

195. The Electronic Structure of Pentaprismane ($C_{10}H_{10}$), as Revealed by its Photoelectron Spectrum

by Evi Honegger¹⁾, Philip E. Eaton²⁾, B. K. Ravi Shankar²⁾ and Edgar Heilbronner¹⁾

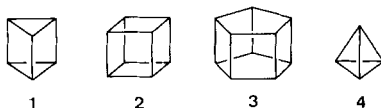
Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel
and Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue,
Chicago, Illinois 60637, U.S.A.

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Summary

The photoelectron (PE.) spectrum of the title compound has been assigned by comparison with the PE. spectrum of cubane (**2**), aided by *ab initio* STO-3G calculations using localized molecular orbitals. On the basis of the information available to date, the most satisfactory orbital sequence, *Koopmans* theorem implied, is, in descending order of energy: band system ①: ($2e'_2$, $3e'_2$, $2e'_1$, $3e'_1$); band system ② ③: $3a'_1$ ($2e'_2$, $2a'_2$); band ④: $2e'_1$. (Sequence of orbitals in parenthesis uncertain.)

Some time ago we discussed the electronic structures of cubane (**2**) [1] and of the tetra(*t*-butyl) derivative of tetrahedrane (**4**) [2] on the basis of their He(I α) photoelectron (PE.) spectra.



In *Figure 1* (solid line) we now present the He(I α) PE. spectrum of pentaprismane (**3**) [3], the highest member known of the series starting with prismane (**1**) [4] and cubane (**2**) [5]. The relevant ionization energies I_j^m corresponding to the positions of the band maxima are collected in the *Table*.

The molecule **3** is a remarkable hydrocarbon, not only because of its rare and pleasing symmetry D_{5h} [3], but also because it incorporates five four-membered rings. Its 25 valence-shell molecular orbitals (*i.e.* excluding the ten linear combinations of the C1s atomic orbitals) span the following irreducible representations of D_{5h} :

$$3 \times A'_1 + 3 \times E'_1 + 3 \times E'_2 + 2 \times A'_2 + 2 \times E'_1 + 2 \times E'_2 \quad (1)$$

¹⁾ Universität Basel.

²⁾ University of Chicago.

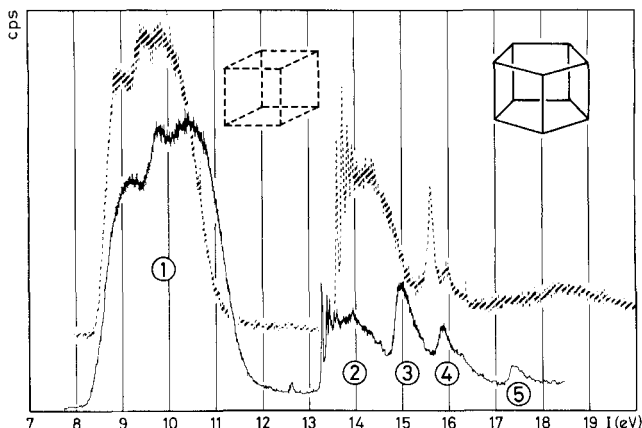


Fig. 1. He(I α) PE. spectra of pentaprismane (3) (solid line) and of cubane (2) (dashed line) [1]

A comparison of the PE. spectra of 2 [1] and 3 (presented in Fig. 1) reveals that they are closely related. Because of the high symmetry of 2 and 3 their interpretation is rather straightforward, as discussed previously in the case of 2 [1] and, in a similar vein, of the tetra(*t*-butyl) derivative of 4 [2]. Indeed an STO-3G calculation [6] for 3 using the following set of structural parameters, $R_{CC} = 156$ pm, $R_{CH} = 108$ pm and strict D_{5h} symmetry, yields the energies ϵ_j of the canonical orbitals ϕ_j listed in the Table. For obvious reasons, the sequence of close-lying states must necessarily be uncertain, but there can hardly be any doubt that both the number and the symmetry of states which cluster around certain values, e.g. those in the vicinity of ~ 10 eV, are most probably correct. This is evident from the regression shown in Figure 2, where we have plotted the observed band positions I_j^m derived from the PE. spectra of 2 and 3 vs. the STO-3G orbital energies ϵ_j . The quality of the regression obtained in this fashion shows that the computed data are significant [7] and that the assignment derived for 2 and 3 are at least compatible with each other.

