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The Photoelectron Spectrum of Cuneane and its Relationship to the Spectra of Cubane and Dihydrocuneane[1]

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The He(Iα) photoelectron spectrum of cuneane (1) has been recorded. The ionization energies of 1 are compared with the corresponding data of cubane (2) and dihydrocuneane (3). The distortion from the vertical to the adiabatic radical cation of 1 is analyzed using the same open-shell MINDO/3 method that has been applied to cubane.

Cuneane (1) along with cubane (2) is one of the most highly strained $(CH)_8$ hydrocarbons. It is formed from cubane by a catalysed bicyclo[2.2.0]hexane → bicyclopropyl rearrangement[2].

As we reported in the preceding communication[1], the large strain energy for cuneane ($\Delta H_f^\circ = 460$ kJ mol^{-1} = 110 kcal mol^{-1} according to MM2 calculations[3], $E_{strain} = 529$ kJ mol^{-1} = 126.5 kcal mol^{-1}), although somewhat smaller than for cubane, is sufficient to cause production of vibrationally excited semibullvalene during reduced-pressure thermolysis. The semibullvalene is capable of undergoing further thermal reaction.

1   **2**   **3**

1$_a^+$ **2$_a^+$**   **4**
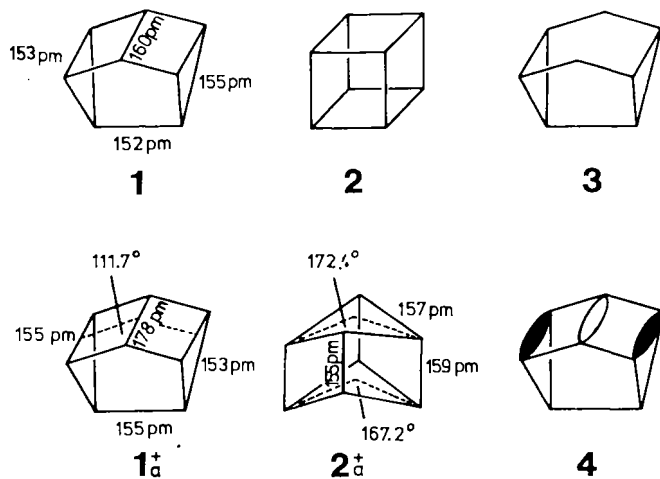
The investigations reported on here were stimulated by the following observation: In spite of the higher ground state and strain energy for cubane, cuneane is more easily electrochemically oxidized than cubane. The oxidation potential of cuneane is lower than that for cubane by 0.2 V, and the adiabatic ionization energy is lower by ca. 0.25 eV[4]. The following working hypothesis may explain the difference. Either the first vertical ionization energy of cuneane is lower than that for cubane and thus leads to an energetically lower onset of the first PE bands (the term adiabatic ionization energy is avoided since the 0—0 transition has not been assigned), or with similar I_1^m values for 1 and 2, the vibrational relaxation and thus the stabilization of the vertical radical cation

1$^{+\cdot}$ is larger than that for 2$^{+\cdot}$. The question which naturally arises from this is, from which orbital does the electron come during oxidation of 1 and 2?

To this end the PE spectrum of 1 was recorded. Figure 1 shows the He(Iα) PE spectra of 1, 2 (first published in ref.[5]) and dihydrocuneane 3[6]. Table 1 shows the ionization energies (maxima of the PE bands correspond to vertical ionization energies).

Table 1. Ionization energies (maxima) I_j^m/eV (error ± 0.03 eV) of 1, 2[5], and 3[6] (assignment according to model calculations[7] with MM2[3] optimized geometry)

	I_j^m	HAM/3 [7a]	STO-3G [7b]
1	9.09	9.31, a_1	7.98, a_1
	9.45	9.87, a_2	8.84, a_2
	10.02	10.16, b_2	8.85, b_2
	10.63	11.19, b_1	10.48, b_1
	11.11	11.42, a_2	10.57, a_2
	11.61	11.76, a_1	11.31, a_1
	13.27	13.22, b_2	13.66, b_2
2	9.00–9.10	10.16, t_{2g}	9.28[5], t_{2g}
	9.55–9.60		
	9.85–9.90	10.72, t_{2u}	9.39, t_{2u}
	13.75	13.57, e_g	14.71, e_g
3	9.12	9.57, a_2	8.60, a_2
	9.60	9.84, a_1	9.10, a_1
	10.25	10.53, b_1	9.94, b_1
	10.67	10.67, b_2	10.04, b_2
	11.25	11.38, a_2	11.13, a_2
	12.25	12.70, a_1	12.50, a_1

