

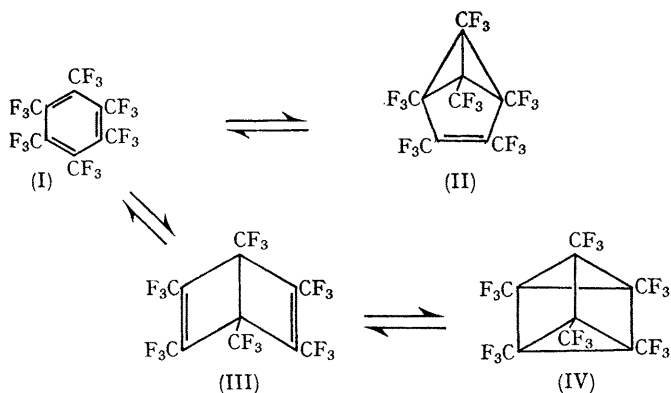
## The Valence-bond Isomers of Hexakis(trifluoromethyl)- and Hexakis(pentafluoroethyl)-benzenes

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THE preparation and properties of three non-planar valence-bond isomers of substituted benzenes, *para*-bonded or Dewar benzenes (bicyclo[2,2,0]hexa-2,5-dienes), benzvalenes (tricyclo[3,1,0,0<sup>2,6</sup>]hex-3-enes), and prismanes (tetracyclo[2,2,0,0<sup>2,6</sup>,0<sup>3,5</sup>]hexanes) have created much interest.<sup>1,2</sup> We now report both the photochemical formation and notable thermal stability of all three valence-bond isomers of hexakis(trifluoromethyl)benzene, and related studies based on hexakis(pentafluoroethyl)benzene.

Hexakis(trifluoromethyl)benzene (I)<sup>3</sup> absorbs in the u.v. region at 212 ( $\epsilon$  10,150) and 283 nm. ( $\epsilon$  140). Irradiation (>200 nm.) at room temperature of its solution in perfluoro-*n*-pentane gives its valence-bond isomers in up to 82% yield:



The benzvalene (II) is the major isomer formed in the early stages. Further irradiation gives increasing amounts of the *para*-bonded benzene (III), while substantial amounts of prismane (IV) are formed only upon prolonged irradiation. Typically, the composition of the reaction mixture changes from compounds (I; 21%), (II; 43%), (III; 31%), and (IV; 5%) (50 hr. irradiation) to (I; 18%), (II; 15%), (III; 39%), and (IV; 28%) (100 hr. irradiation).

Irradiation of the pure *para*-bonded benzene in perfluoro-*n*-pentane also gives substantial amounts of prismane (IV). Preliminary studies of the irradiation of the benzvalene in perfluoro-*n*-pentane indicate that its conversion into the *para*-bonded isomer (III) proceeds largely, if not exclusively, *via* the aromatic compound (I).

Hexakis(trifluoromethyl)benzvalene (II) is a volatile liquid, b.p. 136°,  $\nu_{\max}$  1666 (C:C str.) and 1583 cm.<sup>-1</sup> (cyclopropane ring), the u.v. spectrum of which shows an absorption maximum (221 nm.,  $\epsilon$  1820; in hexane), at shorter wavelength than that of previously reported benzvalenes.<sup>5</sup> The mass spectrum shows a prominent parent-ion, the base-peak corresponding to loss of CF<sub>3</sub>. The <sup>19</sup>F n.m.r. spectrum (relative to external CF<sub>3</sub>·CO<sub>2</sub>H in *n*-C<sub>5</sub>F<sub>12</sub>) shows three band systems of equal intensity at -20.3, -17.55, and -13.9 p.p.m. of the expected A<sub>3</sub>A'<sub>3</sub> P<sub>3</sub>P'<sub>3</sub> X<sub>6</sub>-type.

Hexakis(trifluoromethyl)bicyclo[2,2,0]hexa-2,5-diene (III), b.p. 89°, is surprisingly volatile. It has  $\nu_{\max}$  1709

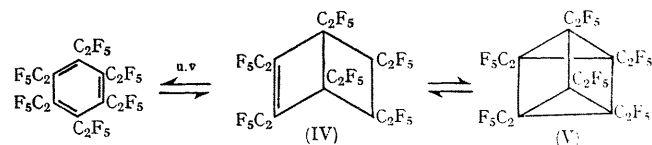
cm.<sup>-1</sup> (C:C str.), and an absorption maximum in the u.v. at 210–211 nm. ( $\epsilon$  620) with a substantial tail. Its mass spectrum shows a prominent parent-ion, with the base-peak corresponding to loss of CF<sub>3</sub>. The n.m.r. spectrum shows two band-systems, of intensity 2:1, at -10.9 and -10.55 p.p.m.

Hexakis(trifluoromethyl)prismane (IV) has a simple i.r. spectrum, showing only a series of m-s bands in the region 1120–1378 cm.<sup>-1</sup>. In its mass spectrum, it shows a surprisingly prominent parent ion (8.0%) for a saturated fluorocarbon; the ion corresponding to loss of CF<sub>3</sub> is very prominent (82.5%), and the base peak corresponds to CF<sub>3</sub><sup>+</sup>. A sharp singlet appears in the n.m.r. spectrum at -12.7 p.p.m.

The three valence-bond isomers show substantial resistance to thermal rearomatization. The benzvalene, in hexafluorobenzene solution, has a half-life of 9 hr. at 170°, the *para*-bonded benzene one of 135 hr. at 170°, while the stability of the prismane falls between these values. In sharp contrast, the half-life of the *para*-bonded isomer of hexafluorobenzene<sup>2</sup> is only 4 hr. at 80°, and the increased thermal stability caused by perfluoroalkylation is presumably

a reflection of the increased steric strain in the parent aromatic compound. This concept can also account, at least in part, for the increased thermal stability of (III) compared with its fluorine-free analogue hexamethylbicyclo[2,2,0]hexa-2,5-diene, the most stable valence-bond isomer hitherto reported (half-life 5.5 hr. at 140°).<sup>1</sup>

Hexakis(pentafluoroethyl)benzene,<sup>4</sup> is practically insoluble (<1%) in perfluoro-*n*-pentane. Prolonged u.v. irradiation of the solution in the presence of much undissolved hexakis(pentafluoroethyl)benzene causes most of the aromatic compound to go into solution, and high yields (>96%) of hexakis(pentafluoroethyl)prismane (V) may be subsequently isolated:



It is noteworthy that, compared with the reaction with hexakis(trifluoromethyl)benzene, photolysis of hexakis(pentafluoroethyl)benzene gives only traces of a compound, spectroscopically identified as the corresponding *para*-bonded benzene (VI), and none of the benzvalene. Hexakis(pentafluoroethyl)prismane, m.p. 179°, shows no unsaturation in its i.r. spectrum, and its u.v. spectrum shows a maximum at 209–210 nm. ( $\epsilon$  290) with a substantial tail. Previously reported prismanes<sup>6</sup> also show substantial absorption for saturated compounds. There are two absorption bands in its n.m.r. spectrum, of relative intensities 3:2, at 4.2 and 32.8 p.p.m. (in hexafluorobenzene). Its thermal stability is again appreciable (half-life 14 hr. at 170° in hexafluorobenzene solution).

The relatively high thermal stability of the benzvalene, hexakis-(perfluoroalkyl)benzenes makes such valence-bond *para*-bonded benzene, and prismane forms of these isomers now available for detailed chemical investigation.

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