

205. *The Crystal Structure of 9:10-Dihydroanthracene and
9:10-Dihydro-1:2:5:6-dibenzanthracene.*

By JOHN IBALL.

The crystal structure of 9:10-dihydroanthracene and 9:10-dihydro-1:2:5:6-dibenzanthracene has been investigated by *X*-rays. The latter compound crystallises in two distinct monoclinic modifications, and in one of them it is possible to demonstrate the presence in the molecule of a centre of symmetry. If it is assumed that the two naphthalene nuclei are planar, it follows that the whole molecule must be planar, as it possesses a centre of symmetry.

IN a recent paper (this vol., p. 405), Campbell, Le Fèvre, Le Fèvre, and Turner discuss the molecular configuration of 9:10-dihydroanthracene and similar compounds. They show that, although for the completely aromatic compounds a planar configuration is required

according to stereochemical considerations, yet for the reduced compounds such as those described in the present paper a planar molecule is not the most stable form. Several compounds of this type, with the CH_2 groups of 9 : 10-dihydroanthracene replaced by other groups, have been shown previously to possess definite dipole moments. These findings were confirmed by those authors, who also found that the dipole moment of 9 : 10-dihydroanthracene was not zero. Thus there is considerable evidence that this type of compound, at least in solution, has a folded structure in accordance with the requirements of stereochemical theory.

Some measurements on the crystal structure of 9 : 10-dihydroanthracene, started some years ago, have now been completed, and it was thought that if the molecule were folded the departure from a plane model would be accentuated in 9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene, which has been prepared in a pure state by Bachmann (*J. Org. Chem.*, 1936, **1**, 347) by hydrolysis of the disodio-compound of 1 : 2 : 5 : 6-dibenzanthracene. The absorption spectrum of a specimen prepared by this method has been examined by Dr. E. M. F. Roe, who gives the following report (a complete account of the spectra of this and similar compounds will be published by Dr. Roe elsewhere): "The absorption spectrum of the specimen of 9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene used in the crystallographic analysis was naphthalenoid in type, as is the case in the other *meso*-saturated dibenzanthracene derivatives, *cis*- and *trans*-9 : 10-dimethyl- and 9 : 9 : 10 : 10-tetramethyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracenes. It is evident therefore that the anomalous type of spectrum reported previously for 9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene (*Proc. Roy. Soc.* 1935, *A*, **152**, 321) was due to contamination of the sample used."

9 : 10-Dihydroanthracene crystallises in short prisms which have been described by Groth ("Chemische Kristallographie," 1919, **5**) as monoclinic prismatic. If this classification is correct, it is shown from the *X*-ray analysis that the molecule must possess either a plane or a centre of symmetry. However, as shown below, there are serious difficulties in fitting the molecule into the unit cell if the space group is of the prismatic class, so it is probable that the lower of the two possible space groups, in which no molecular symmetry is necessary, is the correct one.

In considering the configuration of the molecule of 9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene, one can assume that the two naphthalene nuclei are planar, and if a model is constructed by using, as far as possible, the usual bond distances and valency angles, it is found that the most stable arrangement is one in which the planes of the two naphthalene nuclei are inclined to each other at about 40° . The single bonds by which the two middle atoms are joined to the naphthalene nuclei permit a limited rotation, and the model can be changed through a planar configuration into a mirror image of the first form. Thus it is possible for the molecule to possess a plane of symmetry in either its folded or its planar form, but it can only have a centre of symmetry when it is planar.

9 : 10-Dihydro-1 : 2 : 5 : 6-dibenzanthracene crystallises in two distinct modifications, both of which are monoclinic. The shape of the crystals is similar in each case, being six-sided thin plates parallel to $\{001\}$, and they show in addition the forms $\{100\}$ and $\{110\}$. One form (i) tends to be slightly elongated along *b*, and the other (ii) along *a*. The two forms are easily identified under the microscope by their different edge angles and by their opposite sign of birefringence. If a solution in ethyl acetate is allowed to crystallise slowly by evaporation then the first form predominates, but if a slightly more concentrated solution is used and crystallised overnight, the second form predominates. Both kinds are usually found in the same batch. The two modifications had the same *m. p.*, $218\text{--}219^\circ$ (uncorr.), and there can be no doubt that they are the same compound, for crystals of one kind when dissolved will recrystallise under the appropriate conditions in the other modification.

In the case of (ii) the space group is $C_{2h}^5\text{-}B2_1/c$, and as there are only 4 molecules per unit cell, each molecule must have a centre of symmetry. This means that the molecule must be planar in this modification. From the *X*-ray data it is not possible to decide whether the form (i) belongs to the space group C_{2h}^5 or to C_4^1 . No pyroelectric effect was observed in these crystals, but a negative result with this test is not conclusive. If the space group is C_{2h}^5 the molecule must possess a centre of symmetry or a 2-fold axis of symmetry; the latter possibility is, however, ruled out by the *X*-ray intensities.

Thus it is shown that in at least one of the two crystalline modifications of 9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene the molecule is planar. For the other modification, and also for 9 : 10-dihydroanthracene, it is not possible without a detailed analysis to decide definitely the molecular symmetry. It is possible that the constraints of the solid form are such as to make the molecules planar but that if they were examined in solution it would be found that they take up the folded configuration.

It will be seen that if the molecules of these compounds are folded as suggested by the evidence of Campbell, Le Fèvre, Le Fèvre, and Turner, the unsymmetrically substituted compounds should be capable of resolution into optical isomers, but, as pointed out by these authors, attempts to resolve similar isomers have been unsuccessful (Bennett, Lesslie, and Turner, J., 1937, 444; Keats, *ibid.*, p. 1592). The fact that the molecule of 9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene can exist in a planar configuration in the solid state suggests that the energy required to transform one isomer into its mirror image is small, and this probably explains why the attempts at resolution were unsuccessful.