The orbital sequence of 3 from HAM/3 and STO-3G calculations agrees with that derived from a qualitative model[6]. From Table 1 and Figure 1 the following conclusions can be drawn:

a) Lowering of the symmetry from $O_h(2)$ to $C_{2v}(1)$ causes the levels t_{2g} and t_{2u} to split. For 1 they are found between 9 and 12 eV.

b) The characteristic gap between 11 and 13.5 eV in the PE spectrum of cubane is also qualitatively present in the spectrum of 1. Splitting of the t levels, however, squeezes it into the region 12 to 13 eV.

c) For dihydrocuneane 3 there are only five ionizations observed between 9—12 eV. As six were identified for 1, one must assign one of them to the new strained bond shared by both four-membered rings.

d) This central σ bond in 1 may interact vicinally with the other two four-membered ring bonds. This σ,σ interaction in four-membered rings is considerable, amounting to ca. −2.0 eV[5]. The antibonding combination 4 is to be expected under the six levels which
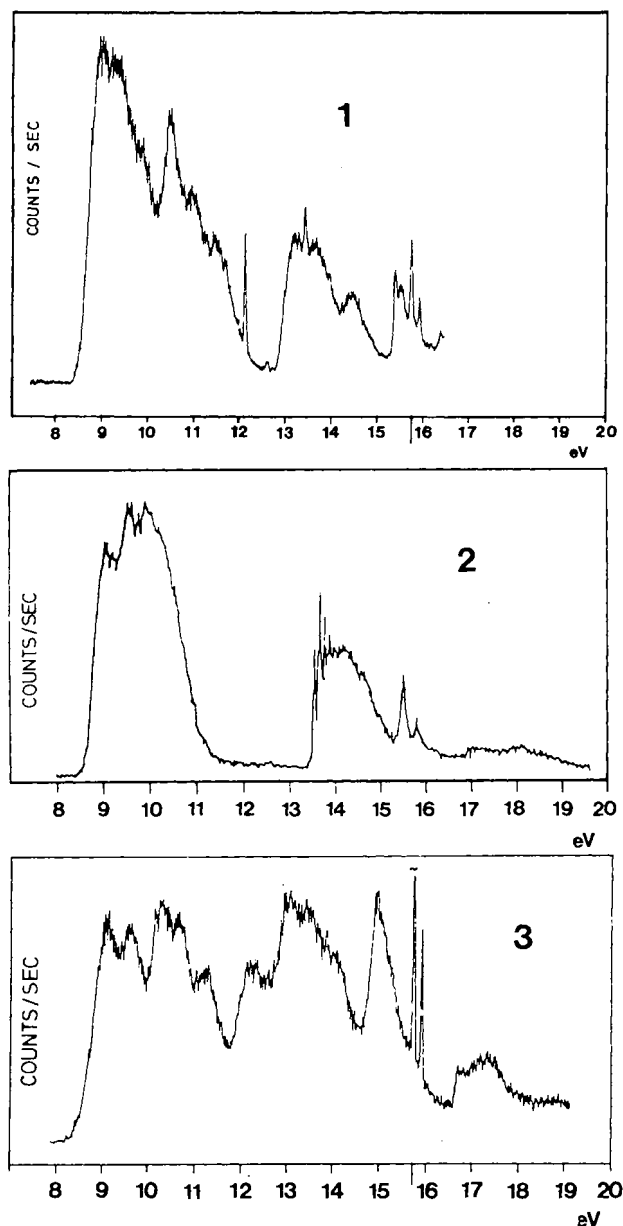
Figure 1. He(Iα) Photoelectron spectra of **1**, **2**[5], and **3**[6]

and cubane: cuneane (**1**) 0.8 eV and cubane (**2**) ca. 1 eV. The minimally larger value for cubane which follows from this estimation is a result of the Jahn-Teller splittings, that result from ejection of a t_{2g} electron. The lower adiabatic ionization of cuneane compared with cubane runs parallel to the low vertical ionization energy of **1** and is also reflected in the oxidation potential[4].

