Acta Cryst. (1953). **6**, 540

The Crystal Structure of Flavanthrone

By H. P. Stadler

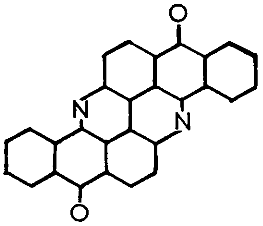
Department of Physical Chemistry and Coke Research, University of Durham, King's College, Newcastle-upon-Tyne 1, *England*

(*Received* 30 *December* 1952)

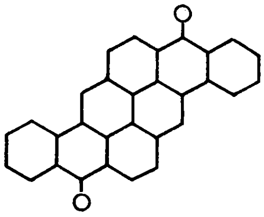
The crystal structure of flavanthrone, $C_{28}H_{12}O_2N_2$, has been determined from $\{h0l\}$ and $\{hk0\}$ intensities by molecular transforms and refined by Fourier methods. The spacegroup is $P2_1/a$ with $a = 27{\cdot}92$, $b = 3{\cdot}80$, $c = 8{\cdot}10$ Å ($\lambda = 1{\cdot}542$ Å) and $\beta = 95°$, $z = 2$. Molecules were assumed planar; the best fit was obtained with the plane given by $0{\cdot}272x - 0{\cdot}907y + 0{\cdot}298z^* = 0$. This makes the interplanar distance 3·44 Å, in good agreement with similar structures. Interatomic distances were calculated from a table of coordinates with standard deviations of 0·03 Å.

In their investigation on the coking properties of various organic compounds, Blayden, Gibson & Riley (1945) examined the variation of line broadening with carbonization temperature and found that certain vat dyes gave carbonization characteristics similar to coking-coal bitumens.

It was decided to continue their work using single crystals in order to get more detailed information about the thermal decomposition processes, and, after a preliminary investigation, flavanthrone and pyranthrone (see diagram) were chosen as suitable working substances. First of all the crystal structure of these compounds had to be determined, and that of flavanthrone is the subject of this paper.



Flavanthrone, $C_{28}H_{12}O_2N_2$.



Pyranthrone, $C_{30}H_{14}O_2$.

Crystals of flavanthrone can be obtained by sublimation *in vacuo*, and although most of the crystals so produced were found to be twins on $(40\bar{1})$, or (100), or intergrowths of various orientations which could not easily be distinguished from single crystals optically, it was eventually possible by X-ray methods to sort out a few single crystals suitable for structure determination. The cell dimensions were found to be

$$a = 27{\cdot}92,\ b = 3{\cdot}80,\ c = 8{\cdot}10\ \text{Å},\ \beta = 95°,$$

(Cu $K\alpha = 1{\cdot}542$ Å), space group $P2_1/a$; $\delta_{\text{obs.}} = 1{\cdot}62$, whence $z = 2$. $\{h0l\}$ and $\{hk0\}$ intensities were estimated from Weissenberg photographs about $[b]$ and $[c]$.

Since the molecule can be assumed to be flat with its centre of symmetry coincident with that of the unit cell, the most promising approach to the solution of the structure appeared to be the use of molecular structure factors (Knott, 1940). A bond length of 1·40 Å was assumed throughout and the difference between C, N and O was neglected to simplify the calculation of the Fourier transform of the molecule. The transform cast in a suitable form for evaluation by Beevers–Lipson strips was

$$\begin{aligned} T = {} & (\cos 4x + \cos 2x)(\cos 5y + \cos 3y + 2\cos y) \\ & + (\cos 5x + \cos x)(\cos 4y + \cos 2y + 1) \\ & + (\cos 7x + \cos x)\cos 2y - (\sin 4x + \sin 2x) \\ & \times (\sin 5y + \sin 3y) - (\sin 5x + \sin x)\sin 4y \\ & - (\sin 7x + \sin 5x)\sin 2y \end{aligned}$$

and gave contours as shown in Fig. 1. A preliminary report of this work has been given at the 1950 X-R.A.G. conference (Wilson, 1951).

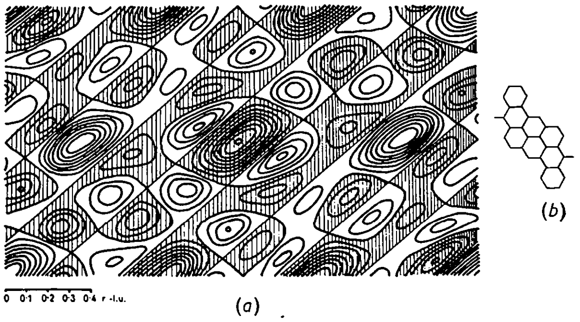


Fig. 1. (*a*) Molecular transform of flavanthrone. For the calculation of the transform all atoms were assumed to have equal scattering power and all bonds were taken as 1·40 Å long. The transform repeats at 2·2 and 1·27 reciprocal-lattice units respectively (for Cu $K\alpha$). It is calculated for a molecule oriented as in (*b*).

