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On the crystal and molecular structure of fluorene.

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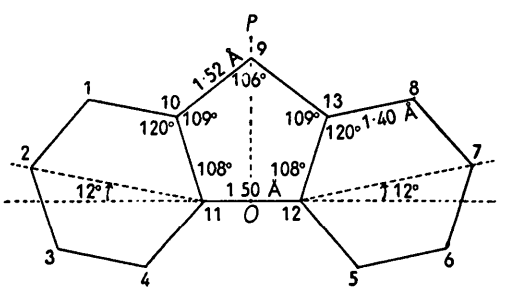
According to the X-ray analysis of crystalline fluorene by Iball (1936), the two six-membered rings in the fluorene molecule are each tilted up about 20° out of the plane of the five-membered ring. In contrast, recent stereochemical (Weisburger *et al.*, 1950) and ultra-violet spectroscopic (Merkel & Wiegand, 1947, 1948) studies on fluorene and an X-ray analysis (Fenimore, 1948) of the closely related bifluorene (dibiphenylene-ethylene) molecule indicate a uniplanar structure for the fluorene carbon skeleton. Since the details of the fluorene structure are of some interest from the point of view of valence theory and chemical reactivity (Lothrop, 1939) and in relation to carcenogenicity of fluorene derivatives (Miller *et al.*, 1949; Sandin *et al.*, 1952), a new X-ray analysis of fluorene has been undertaken in this laboratory.

Crystals of fluorene have been found to be orthorhombic, of space group *Pna* or *Pnam*, with four molecules per unit cell, and with $a = 8{\cdot}50$, $b = 5{\cdot}71$, $c = 19{\cdot}00$ Å, in essential agreement with the data of Iball. With the use of the Weissenberg multiple-film technique and Cu $K\alpha$ radiation, data have been obtained for the zero and higher layers for rotations about the three principal axes. In all, 210 reflections have been recorded and their intensities estimated visually, the number being limited so far because of difficulties in preserving the volatile crystal specimens. Limited success in preserving the crystals was attained by coating them with diluted colorless nail polish.

The distribution of peaks in a Patterson projection [010] strongly suggested space group *Pnam*. The planar model below (similar to Iball's first trial structure and to Fenimore's model for half the bifluorene molecule) was adopted. Satisfactory preliminary agreement between calculated and observed structure factors for the reflections of the three principal zones was obtained for a structure having the model molecule oriented parallel to z with the point O at $x/a = 0{\cdot}353$, $y/b = 0{\cdot}431$, $z/c = 0{\cdot}250$, with an angle of 30·5° between the line OP and the y axis. The reliability factor $\Sigma(||F_o| - |F_c||) \div \Sigma|F_o|$ was 0·22. The value of B in the temperature factor was $4{\cdot}6 \times 10^{-16}$ cm².



Electron-density projections [100], [010], and [001] were computed using X-RAC. The [100] projection shows each molecule, but not each atom, resolved. In the [010] projection carbons 2, 3, 7, 8, 10, 11, 12, and 13 are clearly resolved, and their positions show the approximate correctness of the angular orientation of the benzene nuclei as given in the model. In the [001] projection, each molecule is seen edgewise as one link in a zigzag chain. The shape and distribution of contours in this projection are consistent only with a structure in which deviations from uniplanarity are no more than trivial.

The essential correctness of the proposed planar structure of fluorene is regarded as established. The process of refinement is being carried out, and efforts are being made to record more of the 1090 reflections theoretically accessible using Cu $K\alpha$ radiation, in the hope of achieving a very accurate structure determination.

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