The Crystal Structure of a Heterohelicene

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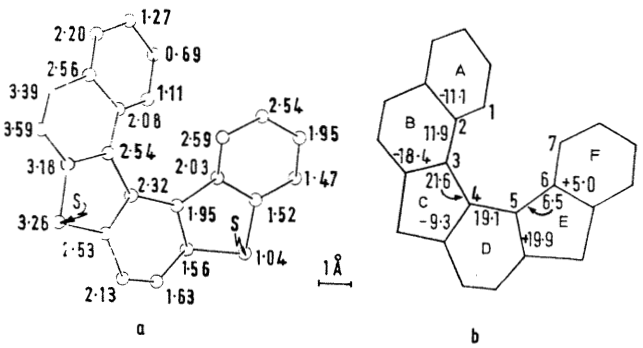
Summary The crystal structure of benzo[*d*]naphtho[1,2-*d'*]benzo[1,2-*b* : 4,3-*b'*]dithiophen has been determined.

THE structures of helicenes and heterohelicenes[1] have aroused considerable interest. We give here a preliminary account of the structure of one of these compounds, *viz.* benzo[*d*]naphtho[1,2-*d'*]benzo[1,2-*b* : 4,3-*b'*]dithiophen, as found by *X*-ray diffraction.

The compound and the crystals were prepared by Wynberg and Groen.[1b] The crystals are monoclinic, space group $P2_1$, $Z = 2$. The cell dimensions at 115° K are: $a = 10{\cdot}896$, $b = 8{\cdot}207$, $c = 9{\cdot}444$ Å, $\beta = 111{\cdot}74°$. The intensities of 2376 independent reflections measured at 115° K on an automated Nonius diffractometer with Zr-filtered Mo radiation were used in elucidating the structure. In the present stage of the least-squares refinement $R = 0{\cdot}14$. The thermal parameters indicate the presence of some disorder which has to be studied further. The structure of the molecule is shown in the Figure.



FIGURE

Structure of a heterohelicene molecule

(a) *Projection of the molecule on the* (010) *plane. The relative heights of the atoms are given in* Å.

(b) *Numbering of some of the atoms and dihedral angles for the 'helix'* 1—7. *At bond* 2–3 *the angle* 123 ∧ 234 *is given* etc. *The angles between the successive planes* (*see text*) *are given in degrees at the lines of intersection of the planes.*

It is impossible for the molecule as a whole to be planar as this would make the distances between the carbon atoms of the terminal rings A and F impossibly small. Nevertheless the individual benzene and thiophen rings in the molecule do not deviate much from planarity. The deviations of the atoms from the best planes through the rings range from 0·00 to 0·08 Å. The bond lengths and angles in the rings do not show significant deviations from those observed in benzene or thiophen molecules.

The conformation of the molecule may be described by considering the angles between the successive best planes through the rings. It appears that in three cases the angle between the normals of two successive planes is negative [indicating that the normals have their point of intersection below the molecule of (b) in the Figure], but in two cases (for D∧E and E∧F) a positive angle is found. The angles between the planes vary from −18·4 to +19·9°. The atoms 1—7 form an irregular helix. The irregularity in this helical structure is reflected by the variation in the dihedral angles at the bonds 2–3—5–6 [Figure (b)], for which angles equal values would have been expected in the case of a regular helix.

The conformation of the molecule results in quite large distances between the atoms of the rings A and F. The shortest distance, 1–7 (2·91 Å) is 0·3 Å smaller than the sum of the Van der Waals radii of two CH_2 groups.[2] The observed value is in good agreement with the value of 3 Å predicted for the corresponding shortest distance in hexahelicene.[3]

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[1] (a) H. Wynberg and M. B. Groen, preceding communication. (b) H. Wynberg and M. B. Groen, *J. Amer. Chem. Soc.*, 1968, **90**, 5339, and refs. cited therein.

[2] L. Pauling, "The Chemical Bond," Cornell University Press, Ithaca, N.Y., 1967.

[3] M. A. Herraez Zarza and F. Sanchez, *Anales Real Soc. espaň. Fis. Quim.*, 1965, **61**, *B*, 953.