Table. Ionization and orbital energies of pentaprismane (3)

Band	I_j^m [eV]	Orbital ^{a)}	ϵ_j^a [eV]
①	9.2	$\left\{ \begin{array}{l} 2e_2'' \\ 3e_2'' \\ 2e_1'' \\ 3e_1'' \end{array} \right\}$	9.32
	9.8		9.69
	(10.2)		9.83
	(10.4)		9.98
②	13.2 ₅	$\left\{ \begin{array}{l} 2e_2'' \\ 2a_2'' \end{array} \right\}$	13.86
	(13.9 ₀)		14.15
③	14.9 ₅	3a ₁ '	14.69
④	15.8 ₅	2e ₁ '	16.05
⑤	17.3 ₅	1e ₂ '	17.10

^{a)} Orbital symmetry and orbital energies according to the *ab initio* STO-3G calculation discussed in the text.

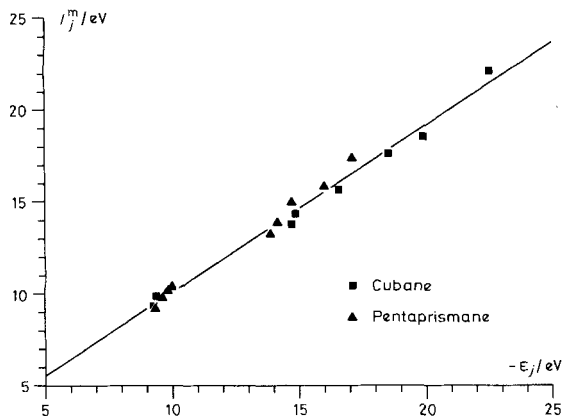


Fig. 2. Comparison of observed ionization energies I_j^m (eV) with STO-3G orbital energies ϵ_j (eV) for cubane (2) and pentaprismane (3)

Indeed, a correlation coefficient $r=0.993$ leads to a Fisher z value of $z=(\ln[(1+r)/(1-r)])/2=2.8$, which is removed by roughly $10\sigma(z)$ from the z value expected for the corresponding random correlation which takes the ordering within each set of data (*i.e.* for 2 and 3) into account [7].

It is of some interest to compare the significant features of the electronic structure of 3 with those of other strained hydrocarbons, in particular those of cubane (2) [1]. To this end, the canonical molecular orbitals φ_j (CMO) of the occupied manifold are subjected to a localization procedure, *e.g.* the one proposed by Foster & Boys [8]. In Figure 3 are shown the matrix elements $\langle \lambda_i | \mathcal{F} | \lambda_j \rangle$ of the Fock matrix in localized basis, *i.e.* referring to the localized molecular orbitals λ_i (LMO). For brevity we designate the LMO's λ_{CC} by λ_a or λ_e , depending on the axial or equa-

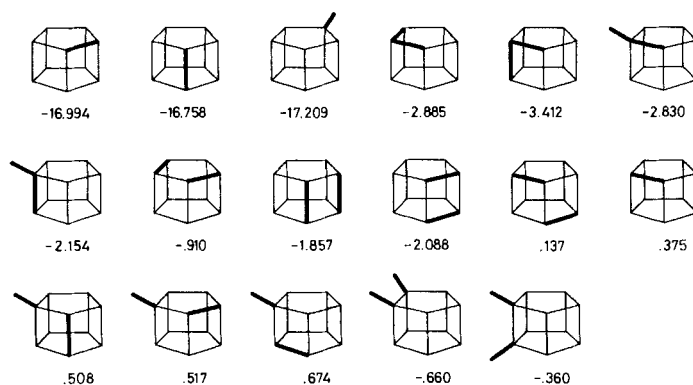


Fig. 3. Matrix elements in eV for the STO-3G model of pentaprismane (3) in localized basis (The values given refer to the self-energy of the localized orbital λ_j (LMO) indicated by a heavy line in the first three formulae or to the cross-term between the two LMO's λ_i, λ_j indicated. All other values are given by symmetry)

