

PHOTOELECTRON SPECTRA OF POLYUNSATURATED [4,4,2]PROPELLANES¹

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Abstract—The photoelectron spectra of the six propellanes 1 to 6 have been recorded. Those bands which correspond to ejection of an electron from a π -orbital have been assigned, using the concept of through bond and through space interaction. Homoconjugative interaction between the π -systems of the two butadiene moieties of 6 is of the same order as that of the π -orbitals in norbornadiene.

Polyenic propellanes seem to be suitable templates for investigation of the interaction of semilocalized π -orbitals. The recent synthetic availability of [4,4,2]propell-11-ene (1) and a number of more highly unsaturated analogs (2-6)²⁻⁴ presented the opportunity to evaluate the level of such effects. That interactions are present in such systems is attested to by the significantly different electronic spectra of, for example, 4 [$\lambda_{\text{max}}^{\text{isooctane}}$ 268 (ϵ 2,400) and 276sh nm (2,100)] and 6 [$\lambda_{\text{max}}^{\text{isooctane}}$ 247 (ϵ 2,500) and 290 nm (2,100)].² However, such shifts in band positions are due not only to overlap controlled electron delocalization of "through space" and/or "through bond" type,⁵ but also to a large extent to energy delocalization in the electronically excited state.⁶ Trying to gain insight into the former type of mechanism, we have recorded the photoelectron (PE.) spectra of hydrocarbons 1 to 6. The results are summarized in Table 1 and in the correlation diagrams of Figs 1 and 2. The orbital energies ϵ_j correspond, according to Koopmans' theorem,⁷ to the vertical ionization potentials $I_{v,j}$, i.e., to the position of the PE. band maxima: $\epsilon_j = -I_{v,j}$.

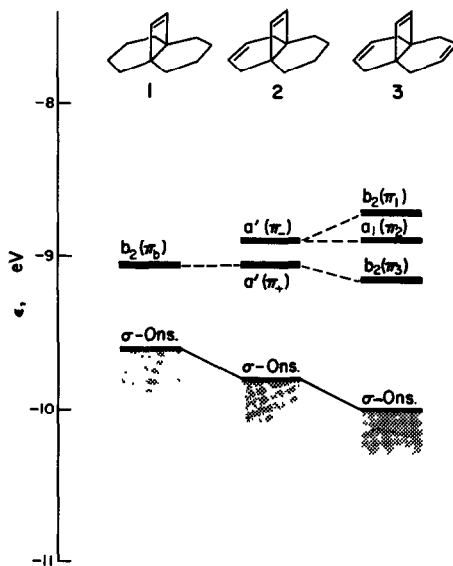


Fig 1. Correlation diagram for the "observed" orbital energies of the compounds 1 to 3 (see Table 1).

Table 1. Vertical ionization potentials $I_{v,j}$ (in eV) for the hydrocarbons 1 to 6

The following abbreviations have been used for the characterization of the π -orbitals: $\pi_+ = (\pi_a + \pi_b)/\sqrt{2}$ or $(\pi_b + \pi_c)/\sqrt{2}$; $\pi_- = (\pi_a - \pi_b)/\sqrt{2}$ or $(\pi_b - \pi_c)/\sqrt{2}$; $\pi'_+ = (\pi_d + \pi_e)/\sqrt{2}$; $\pi'_- = (\pi_d - \pi_e)/\sqrt{2}$.

Band Compd.	1	2	3	4	5	I_v (σ -Onset)					
	$I_{v,1}$	Orbt.	$I_{v,2}$	Orbt.	$I_{v,3}$	Orbt.	$I_{v,4}$	Orbt.	$I_{v,5}$	Orbt.	I_v (σ -Onset)
1	9.0 ₅	$b_2(\pi_b)$									9.6
2	8.9	$a'(\pi_+)$	9.0 ₅	$a'(\pi_+)$							9.8
3	8.7	$b_2(\pi_1)$	8.9	$a_1(\pi_2)$	9.1 ₅	$b_2(\pi_3)$					10.0
4	8.0	$a'(\pi'_-)$	9.0 ₅	$a'(\pi_b)$	10.5	$a'(\pi'_+)$					10.0
5	8.0	$a'(\pi'_-)$	9.0 ₅	$a'(\pi_-)$	9.2	$a'(\pi_+)$	10.5	$a'(\pi'_+)$			10.0
6	8.1	$a_2(\pi_4)$	8.5	$b_1(\pi_3)$	9.2	$b_2(\pi_b)$	10.3	$b_2(\pi_2)$	~10.8	$a_1(\pi_1)$	10.5