The orientation of the transform in its own plane with respect to the reciprocal lattice can most easily be determined from the correspondence of intense regions in high orders, if these occur, since the agreement there is very sensitive to rotation. In the case of flavanthrone the approximate sixfold symmetry due to the constituent benzene rings gave rise to several alternatives, which had to be eliminated by packing considerations and by comparison of the agreement for the low orders. Once the position of best fit had been determined the signs of the structure factors could be read off directly, thus obviating the need for a complete set of structure-factor calculations. The phases for 67 $\{h0l\}$ planes were thus determined and gave a Fourier projection of excellent resolution (Fig. 2). The inclination of the molecule to the plane of projection, as estimated from the foreshortening of the bonds, was about 25°, with a direction of maximum slope perpendicular to the line joining the atoms 2–$\bar{2}$ in Fig. 3. This value agrees well with that obtained from packing considerations assuming a benzene ring 'thickness' of 3·4 Å, which seems to hold in similar cases (Table 1).

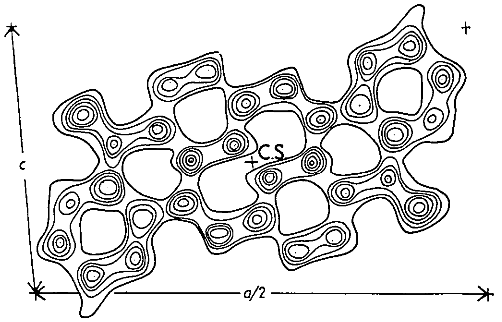


Fig. 2. $\{h0l\}$ projection of flavanthrone using signs obtained from the transform. Contours are drawn at arbitrary intervals. The outlines of half a unit cell are indicated but shifted from its normal origin, C.S., the centre of symmetry of the molecule.

Table 1. *Interplanar distances*

Compound	Distance (Å)	Reference
Coronene	3·38	Robertson & White, 1945
Pyrene	3·52	Robertson & White, 1947
Ovalene	3·4	Donaldson & Robertson, 1949
1 : 12 Benzperylene	3·38	White, 1948
Indanthrone	3·4	Bailey & Wells, private communication
Triphenylene	3·38	Klug, 1950

For the evaluation of structure factors in the $\{hk0\}$ zone the transform was less exact, since it consists there of two different molecular contributions which have to be added or subtracted, and because the approximations used in its evaluation tend to produce the same distortions as the inclination of the molecule. The $F(hk0)$ values were therefore calculated by conventional methods, using the information obtained for the $\{h0l\}$ projection.

The resolution of the $\{hk0\}$ projection is inherently poor and does not lend itself, therefore, to a successive refinement of the atomic positions. It was possible, however, to adjust the y coordinates by varying the inclination of the molecule within narrow limits until the best structure-factor agreement was obtained. The plane of the molecule at the origin was finally given by the equation

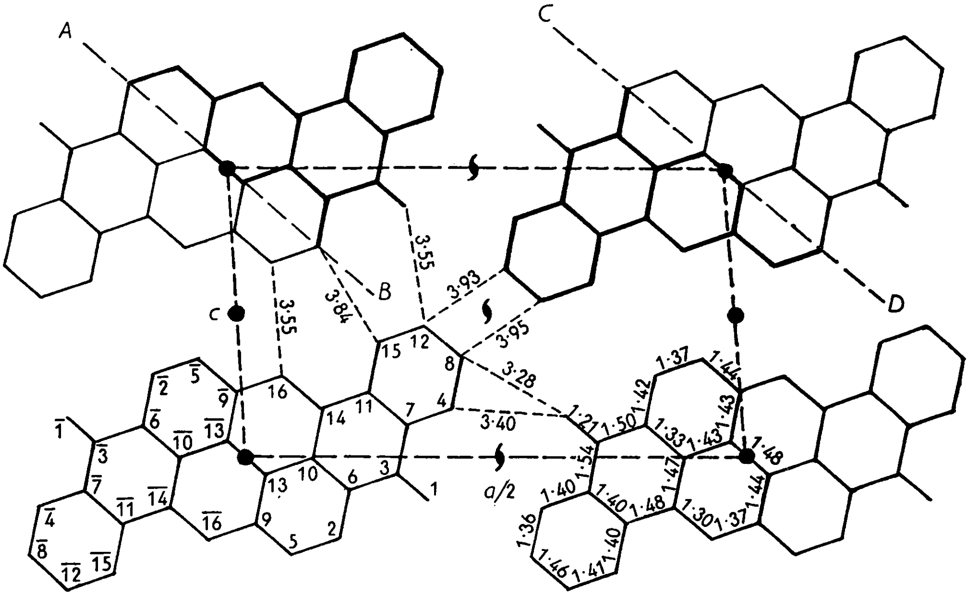


Fig. 3. Diagrammatic representation of the projection of the structure along [010]. Half a unit cell is enclosed in broken lines, the other half being related to it by the centres of symmetry marked by black circles. The positions of the screw axes are also indicated. The broken lines AB and CD are the intersections of the molecular planes with the planes $y = 0$ and $y = \frac{1}{2}$, respectively, and the parts of the molecules above these levels are in heavy outline. The numbering of the atoms is that in Table 2. The shortest distances between atoms of neighbouring molecules are given. Those in successive layers lie between 3·53 and 3·62 Å.

$$0{\cdot}272x - 0{\cdot}907y + 0{\cdot}298z^* = 0\ ,$$

where x, y, z^* are measured along the orthogonal axes $[a]$, $[b]$ and $[c^*]$. This fixes the interplanar distance at 3·44 Å.