torial orientation of the LMO. As has already been observed for cubane (**2**) [1], the main difference between corresponding matrix elements of **3** and of an unstrained hydrocarbon [9] are the large values of the geminal cross-terms $B_{ac} = \langle \lambda_a | \mathcal{F} | \lambda_c \rangle = -3.4$ eV and of the vicinal cross-terms $\Gamma_{aa} = -1.9$ eV, $\Gamma_{ee} = -2.1$ eV of pairs of LMO's facing each other across a four-membered ring, compared to $B_{CC,CC} = -2.9$ eV and $\Gamma_{CC,CC}(\text{syn-planar}) = -1.0$ eV in a saturated, open-chain hydrocarbon. All other cross-terms have their usual values, as shown in Figure 3.

In Figure 4 the CMO's φ_j of **3** are presented schematically as linear combinations of the LMO's λ_j . These diagrams allow a straightforward, *Hückel*-type discussion of the corresponding orbital energies in terms of the matrix elements shown in Figure 3, because of the strict orthogonality of the LMO's, i.e. $\langle \lambda_i | \lambda_j \rangle = \delta_{ij}$.

Band system ①. It is obvious that the first four pairs of CMO's $2e'_2$, $3e'_2$, $2e'_1$ and $3e'_1$, which fall into the narrow gap from -9.32 eV to -9.98 eV could well occur in a different order, depending on small changes in the cross-terms between the LMO's from which they are built. In particular the use of a minimal basis set in the STO-3G procedure could affect the matrix elements given in Figure 3 enough to make the sequence given above an artefact. From an experimental point of view nothing can be deduced from the broad band system spanning the ionization energy interval from 8.5 to 11.5 eV, because each of the individual four bands is presumably distorted and partially split by a *Jahn-Teller* effect. We shall therefore refrain from refining our assignment of these bands beyond the statement that the band system in this region is due to ionization processes in which an electron is lifted from one or the other of the four pairs of CMO's $2e'_2$, $3e'_2$, $2e'_1$ and $3e'_1$, not necessarily in this order. On the other hand it is probably quite safe to assign these four pairs of CMO's to the broad feature in question, in analogy to the interpretation of the cubane PE. spectrum (cf. Fig. 1) where two degenerate orbital triplets t_{2u} , t_{2g} (order uncertain) are associated with the band system in the same ionization energy region.

Band system ② ③. Because of its higher symmetry (O_h) and smaller number of CMO's cubane (**2**) gives rise to a somewhat less congested spectrum than **3**. As a result its interpretation is certainly simpler and more straightforward. In particular the e_g CMO of **2**, which is entirely centred on the LMO's λ_{CC} (with zero contribution from the λ_{CH}) has been associated with the PE. band at 13.75 eV which exhibits a rather distinctive vibrational fine structure. A very similar band is found at 13.25 eV in the PE. spectrum of **3** and it is very tempting to associate it with the CMO $3a'_1$ which is also confined only to the C, C-bonds of **3** as shown in Figure 4. Comparing the CMO diagrams of e_g of **2** [1] with that of $3a'_1$ of **3** one is led to the expectation that the vibrational mode induced by the removal of an electron should be in both cases of a C, C-stretch type in which two opposed C-atom rings (two four-rings in **2**, two five-rings in **3**) move against each other. However, such an assumption would demand that the calculated orbital order $2e'_2$, $2a'_2$, $3a'_1$ for **3** be changed to either $3a'_1$, $2e'_2$, $2a'_2$ or $3a'_1$, $2a'_2$, $2e'_2$. In view of the scatter of points in the regression of Figure 2 such a reversal can not be excluded, especially if the limitations of *Koopmans* approach, applied to a minimal basis set model is