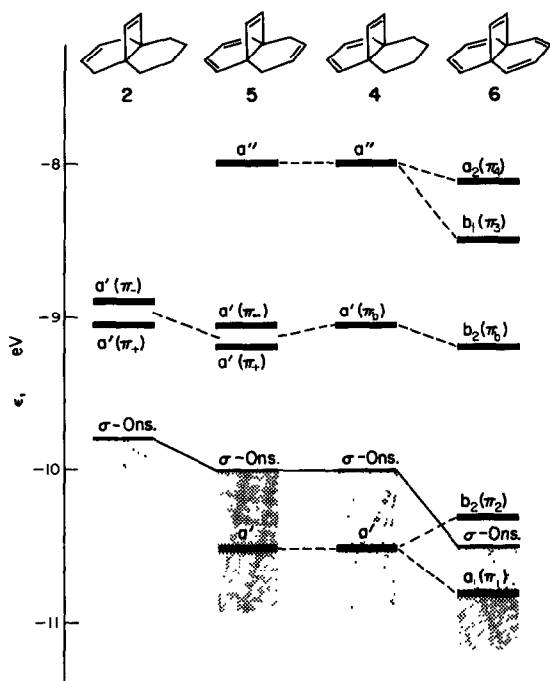
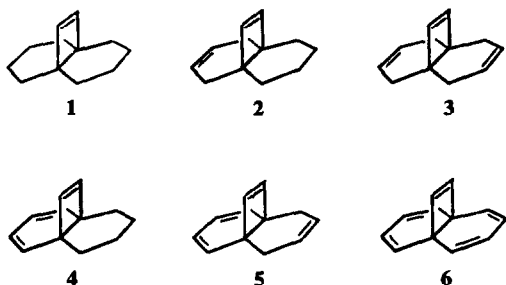
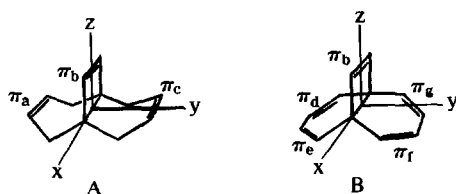


Fig 2. Correlation diagram for the "observed" orbital energies of the compounds 2, 4, 5 and 6 (see Table 1).



The exact conformations of compounds 1 to 6 are not known. For the purpose of the following discussion we have assumed idealized conformations of C_s (2, 4, 5) and C_{2v} (1, 3, 6) symmetry, which place the basis π -orbitals in the relative orientations shown in diagrams A and B.



The orbital labels in Table 1 and in Figs 1 and 2 refer to these symmetries. For convenience we

have dropped the normalizing coefficients of the linear combinations given in brackets.

Correlation 1----2----3

Although assignment of the "observed" π -orbital energies of 1, 2 and 3 to particular orbitals may seem to be straightforward, we believe that it is not possible to derive a unique assignment in view of the complexity of the interaction mechanism between π_a , π_b and π_c . Indeed, the small differences in observed orbital energies are probably the resultant of partially compensating "through space" and "through bond" interactions,⁵ the size of which depends critically on the exact conformation of the molecules.

Previous experience⁸ has shown that the successive introduction of non-conjugated double-bonds into a mono- or polycyclic monoene shifts the mean of the π -orbital energies $\bar{\epsilon}(\pi)$ by -0.1_s to -0.2 eV, per added double bond towards lower energies. In contrast, we observe that $\bar{\epsilon}(\pi)$ is shifted positively along the series 1, 2, 3: $-\bar{\epsilon}(\pi) = 9.0_s$ eV for 1; $8.9_s - 9.0$ eV for 2; 8.9 eV for 3. This can be construed as an indication that there must be substantial interaction with lower lying σ -orbitals, as has been shown previously for cycloocta-1,5-diene (7)⁹ or syn-tricyclo-[4.2.0.0^{2,5}]octadiene (8),¹⁰ where the π -orbitals assume similar relative positions as in 2 or 3.



The π -orbital energies of cyclobutene¹¹ and cyclohexene¹¹ are -9.4 and -9.1 eV respectively. In 1 the cyclobutene ring carries four alkyl substituents in a β -relationship to the double bond, which shifts $A_b \equiv \epsilon(\pi_b)$ by $+0.35$ eV. Similar substitution in a γ -orientation to the double bond of the six membered ring in the unstudied compound 9 would presumably produce a shift of $+0.1$ eV in $A_a \equiv \epsilon(\pi_a)$. The simultaneous presence of π_a and π_b in 2 demands a correction⁸ of -0.1_s to -0.2 eV, which yields basis orbital energies $A_a = -9.1_s$ to -9.2 eV and $A_b = -9.2$ to -9.2_s eV for the π -orbitals π_a and π_b of 2. For simplicity, we shall assume accidental degeneracy, i.e. $A_a = A_b = -9.2$ eV.

The same argument applied to the three basis π -orbitals of 3 will lead to $A_a = A_b = A_c = -9.4$ eV.

