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THE PHOTOELECTRON SPECTRUM OF trans-15, 16-DIMETHYL-DIHYDROPYRENE

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Since its original synthesis[1] trans-15, 16-dimethyldihydropyrene (1), a bridged 14-annulene, and its derivatives have attracted much attention, of particular interest being their unusual magnetic properties[2], UV spectra[3] and their facile photochemical and thermal rearrangement[4] to the corresponding 8, 16-dimethyl-[2. 2]metacyclophane-1, 9-dienes (2). Although "forbidden" by the rules of orbital symmetry conservation[5], the thermal processes proceed at low activation energies. We have recently offered an MO rationalisation of these findings[6]. In order to substantiate our conclusions and to gain further insight into the electronic structure of this class of compounds, we have undertaken a study of their photoelectron (PE) spectra and here report results on the parent hydrocarbon (1).

Figure 1 shows the low energy part of the high-resolution He (I) PE spectrum, recorded on a Perkin-Elmer PS-16 spectrometer which has been modified for relatively unvolatile compounds. Fresh samples have been run at temperatures of 60, 70, 80 and 90°, and the spectra calibrated with rare-gases and naphthalene which has a sharp band[7] at 8. 15 eV. That we observe the spectrum of (1) and not that of a decomposition

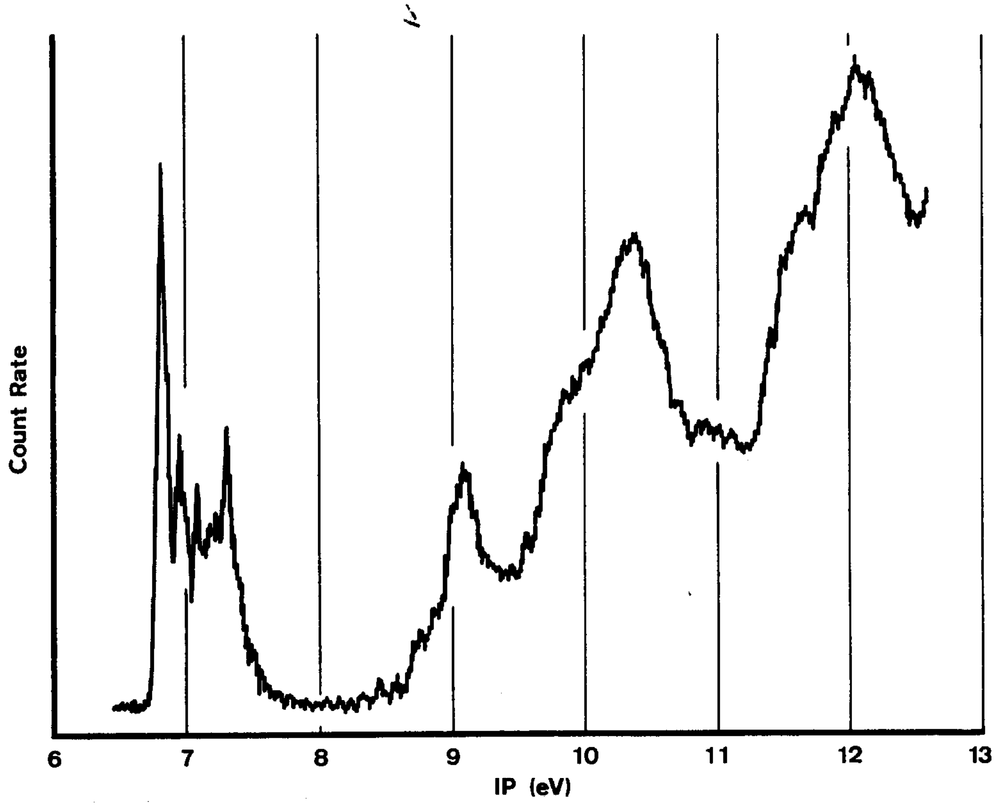

Figure 1. Low energy part of the photoelectron spectrum of (1).

product or that of (2), can be confirmed from the fact that (1) could be recovered after measuring the spectrum, and that it proved to be temperature-independent. No traces of pyrene, which has an IP of 7.72 eV (electron impact value[8]), could be detected.

