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THE ELECTRONIC STRUCTURE OF 1, 6-METHANO-CYCLODECAPENTAENE [1]

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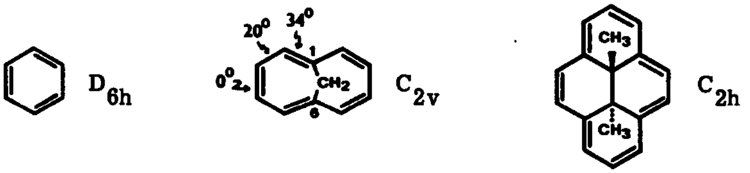
Questions regarding the aromaticity or non-aromaticity are a topic of continuous interest in annulene chemistry, as modern physical methods, prime among them NMR, put the answer within immediate reach. We report here the results of a photoelectron spectroscopic investigation of the title compound (2) [2], directed towards assessing the extent of π electron delocalisation in this non-planar hydrocarbon and, from this, exploring the potential of the PE technique for providing aromaticity criteria. To allow meaningful correlations, the PE spectrum of (2) will be discussed in conjunction with the PE data of benzene (1) [3] and trans-



(1) (2) (3)

15, 16-dimethyldihydropyrene (3) [4]. Neglecting the inner bridge, (2) and (3) can be envisaged as the respective second and third members of the $(4n+2)\pi$ annulene series comprising a neutral $(4n+2)$ carbon framework. Unlike (1) and (3), however, the perimeter of (2) lacks the geometrical pre-requisite for aromaticity, the dihedral angles between successive p_z-AO's being in the range $0 - 34^{o}$ [5] (cf. scheme).

It is clear that evidence for the resulting - possibly not very dramatic - inhibition of π electron delocalisation should be sought in the π ionisation potentials which are the quantities most directly related to the molecular structure, rather than in NMR chemical shifts which depend on a number of unknowns.

The salient features of the PE spectrum reproduced in fig. 1 are as follows. (i) A series of four relatively sharp bands in the region below 11 eV, of which the first two overlap considerably (corrected intensity ratio 2.00 : 1.1 : 0.9). To the extent that sharpness of a band is taken to indicate a π ionisation process, the four highest occupied MO's in (2) have to be classified as (almost) pure π levels, with very little delocalisation over the σ framework.

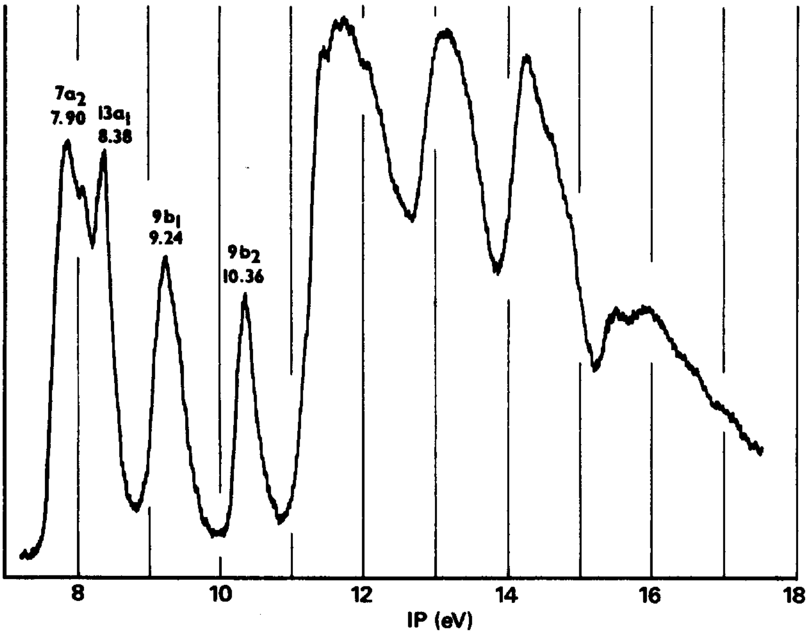


Fig. 1. The photoelectron spectrum of 1, 6-methano-cyclodecapentaene (2), with interpretation. The symmetry designation follows the ab-initio convention and refers to C_{2v}.

(ii) A first IP of 7.90 eV, which is precisely that predicted by Hückel theory for a cyclically conjugated D_{10h}-perimeter according to the equation $IP(eV) = \alpha + x_{HMO}\beta$, where the constants α and β have been calibrated with the aid of the experimental orbital energies of $1e_{1g}$ in (1)[3] and $12b_g$ in (3)[4]. (iii) A σ band onset at 11 eV, as in planar hydrocarbons comparable in size to (2). (This finding also excludes the existence of an equilibrium between (2) and the tautomeric bisnorcaradiene in the gas phase). (iv) Vibrational structure in the first band component, showing an interval close to that found in the $1a_u$ band of naphthalene,[3] and indicating ionisation from a π level with the same nodal properties, i.e., a_2 within C_{2v}.

Thus the gross features of the spectrum closely parallel those of other planar, fully delocalised aromatic hydrocarbons, in particular naphthalene, and also those of (3); the region above 10 eV in the latter case however being obscured because of ionisation from σ levels of the saturated bridge. Given the severe distortions of the peripheral ring in (2), its PE spectrum appears at first glance to be singularly unexciting.