The $\{h0l\}$ projection was refined by two successive syntheses and recalculation of structure factors, and two difference syntheses. For the calculation of structure factors only the atoms C, N and O were taken into account. The effect of the six hydrogens in the asymmetric unit $C_{14}H_6ON$ was neglected. The geometrical part of the last set of structure factors was calculated on the Hollerith equipment in the Chemistry Department of the University of Leeds, and it is a great pleasure to acknowledge my indebtedness to Prof. E. G. Cox and his staff for these calculations.

The F_o values were put on an absolute scale by plotting $\log F_c/F_o$ v. $\sin^2\theta$ and using the scale factor determined by the intercept at $\sin^2\theta = 0$. The slope of this plot gave a value of the temperature factor $B = 6{\cdot}26\times10^{-16}$ cm.^{2} and this was used, together with McWeeny's scattering factors (1951), to calculate the agreement factor $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o| = 16\%$ for the final x and z coordinates. These are given in Table 2.

Table 2. *Fractional coordinates*

Atom	x/a	y/b	z/c
O_1	0·179	0·273	−0·171
C_2	0·086	0·004	−0·277
C_3	0·149	0·275	−0·072
C_4	0·204	0·541	0·153
C_5	0·042	−0·128	−0·333
C_6	0·099	0·138	−0·116
C_7	0·158	0·411	0·107
C_8	0·215	0·668	0·309
C_9	0·005	−0·134	−0·220
C_{10}	0·066	0·137	−0·007
C_{11}	0·121	0·401	0·213
C_{12}	0·180	0·674	0·433
C_{13}	0·019	0·003	−0·058
C_{14}	0·073	0·266	0·164
C_{15}	0·135	0·535	0·371
N_{16}	0·040	0·263	0·268

To assess the accuracy of the results, the procedure recommended by Cruickshank (1949) was followed.

By a three-point parabola method, analogous to that described by Booth (1948) for the location of maxima, the curvature of the peaks is found to be

$$\partial^2\varrho/\partial r^2 = (\varrho_1 - 2\varrho_2 + \varrho_3)/r^2$$

with a mean value of -33 e.Å^{-4} for the $\{h0l\}$ projection.

Since β is not very different from 90°, the standard deviation of the coordinates can be written as

$$\sigma(x) = \sigma(\partial\varrho/\partial x)/(\partial^2\varrho/\partial x^2)\ ,$$

where

$$\sigma\left(\frac{\partial\varrho}{\partial x}\right) = \frac{2\pi}{a^2c}\sqrt{\{\sum_h(\sum_l h^2\Delta F^2)\}}$$

with the summation extending over all the planes in the zone, which gave a value of 1·07 e.Å^{-3}. Therefore, $\sigma(x) = 1{\cdot}07/33 = 0{\cdot}032$ Å. The same value was obtained for $\sigma(z)$.

This accuracy does not allow great emphasis to be placed on the bond lengths given in Fig. 3, nor was this structure determination undertaken with this aim in view. The intermolecular distances, however, are of great interest in connection with the thermal decomposition reaction and for comparison with the chemically very similar but structurally different pyranthrone on which work is still in progress.

This investigation forms part of the fundamental research programme of the British Coke Research Association and I am indebted to the Council of the Association for permission to publish this paper. I am grateful to Prof. W. F. K. Wynne-Jones for his encouragement and to Mr H. E. Blayden for some helpful discussions. My special thanks are due to Prof. E. G. Cox for his continued support and interest and to Dr C. M. Thomson for her assistance in the final stages of this investigation.

References

Blayden, H. E., Gibson, J. & Riley, H. L. (1945). *J. Inst. Fuel*, **18**, 117.

Booth, A. D. (1948). *Fourier Technique in X-ray Organic Structure Analysis*, p. 62. Cambridge: University Press.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Donaldson, D. M. & Robertson, J. M. (1949). *Nature, Lond.* **164**, 1002.

Klug, A. (1950). *Acta Cryst.* **3**, 165.

Knott, G. (1940). *Proc. Phys. Soc., Lond.* **52**, 229.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Robertson, J. M. & White, J. G. (1945). *J. Chem. Soc.*, p. 607.

Robertson, J. M. & White, J. G. (1947). *J. Chem. Soc.*, p. 358.

White, J. G. (1948). *J. Chem. Soc.*, p. 1398.

Wilson, A. J. C. (1951). *Brit. J. Appl. Phys.* **2**, 64.