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THE CRYSTAL AND MOLECULAR STRUCTURE OF 11,11-DIFLUORO-1,6-METHANO-[10]-ANNULENE

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In recent years, the chemistry of aromatic 10-π-electron systems has been extensively developed by Vogel and co-workers (1,2,3). A point of particular interest has been the study of the influence of bridge substituents on the hypothetical equilibrium between 1,6-methano-[10]-annulene and bis-norcaradiene. From n.m.r. spectra and chemical evidence it has been concluded that the difluoro-derivative is in the annulene form, whereas the dimethyl-derivative has a bis-norcaradiene skeleton.

To compare the geometries of the two valence isomers, the determination of the crystal and molecular structure of these two compounds has been undertaken in this Laboratory. In the present work, the data for the difluoro-derivative are communicated.

11,11-difluoro-1,6-methano-[10]-annulene, m.p. =122-123°C, crystallizes in the orthorhombic system, space group $Pna2_1$ (C_{2v}^9,N°33), with cell parameters <u>a</u> =9.233, <u>b</u> =13.235, <u>c</u> =7.055 (±0.001) Å, Z =4.

For structure determination and refinement, 856 independent reflexions were collected by Cu K_α multiple-film Weissenberg technique (out of 985 present in the Cu K_α sphere) and visually measured. Of these reflexions, 220 were too weak to be observed ('less than'). The solution of the structure was obtained in two steps. First, the orientation of the molecule with respect to crystallographic axes was determined by an automatic comparison between the three-dimensional Patterson synthesis around the origin and the intramolecular vectors of a plausible model, as a function of three Eulerian angles; the second step consisted in calculating packing energy as a function of molecular position in the unit cell: a sharp minimum corresponded to the correct structure. Refinement was carried on by least squares: in the last cycles anisotropic temperature factors were assigned to carbon and fluorine atoms. The hydrogen atoms were found by a difference Fourier synthesis and were introduced only in structure-factor calculations. The final R factor for all observed reflexions is 7.7%.

The conformation of the molecule is shown in Fig.1; all bond distances and angles are given here as average of 'equivalent' ones, assuming <u>mm2</u> symmetry. The difference between each bond distance and angle and these averages is always less than twice the standard deviation (for each C-C or C-F distance $\sigma = 0.03$ Å; for each C-C-C or C-C-F angle $\sigma = 1.5°$).

The annulene ring is not planar, in agreement with previous data (4); the atoms C(2), C(3), C(4), C(5) and C(1), C(6), C(2), C(5) or equivalents form planar groups. The dihedral angle between these two planes is 15°; the angle between the latter plane and its symmetrically equivalent is 42°. The distance C(1)-C(6) is 2.22 Å and the angle C(1)-C(11)-C(6) is 100°: these values compare closely with those obtained for 1,6-methano-[10]-annulene-2-carboxylic acid (2.257 Å and 99.6°) for which the annulene structure has been established beyond any doubt.

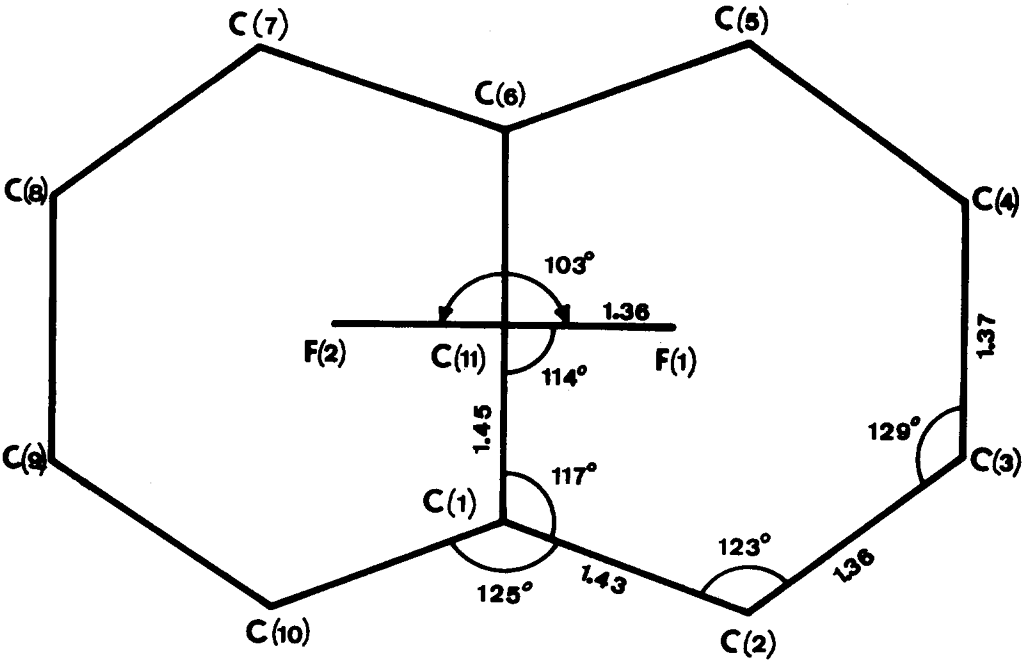

Fig.1 - Average bond distances (Å) and angles in the molecule of 11,11-difluoro-1,6-methano-[10]-annulene

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