A more careful analysis, the details of which are worked out in fig. 2, reveals however that this conclusion is premature. The levels π_4/π_5 and π_2/π_3, which would each be degenerate in the limits of a D_{10h}-perimeter, are seen to be substantially split in the spectrum, mainly as a result of two effects: (i) an inductive raising of the energies of those π levels having non-vanishing coefficients at C1 and C6; (this effect is described in Hückel theory to

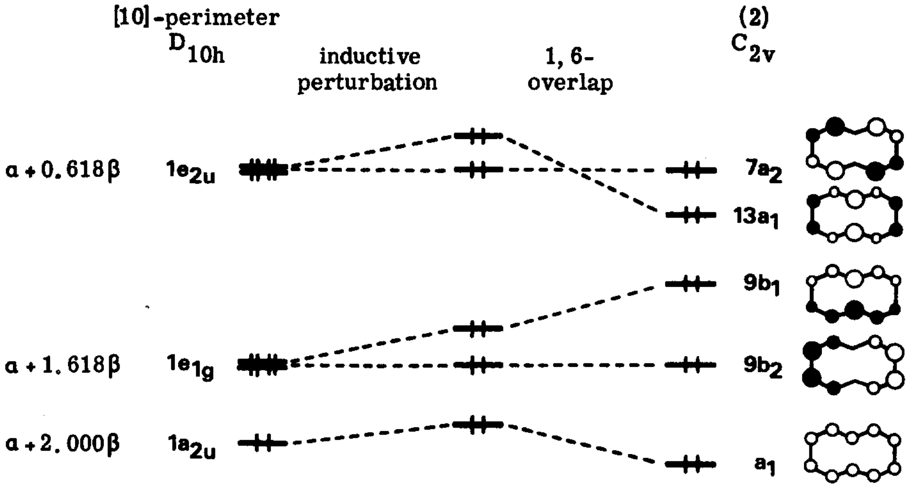


Fig. 2. Influence of the inductive effect of the methylene bridge and of the 1, 6-overlap on the π levels of a D_{10h}-perimeter. The orbital energies are taken from an HMO calculation.

first order by $\delta\varepsilon = \sum_{v} c_v^2 \delta\alpha_v = 2(0.447)^2 \delta\alpha$, where $\delta\alpha$ signifies the change in the Coulomb potential at C1 and C6) and (ii) the transannular interaction between the p-AO's at C1 and C6 (distance[5] 2.26 Å), describable to first order by $\delta\varepsilon = 2c_1c_6\beta_{16} = 0$ or $\pm 2(0.447)^2\beta_{16}$. Neglecting a possible hyperconjugative effect of the bridge, which is expected to be small in (2), $\delta\alpha$ and β_{16} are readily determined from the experimental splittings as +0.8 and -2.0 eV, respectively, and the final π level ordering in (2) then parallels in a formal sense that in naphthalene. The important point to be made is that $7a_2$ and $9b_2$ (cf. fig. 2) remain essentially unperturbed; their energy difference, as deduced from the spectrum, thus permits the assessment of the parameter β which we take in this paper as the prime operational measure of the extent of π electron delocalisation. The result is contrasted in the table with the β values obtained from the PE spectra of some planar hydrocarbons. A substantial reduction in the β value of (2), which is significant at a security level as high as 99 % (Student's t test), is readily apparent in these data. Regardless of whether this effect is due to diminished π-π overlap or to lack of orthogonality between σ and π levels of the perimeter,[6] it remains a fact that (2) does not show the full amount of π electron delocalisation expected for a hypothetical planar [10]-annulene. Conventional techniques such as NMR,[2] ESR[7] and UV[8] did not have a sufficiently high sensitivity to reveal such an admittedly small effect, nor did they indicate the strong perturbation exerted by the bridge on the π levels of the peripheral ring.

Further reductions in the β values have very recently been observed in our laboratory in the case of more severely bent annulenes.

Table. Comparison between the average β values of (2) and those of some planar aromatic hydrocarbons. No reliable estimate is available for (3) to date, as only the two uppermost π levels could be identified in the spectrum.[4]

Hydrocarbon	β (eV)	Hydrocarbon	β (eV)
(2)	-2.46	Perylene[9]	-2.87
Benzene[3]	-2.96	Chrysene[9]	-2.90
Naphthalene[3]	-2.80	1,2-Benzanthracene[9]	-2.91
Anthracene[9]	-2.90	1,2-Benzpyrene[9]	-2.89
Tetracene[11]	-2.76	Benzo[g,h,i]perylene[9]	-2.94
Pentacene[9]	-2.77	Ovalene[9]	-2.81
Phenanthrene[9]	-3.08	Pyrenopyrene[11]	-3.12
Pyrene[10]	-2.70	Anthanthrene[11]	-2.85
Coronene[10]	-2.95	Dibenzochrysene[11]	-2.87
Triphenylene[11]	-3.16	Fluoranthene[11]	-2.97

The preliminary results reported here lend some support to the proposition that aromaticity and non-aromaticity can be defined in a meaningful way by means of PE spectroscopy.

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6. A third possibility - rapid bond shift in the perimeter - cannot be excluded a priori. In this connection we note that a MINDO/2 geometry minimisation for (2) converged to a C_s rather than to a C_{2v} structure, the latter being less stable by ca. 0.4 kcal/mole.

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