Our discussion centres on the first PE band which extends from 6.7 eV (adiabatic IP) to about 7.5 eV and which is split into two components (separation of the maxima about 0.5 eV). The first component consists of a short progression of three vibrational peaks, of which the 0-0 transition is by far the most prominent (vertical IP 6.8_0 eV). The spacing of the peaks, 1150 ± 150 cm^{-1}, is smaller than that in the first bands of related hydrocarbons, e.g. naphthalene[7]; thus the relaxation processes following ionisation seem to affect primarily the topography of the internal butano unit rather than that of the perimeter. No distinct fine structure is discernible in the second band component.

Three questions emerge from these observations: (i) what is the reason for the unprecedented low first IP ? It is the lowest so far observed in a closed-shell hydrocarbon[9]. Pyrene, which possesses also a large, delocalised π system, has a considerable higher first IP; (ii) why is the first band split into two components ? Qualitative MO arguments suggest that all occupied π MO's of the 14-perimeter, except the lowest one, are pairwise degenerate; (iii) even considering the high rigidity of the molecule, it is surprising that ionisation from the topmost occupied π MO excites only one of the large number of possible vibrational modes - and furthermore one that does not appear to be associated with a delocalised π system.

We have calculated the potential energy surface of the neutral molecule and its cation by using the MINDO/2 scheme[10] in conjunction with an iterative SIMPLEX optimisation technique. The primary focus of interest in the geometry optimisation was on the coordinate R (figure 2) which converts (1) into (2); as a low force constant is associated with this nuclear motion, relatively large dimensional changes along R may take place on ionisation. For the open-shell calculations on the cation Dewar's half-electron method was used. The first IP is then equated to the difference in SCF energies between the cation and the neutral molecule. Thus we avoid the use of Koopmans' theorem, the deficiences of which are now well recognised. As seen from figure 2, the calculated adiabatic and vertical first IP's differ by only 0.03 eV - thus reflecting the essentially non-bonding character of the highest occupied MO - and agree well with the experimental values.

Inspection of the wave functions reveals that the highest occupied MO ($20\,a_g$ in the usual notation; point group C_{2h}) is strongly mixed with a σ MO of the internal bridge belonging to the same symmetry species. However the next MO ($12\,b_g$) has a node passing through the carbon atoms 2, 7, 15 and 16 and is confined to the π AO's of the perimeter. The energy difference, $\varepsilon(20\,a_g) - \varepsilon(12\,b_g)$, which is 0.44 eV at R = 1.561 Å, is in good qualitative agreement with the observed splitting of 0.5 eV in the first band.

