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THE SPATIAL STRUCTURE OF TETRABENZO[5,7]FULVALENE[1]

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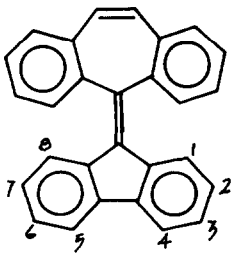
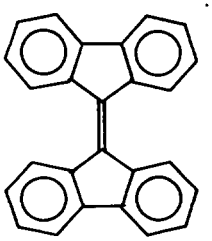
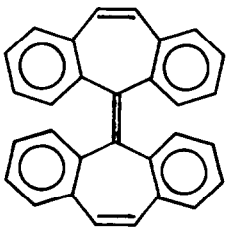
Tetrabenzo[5,7]fulvalene (I),[2] the first known stable "mixed" fulvalene derivative, has so far received little attention. Its experimental dipole moment (0.83 D) reflects a negligible contribution of the "aromatic" dipolar structure (Ia) in the ground state. Undoubtedly, the "fulvenic" properties of (I) are obscured by the heavy annelation. In an attempt to shed light upon the spatial structure of (I), we undertook a detailed study of its nmr spectrum. Previously we have shown that the nmr chemical shifts of the protons ortho to the "pinch" (hereafter "ortho" protons), may serve as a probe for evaluating the conformations of tetrabenzo[5]-fulvalene (II)[3] and trans-tetrabenzo[7]fulvalene ((E)-III).[4,5] The low field absorption of the "ortho" protons of (II) (δ, 8.38 ppm) indicate only a small deviation from planarity and a twist of the "pinch" which still permits significant interactions between the bucking "ortho" protons. By contrast, the shielding of the "ortho" protons of ((E)-III) (δ, 6.58 ppm) indicate a transoid non-planar conformation in which each "ortho" proton lies above (or below) the plane of the opposing aromatic ring of the other half of the molecule. As (I) holds (formally) an intermediary position between (II) and ((E)-III), the chemical shifts of the "ortho" protons of (I) may reveal whether spatially, (I) resembles (II) or ((E)-III).



I



II



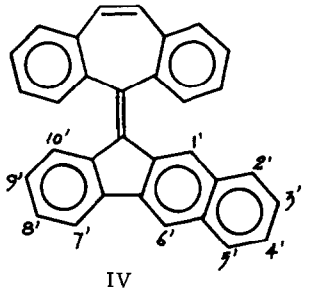
III

The nmr spectrum of (I) (in $CDCl_3$)[8] contains the following signals: δ = 6.45 (dt, J_1 = 8 Hz, J_2 = 2 Hz, 2H), 6.90 (dt, J_1 = 8 Hz, J_2 = 2 Hz, 2H), 7.03 (s, 2H), 7.22 (dt, J_1 = 8 Hz, J_2 = 2 Hz, 2H), 7.37-7.73 ppm (m, 10H). The absence of any absorption at the low field of the aromatic region (below 8.0 ppm) rules out any possible resemblance between (I) and (III). Furthermore, in contrast to ((E)-III), the high field double doublet (at 6.45 ppm) represents not four but only two "ortho" protons. A priori, this absorption may be attributed to the "ortho" protons of either the fluorene moiety or the 5H-dibenzo[a,d]cyclohepten moiety of the molecule. The correct assignment was concluded from the nmr spectrum of the analogous system 5-(11H-benzo[b]-fluorenylidene)-5H-dibenzo[a,d]cycloheptene (IV).

