

- (i) $|V_h + V_{h'}| = 2|V_{211}|, |V_h - V_{h'}| = 0,$
 (ii) $|V_h + V_{h'}| = 0, |V_h - V_{h'}| = 2|V_{211}|,$

so that we can expect that the intensity relation between the two vertices of the hyperbola is reversed for the two cases. This is verified experimentally very well, as shown in Figs. 1 and 2. In case (i), the vertex lying inside both of the Kikuchi bands ($2\bar{1}\bar{1}$) and ($3\bar{1}\bar{2}$) (A_+ in Fig. 2) is actually found to be strengthened. Whereas in case (ii) the outside vertex (A_- in Fig. 2) is strengthened. It is seen that the bright lines appearing in the diffracted spots behave in a corresponding manner. By observing such effects, the relative sign of the two structure amplitudes can be determined uniquely.

We see in Fig. 1 that an intensity distribution similar to that of the extinction lines in the primary spot is found at the crossing point of Kikuchi lines which lies outside the diffraction spots (indicated by an arrow). In fact, by applying our scheme given in Parts I and II

to the theory of Kikuchi pattern (Laue, 1935; Kainuma, 1954) we find that a similar effect of the phase-angle relation is expected in the intensity distribution of Kikuchi patterns. This effect can be observed also at the crossing points of Kikuchi lines in reflexion patterns from natural and cleavage faces.

I wish to thank Prof. Shizuo Miyake for his guidance throughout this work.

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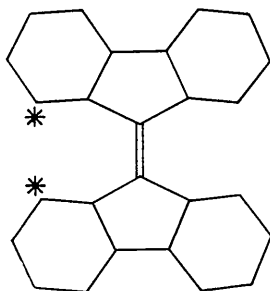
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Steric hindrance in the dibiphenylene-ethylene molecule. By S. C. NYBURG, *Department of Chemistry, University College of North Staffordshire, Keele, England*

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The crystal structure of dibiphenylene-ethylene (bifluorene) has been subject to partial three-dimensional analysis by Fenimore (1948), who concluded that the X-ray data were satisfactorily accounted for by centrosymmetric, essentially planar molecules.



In the planar molecule, the distance between starred carbon atoms would be only 2.5 Å and although, as pointed out by Fenimore, there is chemical and spectroscopic evidence indicative of steric interaction here, there is the more serious problem of the hydrogen atoms attached to the conflicting carbon atoms. Assuming the C-H bond to be 1.0 Å in length and coplanar with the rest of the molecule, the distance between hydrogen centres is only 0.7 Å. The van der Waals diameter for hydrogen is about 2.4 Å and it is evident that unless the C-H bonds are severely bent out of plane the steric repulsion should disturb the molecular planarity. Attention has also been drawn to this by Bell (1952) in connexion with the possibility of producing stereoisomeric derivatives.

The crystallographic data, according to Fenimore, are:

System: orthorhombic.
 $a = 17.22, b = 36.9, c = 8.23$ Å.

Space group: *Pcan*, uniquely determined.
 $Z = 12$.

Four of the molecules are centred on special repeats of that at the origin and are necessarily centrosymmetric. The remaining eight are centred on general repeats of that at approximately $(\frac{1}{2}, \frac{1}{8}, 0.434)$ and, although not required to be centrosymmetric, were assumed to be so.

All the molecules lie close to (031) and (0 $\bar{3}$ 1) planes so that it is the x projection which is critical in deciding the planarity question. Fenimore's analysis of this projection was two-dimensional and the resolution too poor for this question to be settled with certainty. A (0 $\bar{3}$ 1) section of the molecule at the origin was fairly well resolved, but again this is not decisive evidence for or against strict planarity.

Accordingly, it was decided to use all Fenimore's F_o 's and calculated phases to analyse the structure further by three-dimensional x sections.

Fig. 1(a) shows superimposed x sections chosen to pass through (or nearly through) the atoms in the region of the origin. As far as the (left-hand) molecule at the origin is concerned, resolution was sufficiently good to fix the coordinates with reasonable certainty. Resolution on the other molecule, which with Fenimore's parameters is centred on $(0, \frac{1}{8}, \frac{1}{2} + 0.434)$, was not quite so good. This was certainly due to some extent to the fact that the orientation is not exactly that proposed. All the sections for this molecule were consistent with it being rotated slightly in the (031) plane so that the x coordinates of atoms C_{11} and C_{12} are closer to 0.040 than to 0.048 and 0.058 respectively.

Fig. 1(b) shows the positions of some of the atoms derived from the corresponding sections. Regardless of imperfect resolution in specific instances, the results can be unambiguously interpreted.