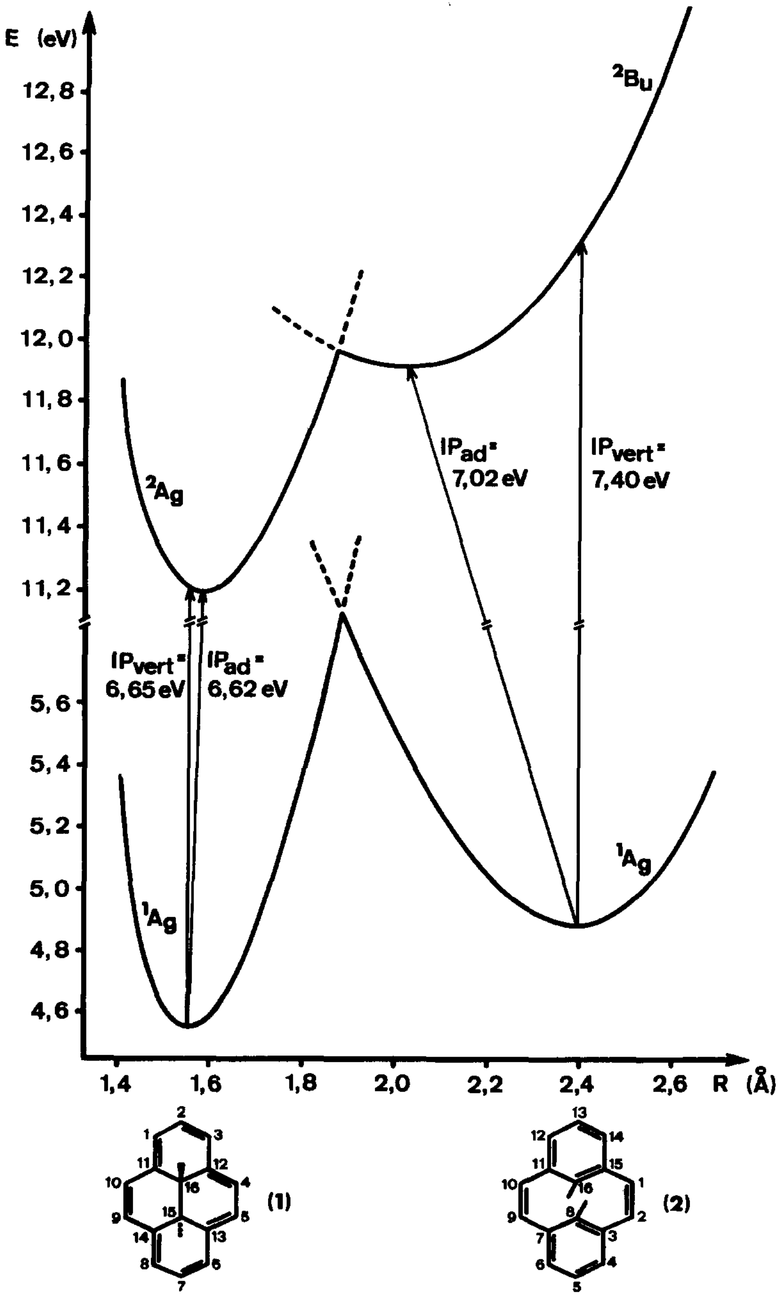

Figure 2. MINDO/2-SIMPLEX potential curves for (1) $\rightleftharpoons$ (2) and $(1)^+ \rightleftharpoons (2)^+$ and calculated IP's. R is the distance C15-C16. The discontinuity at R = 1.89 Å is a manifestation of the forbiddenness of the process (1) $\rightleftharpoons$ (2).

The MO which brings about this sizeable split can be described (in a semi-localised MO picture) as the 'plus-minus-plus' linear combination of the three bonds C15-C17, C15-C16 and C16-C18 and is thus of the same character as the topmost occupied MO of n-butane (first vertical IP 11.1 eV). Molecular models for (1) show that this MO can enter into "hyperconjugation" with π MO's of the same symmetry[11]. However this overlap-controlled σ-π interaction cannot be the sole reason for the low first IP of (1), otherwise the second IP of (1) and the first IP of pyrene should be identical (as are the corresponding MO's). An "inductive" effect must also be operative. This will be further examined when results for the 15, 16-diethyl-, propyl- and butyl-derivatives become available. Increasing the chain length of the internal substituents should increase the splitting between $20a_g$ and $12b_g$ further and lower the first IP accordingly.

As has been discussed elsewhere[6], it is the top-occupied MO, $20a_g$, which makes the interconversion (1) $\rightleftharpoons$ (2) a symmetry-forbidden reaction. Hence ionisation from this MO must reduce the barrier separating the two isomers. Figure 2 supports this view: The calculated force constant d^2E/dR^2 is reduced on ionisation from 5.1 to 3.7 mdyne/Å. It seems therefore likely that the observed progression in the first PE band relates to the symmetry coordinate R. Ionisation from $12b_g$, on the other hand, does not change the molecular force field in such a distinctive manner and hence several vibrational modes are likely to be excited.

While we are confident in our assignment of the first PE band to the MO's $20a_g$ and $12b_g$, considerable scepticism must be placed on the MINDO prediction that the second band centred at 9.1 eV relates to a σ MO, because semi-empirical MO procedures usually display a poor balancing of the relative energies of σ and π levels. A firm assignment must therefore be based on other evidence. Attempts to synthesise fluorinated dihydropyrenes are in progress: it is known[12] that fluoro- and trifluoromethyl substituents stabilise σ MO's, while leaving π MO's essentially unaffected.

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