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THE STRUCTURE OF A CROWDED FULVALENE.
1-METHYL-2-FLUORENYLIDENE-1,2-DIHYDROPYRDINE

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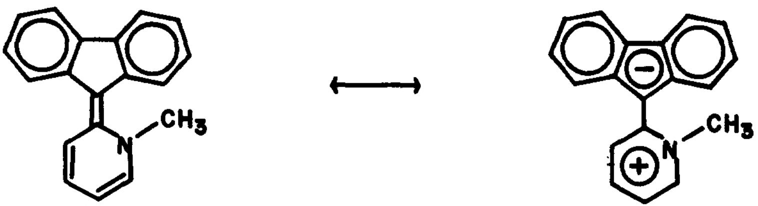
The bond characteristics in fulvenes (e.g. I) and fulvalenes (e.g. II) can be qualitatively described as resulting from the mesomeric superposition of canonical forms Ia (IIa) and Ib (IIb) (1). Although π-electron delocalization is inherent in the charge separated structures, most of the available experimental evidence (2) and recent theoretical work (3) support the idea that these hydrocarbons are characterized by strong bond fixation and small resonance energies. It should be possible to increase the contributions of dipolar structures to the ground state resonance hybrid by the introduction of heteroatomic substituents capable of stabilizing either the + or - charge.

Ia Ib IIa IIb

We have undertaken an X-ray crystallographic investigation of the title compound (III). This material, which is iso-π-electronic with the dibenzo derivative of sesquifulvalene(II), provided the opportunity to determine if



IIIa IIIb

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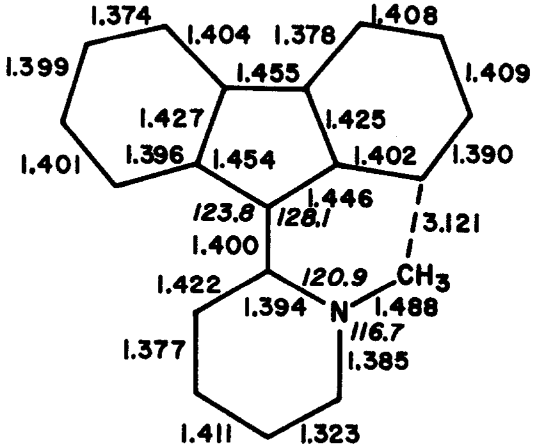
severe intramolecular crowding (4) could result in appreciable charge separation (e.g. IIIb) in the ground state (5). Our preliminary results are reported in this communication.

A sample of III was obtained from Dr. E. M. Evleth. The compound crystallizes in the orthorhombic space group Pbca with unit cell parameters of $\underline{a}$ = 16.68, $\underline{b}$ = 17.32, and $\underline{c}$ = 9.49 Å. Crystal density measurements were consistent with eight molecules per cell. Three-dimensional X-ray diffraction data were collected with CuKα radiation on a Weissenberg camera and the film intensities were measured with a microdensitometer. The structure was solved by the symbolic addition procedure and has been refined with full matrix least-squares to an $\underline{R}$ index of 0.094.

Bond lengths (Å) and a few angles (°) are shown in the accompanying drawing. The inter-ring bond length (C(2)-C(9') = 1.400 Å), which is long for a formal double bond, and distances in the dihydropyridine ring show the effects of electron delocalization. The C(5)-C(6) distance is normal for an ethylenic linkage.



The fluorenylidene ring shows only slight deviations from planarity with an angle of 6° between the planes of the two benzene rings. This feature is substantially different from the "butterfly" shape observed in several crowded anthrones (6) and in tetrabenzopentafulvalene (7). There are small, but significant, deviations from planarity in the dihydropyridine moiety and the mean plane of the six atoms intersects the central five atom plane of the fluorenylidene group at an angle of 38°. The exocyclic bond angles at C(9') and N show the effects of the methyl group-benzene ring crowding.

We believe that the bond lengths and molecular conformation offer evidence for π-electron delocalization. Further studies to obtain dipole moment and rotational barrier data for this compound and several derivatives are in progress.

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