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Crystallographic evidence for non-planarity of 9:10-dihydro-1:2:5:6-dibenzanthracene molecule. By F. H. HERBSTEIN, *National Physical Research Laboratory, Council for Scientific and Industrial Research, Pretoria, South Africa*

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The crystal structure of 9:10-dihydro-1:2:5:6-dibenzanthracene has recently been analysed by Iball & Young (1958) by two-dimensional methods (space group $P2_1/a$; molecular symmetry $C_i - \bar{1}$; $R(0kl) = 0.121$, 108 reflexions; $R(h0l) = 0.156$, 130 reflexions; $R(hk0) = 0.151$, 77 reflexions). Iball & Young calculated (by the method of least-squares) that the mean plane of the molecule was given by:

$$0.7677x' - 0.3835y' - 0.5135z' = 0. \quad (1)^*$$

The orthogonal axes x' , y' , z' were taken along a , b and d_{001} respectively. It was pointed out that the essential planarity of the molecule was not 'in accord with predictions from normal stereochemical considerations.' The unexpected molecular conformation has been explained elsewhere (Herbstein, 1959) as caused by the need to minimize the repulsion between the *lin* hydrogen attached to carbon A and that attached to carbon D , and similarly for the hydrogens at A' and D' (Fig. 1). These repulsions

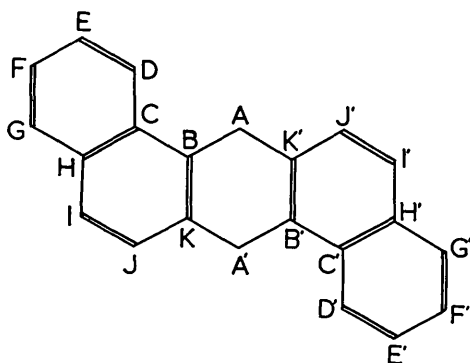


Fig. 1. Nomenclature of atoms.

would be greater in a folded molecule. In terms of these somewhat rough calculations the molecule would be expected to be planar.

A closer examination of Iball & Young's results shows that the perpendicular distances of some atoms from plane (1) (see column 1 of Table 1) are significant. In addition these displacements appear to be systematic: atoms B , C , K are significantly above the mean molecular plane and atoms F and G significantly below. The possibility therefore exists of a systematic deviation of the molecular shape from strict planarity.

One possible description of the molecule is that it has a zigzag (or biplanar) structure, with planar 'naphthalene' groupings inclined at small angles to a planar central ring. As the molecule is centrosymmetric the two 'naphthalene' groupings must be parallel. The experimental coordinates of the carbon atoms (Iball & Young, 1958) have been

* This equation differs slightly from that given by Iball & Young; it has been recalculated by electronic computer and a misprint in the coefficient of z' has been corrected.

Table 1. *Perpendicular distances Δ_i (in Å) of atoms from planes given in text*

Standard deviation $\sigma(X_i) = 0.013$ Å by Cruickshank's (1949) method

Atom	Plane (1)	Plane (2)	Plane (3)
A	0.001	-0.000 ₈	(0.087)
B	0.047 (c)	0.000 ₉	-0.014
C	0.081 (c)	—	0.050 (c)
D	0.011	—	-0.021
E	0.019	—	0.015
F	-0.059 (c)	—	-0.028 (a)
G	-0.039 (b)	—	-0.005
H	0.010	—	0.015
I	0.005	—	0.014
J	0.005	—	-0.016
K	0.044 (c)	-0.000 ₈	-0.010
$10^3 \sum_i \Delta_i^2$	16.19	0.002	4.98*
R.m.s. displacement	0.039	0.000 ₈	0.022*

* Excluding atom A .

Displacement significant at 5% level ($\Delta/\sigma > 1.645$) shown by (a), at 1% level ($\Delta/\sigma > 2.327$) by (b), and at 0.1% level ($\Delta/\sigma > 3.090$) by (c).

used to test this hypothesis, with the following results: the central ring $ABKA'B'K'$ is planar, its equation being

$$0.7509x' - 0.3754y' - 0.5433z' = 0. \quad (2)$$

The r.m.s. displacement from (2) is 0.0008 Å, the actual displacements being given in column 2 of the table. The 'naphthalene' groupings are nearly planar, the equation for atoms $BCDEFGHIIJK$ being

$$0.7773x' - 0.3935y' - 0.4909z' + 0.0912 = 0. \quad (3)$$

The r.m.s. displacement is 0.022 Å, and C is the only atom that is significantly displaced from (3) ($\Delta/\sigma = 3.85$) (see column 3 of Table 1). The zigzag model of the centrosymmetric molecule consists of a planar central six-membered ring to which two parallel, planar 'naphthalene' groupings are attached. These 'naphthalene' groupings make angles of $176^\circ 28'$ with the central ring; the perpendicular distance between the planes of the 'naphthalene' groupings is 0.18 Å.

