

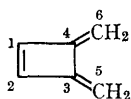
3,4-Dimethylenecyclobutene—Alternant or Non-alternant?

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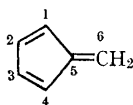
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THE properties of 3,4-dimethylenecyclobutene (I),^{1,2} a cyclic isomer of benzene, are of particular interest because of the light they may throw on some problems relating to aromaticity and the value of the distinction between alternant and non-alternant hydrocarbons.³

According to the simple classical structure (I), this hydrocarbon is alternant, but implicit in this is that C-2 and C-4 (or C-1 and C-3) are not



(I)



(II)

neighbours. However such atoms are only about 2.0 Å apart (compare *meta*-carbons in benzene, which are 2.42 Å apart). In terms of self-consistent-field molecular-orbital calculations the possibility arises that an unusually short non-neighbour distance may mean that the corresponding core resonance integral is no longer negligible and then the system may be expected to have perceptible non-alternant properties; in particular it may be distinctly polar.

corresponds to a dipole moment of 0.71 D. (The geometry was estimated by deriving bond lengths from bond orders from the formula:

$$r_{\mu\nu} = 1.514 - 0.178P_{\mu\nu}/(1.05 - 0.05P_{\mu\nu})$$

The methylene carbons were assumed to bisect the ring angles externally.) This is a substantial polarity for a hydrocarbon, not very much smaller than the value calculated for the non-alternant hydrocarbon fulvene (II). An analogous VESCF treatment of the latter yields the charge distribution given in Table 1, corresponding to a dipole moment of 0.79 D. In both molecules the calculated polarity depends strongly on the values assigned to core resonance integrals between non-neighbour carbon orbitals [when these are neglected the calculated moment of (I) is zero and of (II) is 0.98 D].

TABLE 1. Net charges (milliprotonic) on carbon atoms in dimethylenecyclobutene and fulvene

Atom	Dimethylenecyclobutene	Atom	Fulvene
2	-24	3	-5
3	+17	4	-42
5	+41	5	+38
		6	+57

TABLE 2. Energies (ev) of excited states* of dimethylenecyclobutene and fulvene

	Dimethylenecyclobutene		Fulvene	
	(a)	(b)	(a)	(b)
V_1	4.36 (B_1)	4.80	3.18 (B_1)	3.01
V_2	5.30 (A_1)	5.14	3.97 (A_1)	5.23
V_3	5.62 (A_1)	6.19 (B_1)	5.97 (A_1)	6.55 (B_1)
T_1	2.42 (B_1)	2.62	1.93 (B_1)	1.95

* All singly excited configurations included in the CI calculation.

^a Only nearest neighbour $\beta_{\mu\nu}$ included.

^b All $\beta_{\mu\nu}$ included.

By adopting the usual assumption that β_{CC} is proportional to the corresponding overlap integral and taking β_{12} (benzene) = -2.68 ev we obtain for dimethylenecyclobutene β_{24} = -0.76 ev. A VESCF treatment⁴ (neutral atom penetrations were neglected, two-electron Coulomb repulsion integrals were evaluated by an analysis of the benzene spectrum analogous to that of Simmons,⁵ all core resonance integrals were included) yields the charge distribution given in Table 1, which

The inclusion of non-neighbour core resonance integrals also affects the calculated energies of excited electronic states as illustrated in Table 2. The calculated dipole moments and spectroscopic intervals of course depend on the functional dependence of $\beta_{\mu\nu}$ upon internuclear distance and it is by no means certain that the assumed proportionality to $S_{\mu\nu}$ is reliable. It may be that we are underestimating the values of these non-neighbour interactions [this is suggested by the

recent accurate experimental value (0.80 D) of the dipole moment of azulene⁶]. From further detailed comparison of physical properties such as dipole moments and u.v. spectra of selected hydrocarbons with results of molecular-orbital calculations, an answer to this question may be provided. This would illuminate the value of the

concept of alternant and non-alternant hydrocarbons.

The deficiency at present is experimental. We are currently studying the microwave spectra of dimethylenecyclobutene and fulvene to obtain some of the necessary data.

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