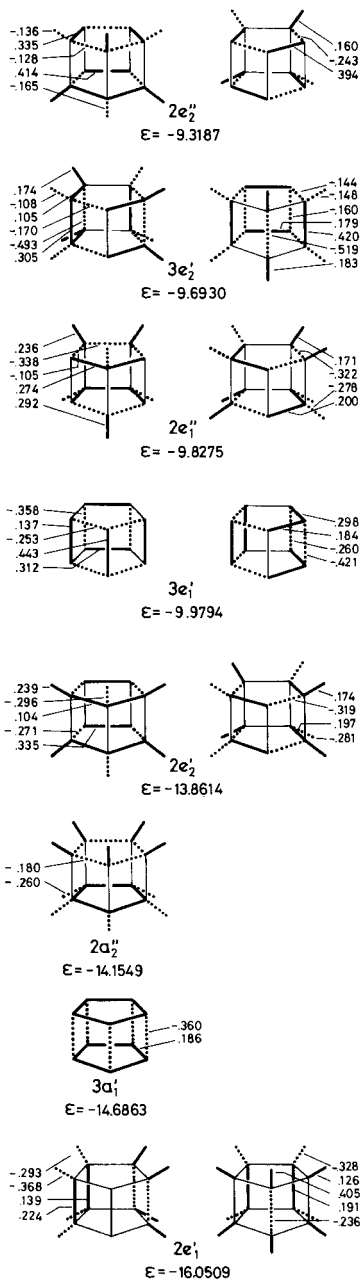
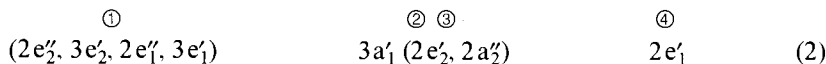


Fig. 4. Schematic representation of the occupied canonical molecular orbitals (CMO's) of pentaprismane (3) in localized basis, as computed according to the STO-3G scheme (Thick solid and dotted lines correspond to localized orbitals of opposite phase. The values given are the coefficients in the linear combination. Thin lines indicate that the contribution of the LMO is zero or vanishingly small)

taken into consideration. Thus we are lead again to the conclusion that the calculated orbital sequence in the interval -13.86 eV to -14.69 eV presented in *Figure 4* is uncertain.

Band ④. The band starting at 15.6 eV in the PE. spectrum of **2**, shows a wide spacing of its vibrational fine structure, typical for a C, H-stretch frequency. Indeed, this band has been related to a CMO a_{2u} of **2** completely localized on the C, H-bonds with zero contribution from the LMO λ_{CC} . In the PE. spectrum of **3** we find a similar band starting at 15.85 eV. The relevant orbital $2e'_1$ shown in *Figure 4* is again mainly localized on the C, H-bonds, albeit not to the same extent as a_{2u} of **2**. This could be the reason why the vibrational fine structure of band ④ is not as well developed as that of the corresponding band in the spectrum of **2**.

From the above discussion it is obvious that one is still far removed from a complete assignment of the PE. spectrum of **3**. However, correlation with the PE. spectrum of **2**, aided by the results derived from an *ab initio* STO-3G calculation leads to a satisfactory interpretation of its gross features. For the moment the most satisfactory assignment is



where the sequence of the orbitals in parenthesis is uncertain.

Appendix. – In previous and forthcoming contributions [9] [10] we have investigated the usefulness of localized molecular orbitals λ_j (LMO) for the study of the electronic structure of hydrocarbons in particular with regard of the interpretation of their PE. spectra. The central question concerns the degree of transferability of the matrix elements of the *Fock* matrix F_λ in localized basis, and an assessment of the relative importance of cross-terms between geminal, vicinal or further separated pairs of LMO's. For aliphatic and for alicyclic, unstrained hydrocarbons it has been found that the low-lying orbitals responsible for the so-called 2s-part of the PE. spectrum (accessible through the use of He(II) radiation) are obtained in a sufficiently good approximation by restricting the matrix elements to the diagonal self-energies A_j of the LMO's λ_j and to their geminal cross-terms $B_{ij} = \langle \lambda_i | \mathcal{F} | \lambda_j \rangle$. The outer valence shell orbitals (yielding the so-called 2p-part of the PE. spectrum) demand the inclusion of vicinal cross-terms $\Gamma_{ij} = \langle \lambda_i | \mathcal{F} | \lambda_j \rangle$, i.e. those where the LMO's λ_i, λ_j are separated by one bond.

