The Crystal Structure of Hexahelicene

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Summary The crystal structure of the 1 : 1-hexahelicene–4-bromo-2,5,7-trinitrofluorenone complex has been solved.

HEXAHELICENE (phenanthro[3,4-*c*]phenanthrene) was first synthesised by Newman and Lednicer.[1] The precise conformation of this severely overcrowded aromatic molecule can only be determined by X-ray crystal analysis, and to facilitate this work Professor Newman kindly supplied us with good crystals of the 1 : 1-hexahelicene–4-bromo-2,5,7-trinitrofluorenone complex (Figure 1).
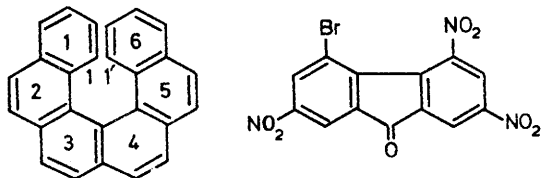

FIGURE 1

The crystals are triclinic, space group $P\bar{1}$, with four molecules of $C_{26}H_{16} : C_{13}H_4O_7N_3Br$ in a unit cell of dimensions $a = 9.30$, $b = 20.63$, $c = 18.90$ Å, $\alpha = 114.9$, $\beta = 93.7$, $\gamma = 98.7°$. There are therefore 100 non-hydrogen

atoms in the asymmetric crystal unit. Some 6300 independent structure amplitudes were evaluated from intensity data estimated visually from Weissenberg photographs, and the positions of the two bromine atoms were obtained from an analysis of the Patterson function. From this starting point, successive structure factor calculations and three-dimensional Fourier syntheses gradually revealed the positions of all the other non-hydrogen atoms. The value of R is now 19%, and refinement by least-squares methods has commenced.

In the unit cell of the complex two of the four hexahelicene molecules are the left-handed enantiomer and two are right-handed, each of the former being related to the latter through the centre of symmetry. Each 4-bromo-2,5,7-trinitrofluorenone molecule is sandwiched between two hexahelicene molecules with the three rings of the former compound lying nearly parallel to rings 1, 2, 3 and rings 4, 5, 6 of the two adjacent hexahelicene molecules (Figure 1) at approximately van der Waals separation distances.

The results of our analysis at this stage show clearly that the hexahelicene structure is achieved with little deviation from the values expected for bond lengths and angles in benzene rings. The distortion from planarity which is

required of the individual rings is not uniformly distributed as is shown by the root-mean-square distance of the atoms from the best plane through each benzene ring (Figure 2). The dihedral angles between the best planes of neighbouring rings are also shown in Figure 2 at the ring junctions.

The distance between the closest pair of non-bonded carbon atoms (1 and 1' in Figure 1) is 3·05(4) Å, which is in good agreement with the value of 3·004 Å obtained from theoretical calculations[2] and is significantly less than the value predicted from the van der Waals radii of two CH_2 groups. In the recently reported structure of a hetero-helicene, benzo[d]naphtho[1,2-d']benzo[1,2-b : 4,3-b']dithio-phen, [3] in which benzene rings 3 and 5 of hexahelicene are replaced by thiophen rings, the corresponding separation distance was found to be 2·91 Å.
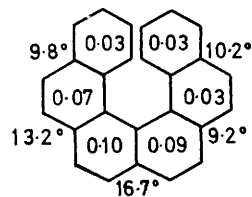
FIGURE 2

[1] M. S. Newman and D. Lednicer, J. Amer. Chem. Soc., 1956, 78, 4765.
[2] M. A. Herraez Zarza and F. Sanchez, Anales Real Soc. españ., Fís. Quím, 1965, 61 B, 953.
[3] G. Stulen and G. J. Visser, Chem. Comm., 1969, 965.