EXPERIMENTAL.

9 : 10-Dihydroanthracene.—The crystals of this substance were short prisms showing the forms {110}, {001} and {101}. According to Groth (*op. cit.*), they are monoclinic prismatic with axial ratios, 1.2490 : 1 : 1.7644, $\beta = 113^\circ 41'$. The following angles are also given: $m : m' = (110) : (\bar{1}10) = 82^\circ 20'$; $m : c = (110) : (001) = 74^\circ 40'$; $g : c = (\bar{1}01) : (001) = 71^\circ 30'$. X-Ray analysis gives the following dimensions for the unit cell: $a = 7.70$, $b = 6.21$, $c = 11.09$ Å., $\beta = 113^\circ$; 2 mols. of (C₁₄H₁₂) per unit cell; d (obs.), 1.212 g./c.c.; d (calc.), 1.222 g./c.c. Photographs taken on Weissenberg and on moving-film cameras about each of the above axes showed that the only halving was (0*k*0) halved when k is odd. The space group is therefore either $C_{2h}^2 - P2_1/m$ or $C_2^2 - P2_1$. The crystals show negative birefringence with $\beta = b$ and γ emerging at an angle to (001); the optic axial angle is large. No pyroelectric effect was observed.

If the correct space group is $C_{2h}^2 - P2_1/m$ it would mean that the molecule has either a plane or a centre of symmetry. A centre of symmetry would result in there being one molecule at (000) and a reflected molecule at (0 $\frac{1}{2}$ 0). This is not permissible owing to the short length of b , for even if the molecule is perfectly flat and perpendicular to b , there are only 3.1 Å. between the two molecules. The fact that the optic direction β is along b , and the observed intensities of the (0*k*0) planes show that the molecule cannot be perpendicular to b . The only plane of symmetry which the molecule is likely to possess is one passing through the two middle carbon atoms, and as this plane must be parallel to (010) the length of the molecules (OA; I) would be along b . The length of b is too small to allow this. Thus the correct space group must be $C_2^2 - P2_1$. This space group gives no indication of the molecular symmetry, and without a detailed analysis it is not possible to decide whether the molecule has a planar configuration or one in which the benzene rings are inclined to each other.



9 : 10-Dihydro-1 : 2 : 5 : 6-dibenzanthracene.—*Form* (i). The unit cell of this form has the following dimensions, etc.: $a = 14.24$, $b = 5.27$, $c = 24.90$, d (001) = 18.98 Å., $\beta = 130.2^\circ$; 4 mols. of (C₂₂H₁₆) per unit cell; d (obs.), 1.296 g./c.c.; d (calc.), 1.306 g./c.c. The halvings observed on moving-film photographs were: (hkl) halved when ($h + k$) is odd, and ($h0l$) halved when h or l is odd. The space group is therefore either $C_{2h}^6 - C2/c$ or $C_2^4 - C2$. From the halvings it is seen that the cell is face-centred on the c face, and this was confirmed by taking a rotation photograph about the diagonal of the c face. The crystals show positive birefringence with $\beta = b$, and α is inclined at a small angle to the perpendicular to (001). No pyroelectric effect could be detected when the crystals were cooled in liquid air. This suggests that the correct space group is C_{2h}^6 , but a negative result cannot be taken as decisive.

In the space group $C_{2h}^6 - C2/c$, with only four molecules per cell, the molecule must have either a centre of symmetry or a 2-fold axis of symmetry. The only possible axis of symmetry is

one perpendicular to the mean plane of the molecule, and as this plane would have to be parallel to (010) the reflexions from the (0*kl*) planes should be strong, whereas actually they are absent. Therefore if the correct space group is C_{2h}^2 the molecule must have a centre of symmetry and so would have a planar configuration.

Form (ii). The following are the unit cell dimensions for this crystal form: $a = 9.49$, $b = 6.76$, $c = 24.38$, $d(001) = 22.70$ Å., $\beta = 111.4^\circ$. This cell is face-centred on the b face, but this c axis has been chosen so as to compare this cell with the previous one. (The primitive cell is pseudo-orthorhombic, with a and b as above and $c = 11.34$ Å.; β is now approximately 90° .) The cell chosen contains 4 mols. of $(C_{22}H_{16})$, d (obs.), 1.258 g./c.c.; d (calc.), 1.278 g./c.c. The halvings observed on moving-film photographs taken about each crystallographic axis and about the ac diagonal are: (hkl) halved when ($h + l$) is odd, ($h0l$) halved when h or l is odd, and (0*kl*) halved when k is odd. The space group is therefore $C_{2h}^2 - B2_1/c$. The crystals have a negative sign with $\beta = b$ and γ approximately along c .

In the space group $B2_1/c$ with only 4 molecules per unit cell each molecule must possess a centre of symmetry, and on the assumption that the naphthalene nuclei are planar and that the usual extranuclear valency angles are used as far as possible, the molecule of this compound can only have a centre of symmetry when the whole molecule is planar.

The author thanks Sir William Bragg and the Managers of the Royal Institution for facilities provided at the Davy-Faraday Research Laboratory, where part of this work was carried out, and Dr. H. S. Childs, who prepared and crystallised 9:10-dihydroanthracene. He is also indebted to Professor J. W. Cook, F.R.S., for a specimen of 9:10-dihydro-1:2:5:6-dibenzanthracene, and to the British Empire Cancer Campaign for a grant to the Hospital which has assisted this work.

RESEARCH INSTITUTE, ROYAL CANCER HOSPITAL (FREE),
FULHAM ROAD, LONDON, S.W.3.

[Received, May 10th, 1938.]