The molecules are, within the imposed limits, identical

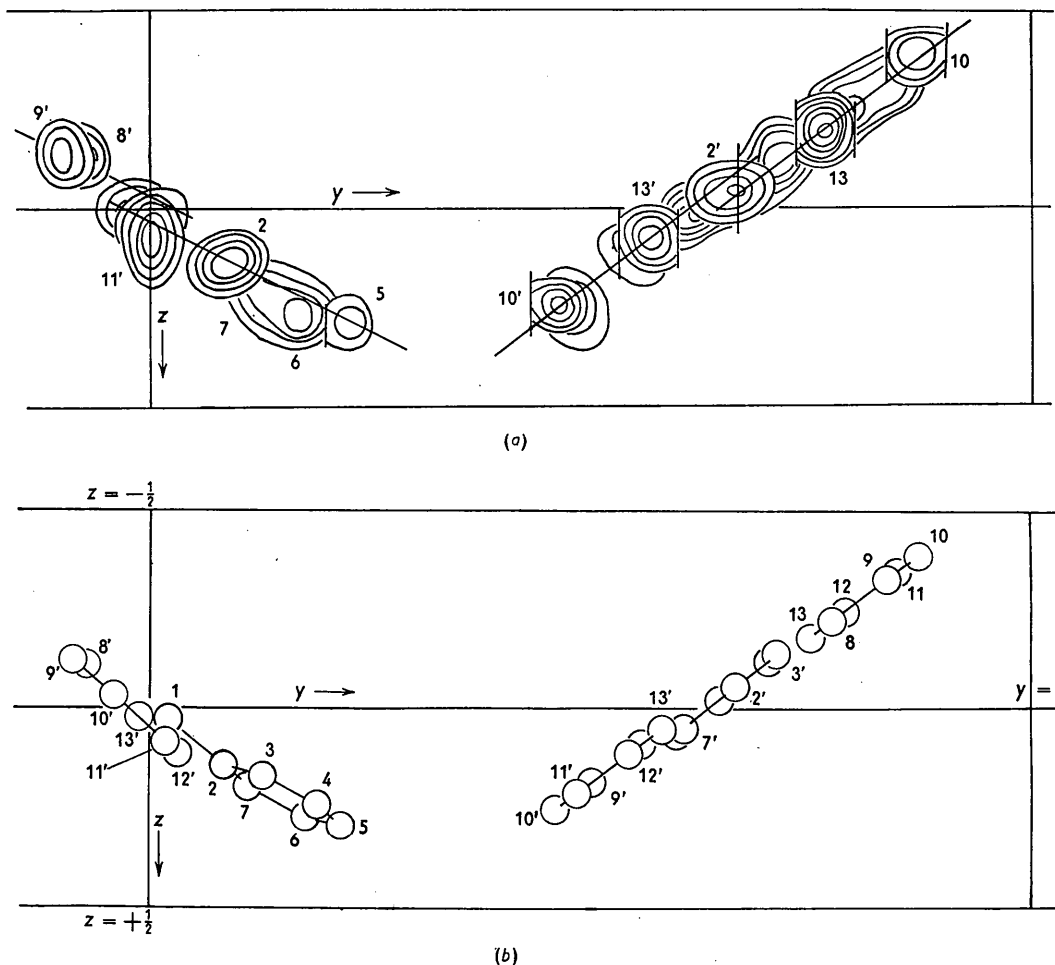


Fig. 1. (a) Sections parallel to the bc plane looking towards $+x$. (b) Positions of the atoms.

in configuration and of the form shown in Fig. 2. Steric repulsion at the hydrogen atoms causes two distortions from planarity. First, a tilting of the phenylene nuclei about an axis parallel to the C_7-C_8 bonds, and secondly bending of the benzene rings up and down about the C_2-C_7 and the C_8-C_{13} bonds. The extent of the bending cannot be fixed with certainty, but is about 10° in both cases.

One feature of the distortions which can be immediately seen on the $x = 0$ section is the failure of lines joining C_2C_5 and C_2C_5' to intersect at the molecular centre. This is shown by heavy lines in Fig. 1(a) and by broken lines in Fig. 2.

The molecule is seen to possess a plane of symmetry,

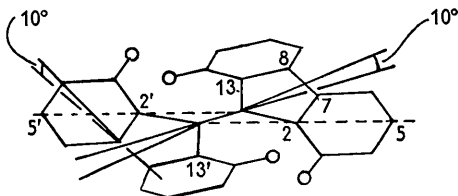


Fig. 2. Form of the molecule, showing conflicting hydrogen atoms.

and is thus not enantiomorphous. However, suitable derivatives disubstituted for example at C_5' and at C_9 should, as proposed by Bell, be resolvable. The deep red colour of the parent substance and of derivatives is, however, a serious experimental handicap to the detection of what is probably only a small optical activity.

Oscillation photographs of dibiphenylene-ethylene show diffuse extra layer lines and these led Taylor (1935) to assign a cell having twice the a repeat. The cause of these diffuse lines is not known but it is tempting to suggest that they are caused by the occasional location of a molecule with the wrong 'sense', i.e. with the benzene rings which should be tilted 'up' replaced by rings tilted 'down'. A full discussion of this and the stereochemical details must await a fully refined analysis.

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