Similar shortenings of the normal C–N single bond lengths of 1·47 Å have been found in other heterocyclic compounds and have been listed by Brown (1949). Of the two C=O bond lengths C_9–O_{15} is 1·21 Å and C_{10}–O_{16} is slightly longer at 1·23 Å. The four single C–C bonds, C_{10}–C_{14}, C_{10}–C_{13}, C_9–C_{11}, C_9–C_{12}, have lengths 1·49, 1·50, 1·48, and 1·50 Å respectively. The nitrogen atom is intramolecularly hydrogen-bonded to the adjacent oxygen atom, the N–H bond length being 1·01 Å as deduced from the hydrogen position measured from the [*b*] difference synthesis.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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On the treatment of unobserved reflexions in the least-squares adjustment of crystal structures.

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(*Received* 15 *December* 1954 *and in revised form* 31 *December* 1954)

In the refinement of crystal structures by the least-squares method, the problem is often complicated by the question of what is the proper way to deal with unobserved reflexions, i.e. reflexions for which $0 \leqslant F^2 < F^2_{\text{min.}}$. It is obvious that an observation that a particular reflexion has a value in a certain range, in particular the range above, may be fully as important in the determination of a structure as observations of a more precise nature. It is the purpose of this note to point out a method of dealing with unobserved reflexions which is demanded by the spirit of least-squares adjustments.

Now the problem of least squares is to find (under the minimum variance criterion) the expected values for a set of parameters under the condition that a set of linear combinations of these parameters (the observables) have been observed to have certain values. These values are by their very nature unprecise; else there would be no need to call on the least-squares procedure. Actually, we may generalize the statement to say that we observe certain conditions which the observables must satisfy. The solution of the least-squares problem tells us that the best values of the parameters are given by the solutions of the *normal equations* with the value of each observable being taken as its *expected value* or *mean* (μ) under the conditions which the observations impose, together with any conditions we may assume about its possible value, and weighted inversely proportional to its variance (σ^2) under these conditions.†

The application of this point of view to observed reflexions is straightforward, the mean value of the distribution of the corresponding observable being simply the observed value.‡ The weights are chosen by a more or less direct analysis of the experimental errors, usually combined with some scheme which contributes computational simplicity.

For unobserved reflexions, the best procedure is to determine the mean value and variance of an observation in the unobservable range, assuming that the probability distribution is the theoretical one for the space group under consideration (in the later stages of refinement, for the actual structure). Howells, Phillips & Rogers (1950) have derived the distributions for the space

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* National Science Foundation Post-Doctoral Fellow, 1954–55.

† The case of correlated observational errors and the consequent non-diagonal weight matrix will not be discussed here. However, see W. C. Hamilton & Verner Schomaker, *The Method of Least Squares in Electron Diffraction* (to be published) for a more detailed discussion of some of these points.

‡ This is the case if an observation yields a definite *number.* If the intensities are visually estimated to lie in a certain range, the analysis below might well be more suitable.