57. Radical Cation States of 2,3,5,6,7,8-Hexamethylidenebicyclo[2.2.2]octane[1])

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Summary

The photoelectron spectrum of the title compound is reported and assigned by correlation with the photoelectron spectra of related molecules.

The photoelectron spectra of 2-methylidene- (**1**) and 2,3-dimethylidene-bicyclo[2.2.2]octane (**2**) have been recorded and discussed by *Klessinger et al.* [1]. Recently, we have reported the photoelectron spectrum of 2,3,5,6-tetramethylidene-bicyclo[2.2.2]octane (**3**) [2]. In *Figure 1* is shown the He(Iα) photoelectron spectrum of the title compound (**4**), the synthesis of which will be described elsewhere [3].

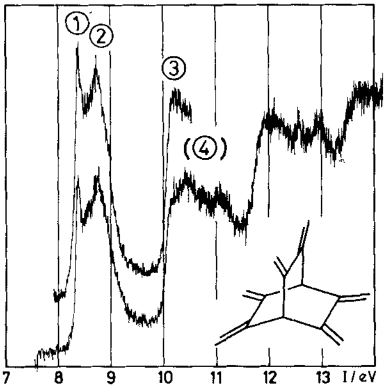

Fig. 1. He(Iα) photoelectron spectrum of [2.2.2]Hericene. Band maxima positions I_j^m: ① 8.38 eV; ② 8.75 eV; ③ 10.2_0 eV; ④ $\sim 10.7_5$ eV.

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[1]) The general name [l.m.n]hericene is proposed for bicyclo[l.m.n]alkanes with l+m+n methylidene groups, after the latin name *hericeus* for hedgehog. Thus the title compound would be called [2.2.2]-hericene.

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The main attraction of **4** is its high symmetry, which is ideally D_{3h}. This is also true statistically, if the molecule flip-flops between lower symmetrical (D_3?) conformations. As a result the sequence of the six molecular orbitals $a_1''(\pi)$, $e''(\pi)$, $a_2'(\pi)$ and $e'(\pi)$ of **4** which are essentially linear combinations of the six exocyclic double bond orbitals π_μ, is completely determined by symmetry (assumed D_{3h}). Following the example of *Bruckmann & Klessinger* [4], it is possible to express the corresponding orbital energies in terms of four parameters into which the competitive influence of 'through space' and 'through bond' interactions [5] has been absorbed (*cf.* discussion in [2]). If B stands for the direct conjugative interaction of two vicinal π-orbitals, Γ for the homoconjugative interaction of two π-orbitals *e.g.* in positions 2 and 6, Δ for the interaction of two π-orbitals across the ring, *e.g.* in positions 2 and 5 and if A stands for the self energy of a π-orbital, then the following orbital energies are obtained:

$$\begin{aligned}
\varepsilon(a_1''(\pi)) &= A - B - 2\Gamma + 2\Delta \\
\varepsilon(e''(\pi)) &= A - B + \Gamma - \Delta \\
\varepsilon(a_2'(\pi)) &= A + B - 2\Gamma - 2\Delta \\
\varepsilon(e'(\pi)) &= A + B + \Gamma + \Delta
\end{aligned} \tag{1}$$

(With reference to the nomenclature used in [2] we have $A \equiv A_\mu$, $B \equiv B_{ab}$, $\Gamma \equiv B_{ad}$, $\Delta \equiv B_{ac}$.) Assuming the validity of *Koopmans'* approximation, the orbital energies (1) correspond, except for the sign, to the band positions. Whereas the first three can be read off the spectrum of **4** shown in *Figure 1*, the position of band ④ is somewhat uncertain because it is overlapped by others which are due to the removal of an electron from σ-type orbitals. However, a reasonably safe value can be extrapolated as follows: The mean ionization energies of **2** (9.26 eV) and **3** (9.43 eV) differ by 0.17 eV, due to the relatively higher sp^2 character of **3**. If the same trend holds for a comparison of **3** with **4**, then the e'-band ④ should lie close to 10.7_5 eV. The same estimate is obtained if a shift of 0.17 eV is applied to the band position of the a_1-band of **3**, the energy of which, expressed in A, B, Γ and Δ is equal to $\varepsilon(e'(\pi))$, *i.e.* $\varepsilon(a_1(\pi)) = \varepsilon(e'(\pi)) = A + B + \Gamma + \Delta$. Solving (1) for the values $\varepsilon(a_1''(\pi)) = -8.38$ eV, $\varepsilon(e''(\pi)) = -8.75$ eV, $\varepsilon(a_2'(\pi)) = -10.2_0$ eV and $\varepsilon(e'(\pi)) = -10.7_5$ eV yields $A = -9.60$ eV, $B = -0.97$ eV, $\Gamma = -0.15$ eV and $\Delta = -0.03$ eV, in excellent agreement with the previous results obtained for **2** and **3** [1] [2] [5]. Thus the correlation shown in *Figure 2* is straightforward.

A notable feature of band ① is that it corresponds to the removal of an electron from the $a_1''(\pi)$ orbital of **4** which is the only one of this symmetry in the molecule. Thus the resultant ground state $^2\tilde{X} \equiv {}^2A_1''$ of $\mathbf{4}^+$ cannot mix with any other *Koopmans'* state of the radical cation under strict D_{3h}-symmetry. Furthermore the positive hole is localized to 1/6 in each double bond and we expect a sharp $0 \rightarrow 0$ transition, as is indeed observed. The higher vibrational components are overlapped by the wide band ② corresponding to the ejection of an electron from $e''(\pi)$. Note

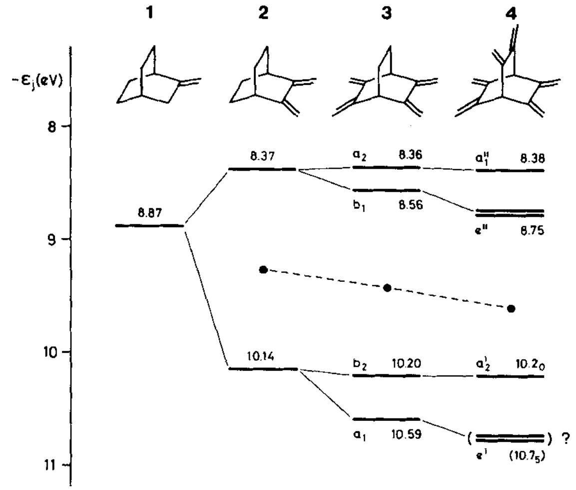

Fig. 2. Correlation diagram for the compounds 2-methylidene- (**1**), 2,3-dimethylidene- (**2**), 2,3,5,6-tetramethylidene- (**3**) and 2,3,5,6,7,8-hexamethylidenebicyclo[2.2.2]octane (**4**).

that the orbital $a_2'(\pi)$ is also the only one of its kind within **4**, but the expected vibrational fine structure of band ③ is presumably perturbed by the close lying σ bands, perhaps as a consequence of vibronic mixing.

Although '[2.2.2]hericene' (**4**) is undoubtedly an esthetically pleasing molecule, its photoelectron spectroscopic behaviour offers no surprises.

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