It may seem surprising, at first glance, that the differences in energy between the vertical and adiabatic ionization of **1** and **2** are so similar. The photoelectron from **1** comes from orbital **4** (a_1 symmetry) which is mainly delocalized over three bonds. The t_{2g} photoelectron from **2** however is removed from an orbital delocalized over 12 bonds[5]. To be able to compare the adiabatic radical cation of **1** in its electronic ground state with the radical cation of cubane[5], its structure was calculated using an open-shell MINDO/3 method[9]. In **1a**$^+$ the bond lengths found are given. The most pronounced effect was found for the 1,5 bond. The increase from 160 pm to 178 pm agrees with the fact that the photoelectron is removed from an orbital which is significantly localized in this bond (cf. **4**). The first adiabatic ionization energy of **2** $I_1^a(2) = \Delta_f H(\text{cubane}^+) - \Delta_f H(\text{cubane}) = 8.2$ eV[5] is in reasonably good agreement with observation. For **1** we obtain $I_1^a(1) = \Delta_f H(\text{cuneane}^+) - \Delta_f H(\text{cuneane}) = 7.8$ eV. The calculated difference $\Delta I_1^a(2, 1) = 0.4$ eV between the adiabatic ionization energies agrees well with the experimental differences between the onsets of the first PE bands [see f)] $\Delta(\text{onset}) \approx 0.25$ eV. The differences $I_1^v - I_1^a$ estimated from the spectra (0.8 eV for **1** and ca. 1 eV for **2**) are also similar to the calculated values $I_1^v - I_1^a(\text{MINDO}/3)$: 0.50 eV for **1** and 0.63 eV for **2**.

Experimental

Cuneane (**1**, pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane), cubane (**2**, pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane) and dihydrocuneane (**3**, tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane) were prepared according to established procedures[2,10,11]. PE spectra were recorded on a UPG-200, Leybold-Heraeus, instrument.

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1: 20656-23-9 / **2**: 277-10-1 / **3**: 765-72-0

are observed in the range 9−12 eV. The HAM/3[7a] method predicts that this vicinal antibonding σ orbital **4** is the HOMO for **1**.

e) Both ^2T states of the cubane radical cation are Jahn-Teller unstable and this results in a complex band envelope. It is thus not possible to assign with certainty the three Jahn-Teller maxima of the first PE band to these states. One possibility is that the second maximum at 9.6 eV is to be interpreted as the central maximum of the $^2T_{2g}$ state. According to the Franck-Condon approximation, the central maximum would coincide with the energy of the upper state at the symmetrical position and the two outer maxima are symmetrical about it[8]. This position (9.6 eV) is also the centroid of the band system[5]. According to this interpretation the vertical ionization to an ion with the nuclei in the same symmetrical position would be easier for cuneane (**1**) than for cubane (**2**).

f) The published[4] adiabatic ionization energies for **1** (8.18 eV) and **2** (8.46 eV) agree on the whole with the onset of the PE bands: $I(\text{onset})$ (**1**) ≈ 8.25 eV, $I(\text{onset})$ (**2**) ≈ 8.5 eV[5]. Taking point e) into consideration we can see that this means that the distortion from vertical symmetrical to adiabatic ions is similar for both cuneane

1) *Small and Medium Rings*, Part 67. − Part 66: K. Hassenrück, H. D. Martin, R. Walsh, *Chem. Ber.* **121** (1988) 369. preceding paper. This is also Part 5 of "C$_8$H$_8$ Hydrocarbons", Part 4 see above.
2) L. Cassar, P. E. Eaton, J. Halpern, *J. Am. Chem. Soc.* **92** (1970) 6367.
3) N. L. Allinger, *J. Am. Chem. Soc.* **99** (1977) 8127.
4) P. G. Gassman, R. Yamaguchi, *J. Am. Chem. Soc.* **101** (1979) 1308.
5) P. Bischof, P. E. Eaton, R. Gleiter, E. Heilbronner, T. B. Jones, H. Musso, A. Schmelzer, R. Stober, *Helv. Chim. Acta* **61** (1978) 547.
6) H. D. Martin, C. Heller, J. Werp, *Chem. Ber.* **107** (1974) 1393.
7) 7a) E. Lindholm, L. Asbrink, *Molecular Orbitals and their Energies. Studied by the Semiempirical HAM Method*, Springer-Verlag, Berlin 1985. − 7b) W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York 1986.
8) J. H. D. Eland, *Photoelectron Spectroscopy*, 2nd ed., p. 181, Butterworths, London 1984.
9) P. Bischof, *J. Am. Chem. Soc.* **98** (1976) 6844.
10) P. E. Eaton, T. W. Cole, *J. Am. Chem. Soc.* **86** (1964) 962, 3157; E. W. Della, H. K. Patney, *Aust. J. Chem.* **29** (1976) 2469.
11) H. C. Volger, H. Hogeveen, M. M. P. Gaasbeek, *J. Am. Chem. Soc.* **91** (1969) 218.

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