Prismane (**3**) happens to be an ideal test case because of its extreme compactness which ensures that even higher cross-terms become rather large because of the spatial proximity of the LMO's. Thus, **3** is in a certain sense the worst possible example for the validity of the above assumptions. In *Figure 5* are shown the results obtained by calculating orbital energies for **3** within the following conventions.

1. These results are obtained by diagonalizing the matrix containing a) the self-energies A_e , (A_a) of the equatorial, (axial) CC-LMO's and A_{CH} of the CH-LMO's on the main diagonal, and b) the corresponding geminal cross-terms B_{ee} , B_{ea} , B_{eCH} and B_{aCH} shown in *Figure 3*.

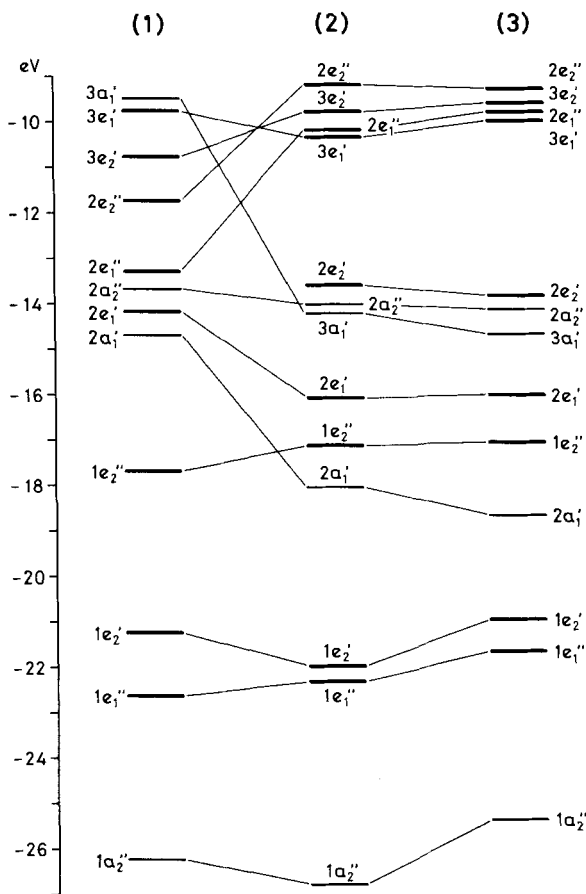


Fig. 5. Comparison of orbital calculations of pentaprismane (3) using localized STO-3G orbitals (cf. Fig. 3) (1) Using only geminal interaction matrix elements; 2) using geminal and vicinal interaction matrix elements, i.e. those presented in Figure 3; 3) using all interaction matrix elements, which leads back to the original CMO's)

2. This calculation uses all the matrix elements given in Figure 3, i.e. those used in 1, plus all vicinal terms Γ_{ij} .

3. Finally diagonalization of the full F_2 matrix leads necessarily back to the CMO's of 3, the highest ones of which are shown in Figure 4.

The results summarized in Figure 5 support rather nicely what has been stated above. The very crude approximation 1 yields the correct sequence and rather precise energies for the low-lying orbitals, e.g. $1e_2'$, $1e_1''$ and $1a_2''$. On the other hand the sequence of the higher orbitals is badly jumbled. Inclusion of the vicinal Γ_{ij} cross-terms in 2 yields the correct ordering (i.e. within the STO-3G model) and a very satisfactory relative spacing. This shows that even in such an extreme case, as in pentaprismane (3), approximation 2 is quite respectable and that it can be used with some confidence for the rationalization of PE. spectra of hydrocarbons.

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