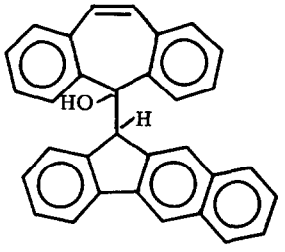
The synthesis of (IV) was carried out in the following manner: Treatment of the deep purple 11H-benzo[b]fluorenyl lithium (from the hydrocarbon and butyl lithium) with 5H-dibenzo[a,d]cyclohepten-5-one in ether-benzene solution under helium afforded 5-(11'-(11'H-benzo[b]fluorenyl))-5-hydroxy-5H-dibenzo[a,d]cyclohepten (V) as colourless needles, mp 280° (from toluene). ν (nujol) 3570 cm^{-1} (OH). Anal. Calcd. for $C_{32}H_{22}O$: C, 90.96; H, 5.25. Found: C, 91.20; H, 5.02. Dehydration of (V) by boiling acetic anhydride containing (2%) sulfuric acid led to the desired hydrocarbon (IV), obtained as pale yellowish needles, mp 275° (from methylcyclohexane) (mixed mp of (IV) and (V), 260°). Anal. Calcd. for $C_{32}H_{20}$: C, 95.02; H, 4.98. Found: C, 95.00; H, 5.23. uv, $\lambda_{max}^{Cyclohexane}$ 225 (4.67), 251s (4.75), 259 (4.78), 292 (4.73), 301 (4.51), 340s (4.04), 378 (3.38), 392s nm (3.30) ($lg\varepsilon$). Nmr, δ ($CDBr_3$) = 6.47 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 1H), 6.77 ("s", 1H), 6.90 (dt, J_1 = 8 Hz, J_2 = 2 Hz, 1H), 7.05 (s, 2H), 7.20-7.84 (m, 14H), 8.00 ppm ("s", 1H). The singlet at 6.77 ppm should be assigned to the only uncoupled "ortho" proton, viz. H-(1'). The other absorption at the high field (at 6.47 ppm) must be due to H-(10'). Thus, the high field region in the spectrum of (IV) represents the two "ortho" protons of the benzofluorene moiety, while the respective protons of the dibenzocyclo-heptene moiety appear in the normal aromatic region. Consequently, the 6.45 ppm double doublet in the spectrum of (I) should be assigned to the two "ortho" protons of the fluorene moiety of the molecule.

The analysis of the remainder of the spectrum of (I) was based on the coupling between

the 6.90 double triplet and the 6.45 ppm double doublet. Irradiation of the former collapsed the latter into a "singlet". Hence, the signal at 6.90 ppm must be assigned to H-(2) and H-(7). The neighbouring double triplet at 7.22 ppm is probably due to H-(3) and H-(6) while the singlet at 7.03 ppm represents the protons of the ethylenic double bond.[7] The remaining multiplet at 7.37-7.73 ppm contains H-(4) and H-(5) of the fluorene moiety,[8,9] as well as all the eight aromatic protons of the dibenzocycloheptene moiety of the molecule.



IV



V

The shielding of 0.78 ppm observed in the absorption of the "ortho" fluorene protons (H-(1) and H-(8)) indicates that these protons lie above (or below) the plane of the opposing aromatic ring of the dibenzocycloheptene moiety. H-(2) and H-(7) are also influenced by this shielding effect, although its magnitude is much smaller (0.33 ppm). On the other hand, the two "ortho" protons of the dibenzocycloheptene moiety do not interact with the π electrons of the fluorene moiety.

In spite of the similarities in the nmr spectra of (I) and ((E)-III), (I) should be viewed sterically, not as a derivative of ((E)-III) (or of 5-diphenylmethylene-5H-dibenzo[a, d]cycloheptene[9]) but rather as an analogue of 9-diphenylmethylenefluorene.[9] Apparently, the ethylenic bridge of the dibenzocycloheptene moiety in (I) does not affect significantly the interaction between the two halves of the molecule. It seems that the planarity of the fluorene moiety of (I) is the dominant feature which determines the conformation of the rest of the molecule. It prevents the existence of a geometrical isomerism. Furthermore, it forces the dibenzocycloheptene moiety out of this plane in such a manner as to bring the aromatic rings above (or below) H-(1) and H-(8) as well as H-(2) and H-(7). Derivatives of 5H-dibenzo[a,d]-

cycloheptene, carrying an alkylamine side chain at position 5, already serve as useful drugs in the chemotherapy of mental diseases.[10,11] In these molecules, the conformation of the side chain vis-à-vis the polycyclic moiety plays an essential role in determining the psycho-pharmacological properties. The conformation of (I),as revealed in the present study, renders it possible that the 1-alkylamino- and 2-alkylamino-derivatives of (I) may well prove to be potent psychotherapeutic agents. The synthesis of such systems is under way.

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