The F test (e.g. Kenney & Keeping, 1956) was applied to the variances (i.e. $\sum_i \Delta_i^2$, where Δ_i is the perpendicular

distance of atom i from the plane considered) calculated for the two molecular models; this showed that the smaller variance found for the zigzag model as compared to the planar model was significant at the $2\frac{1}{2}\%$ level. A more complex model, in which the six-membered rings $ABKA'B'K'$, $BCHIIJK$ and $CDEFGH$ were taken to be planar but not necessarily coplanar, gave better agreement with the experimental results, there being no significant displacement from the planes of the rings. However the F test showed that the improvement on the zigzag model was not significant.

The conclusion to be drawn from these calculations is that the zigzag model of the molecule fits the *experimental atomic coordinates* better than the planar model given by Iball & Young, and that there is less than one chance in forty that this improvement in fit is fortuitous. More accurate experimental results are needed before a decision can be made between the simple zigzag model discussed above or a more complex one. It is also not clear at present whether the deviation from a planar shape is a property of the free molecule or whether this should be ascribed to packing effects. Results from a three-dimensional analysis now in progress (Iball, 1960) should help to settle these points.

The method used for fitting planes to various sets of atomic coordinates by least squares was that given by Schomaker, Waser, Bergmann & Marsh (1959). Its use in the present problem has been facilitated by a pro-

gramme prepared for the Stantec Zebra electronic computer in our laboratory by Mr G. J. Rudolph, whose assistance is greatly appreciated. I am also indebted to Prof. A. J. B. Wiid, Mr C. R. Troskie and Mr G. Gafner for helpful discussions and to Dr J. N. van Niekerk for his interest in this work.

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Comments on the properties of triglycine sulfate. By A. D. BALLATO, *U.S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey, U.S.A.*

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A recent paper by Konstantinova, Sil'vestrona & Aleksandrov (1959) has described the preparation and measurement of triglycine sulfate, where the piezoelectric strain constants $d_{i\mu}$ were obtained by the resonance-anti-resonance method using ϵ^S , the clamped dielectric constant.

Bechmann (1954) has shown that in this case the $d_{i\mu}$ must be computed using ϵ^m , the effective dielectric constant for the mode considered. Since only in the measurement of d_{16} , d_{34} , and d_{22} where thickness shear vibrations are used, can the effective dielectric constant be considered that at constant strain, the determination of the remaining $d_{i\mu}$ must be considered subject to a greater factor of uncertainty than the authors give.

This uncertainty is not so great for d_{14} and d_{36} as it is for d_{21} , d_{23} , and d_{25} since contour modes were used for the former and longitudinal vibrations for the latter. The magnitude of error cannot be calculated because of the paucity of data given, but an estimate may be made using the curves showing the vibration of the dielectric constant ϵ_{22} as a function of frequency for various values of field strength. The curve corresponding to lowest field strength shows a variation of greater than ten to one over the range of frequencies which correspond to the dielectric constants ϵ^T and ϵ^S . The effective piezoelectric constant ρ is proportional to $1/\epsilon$, and so could vary by more than three to one; however, since ϵ^m is between ϵ^T and ϵ^S , this figure gives only an upper bound. The actual error is probably small for all constants with the exceptions noted above.

It should also be pointed out that some of the values for the compliances s^D calculated from the stiffnesses measured by the ultrasonic method are incorrect. The proper values are given below; the calculations were

carried out on the Burroughs Datatron 220 computer in use at this Laboratory, using a matrix inverting program based on the Crout procedure (Hildebrand, 1952).

Table 1. *Elastic compliances s_{ik} for triglycine sulfate*
 Computed from data of

V. P. Konstantinova, I. M. Sil'vestrona & K. S. Aleksandrov.

Elastic compliances	Values
	10^{-13} cm. ² /dyne
s_{1k}	
s_{11}	32.9
s_{22}	69.8
s_{33}	108.5
s_{44}	105.4
s_{55}	107.3
s_{66}	161.5
s_{23}	-57.7
s_{13}	-22.7
s_{12}	-2.9
s_{15}	-1.4
s_{25}	-24.5
s_{35}	40.9
s_{46}	4.4

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