If π_a and π_b of 2 interacted only by a "through space" mechanism (resonance integral β_{ab}) we would expect, relative to $A_a = A_b$, a lower lying orbital $\pi_+ = (\pi_a + \pi_b)/\sqrt{2}$ and a higher lying orbital $(\pi_a - \pi_b)/\sqrt{2}$ such that $(\epsilon(\pi_+) + \epsilon(\pi_-))/2 = A_a = A_b = -9.2$ eV. However, π_+ will interact

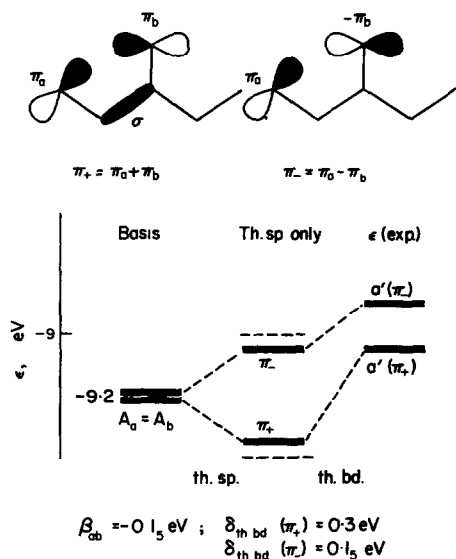


Fig 3. Interaction diagram for the orbitals π_a and π_b in 2. The two linear combinations π_+ and π_- are shown qualitatively. Their interaction has been partitioned into a through space part ($\beta_{ab} = -0.15 \text{ eV}$) and a through bond part ($\delta(\pi_+) = 0.3$; $\delta(\pi_-) = 0.15 \text{ eV}$).

with the CC- σ -orbital as shown in the top diagram of Fig 3 and, perhaps to a smaller extent, with the Walsh-type orbital of the cyclobutene moiety (Walsh orbital of cyclobutane¹² and cyclobutene¹¹; $\epsilon(\sigma; \text{Walsh}) = -11.0 \text{ eV}$ ¹²). This will result in a positive displacement of $\epsilon(\pi_+)$ by an increment $\delta_{\text{th.bd.}}(\pi_+)$. The latter type of interaction may also occur for $\epsilon(\pi_-)$, albeit to a lesser degree: $\delta_{\text{th.bd.}}(\pi_-)$. As a working hypothesis we shall assume that the interplay of these effects results, as shown in Fig 3, in an orbital sequence of π_- above π_+ . This is also the one given in Fig 1 and in Table 1.

If the parameter $\beta_{ab} = -0.15 \text{ eV}$ (see Fig 3) is carried over to compound 3, we obtain with $A_a = A_b = A_c = -9.4 \text{ eV}$ the linear combinations π_1, π_2, π_3 of π -orbitals shown at the top of Fig 4 and the orbital energies $\epsilon(\pi_1) = -9.6 \text{ eV}$, $\epsilon(\pi_2) = -9.4 \text{ eV}$ and $\epsilon(\pi_3) = -9.2 \text{ eV}$. A second order perturbation treatment suggests that the displacement $\delta_{\text{th.bd.}}(\pi_1)$ experienced by $\epsilon(\pi_1)$ of 3 should be roughly three times as large as $\delta_{\text{th.bd.}}(\pi_+)$ in 2, i.e., $\delta_{\text{th.bd.}}(\pi_1) \approx 0.9 \text{ eV}$. This would make $b_2(\pi_1)$ the top occupied orbital in 3. On the other hand $\delta_{\text{th.bd.}}(\pi_3)$ must be almost zero for symmetry reasons and thus $b_2(\pi_3)$ correlates with band 3 in the PE. spectrum of 3. This leaves the central π -orbital at -8.9 eV to be assigned to $a_1(\pi_2)$, which demands $\delta_{\text{th.bd.}}(\pi_2) = 0.5 \text{ eV}$. This displacement is larger than twice $\delta_{\text{th.bd.}}(\pi_-)$ observed for 2, but still within reasonable limits for through-bond interaction with the Walsh orbital of the four-membered ring.

It should be emphasized that the resulting correlation diagram, i.e. the assignment of particular

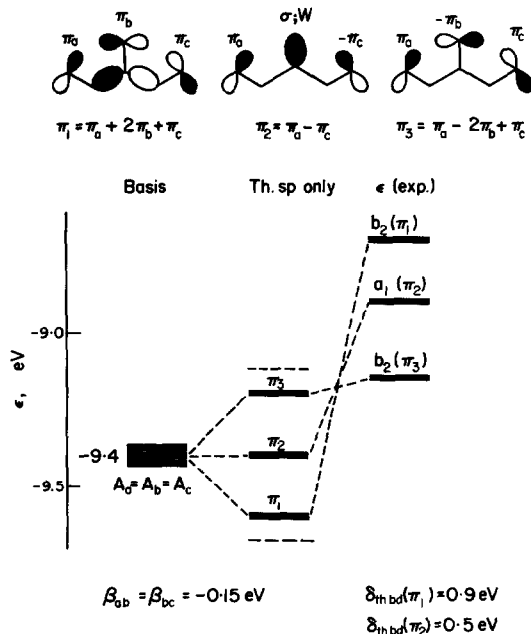


Fig 4. Interaction diagram for the orbitals π_a, π_b and π_c in 3. The linear combinations $\pi_1 \approx \pi_a + 2\pi_b + \pi_c$; $\pi_2 \approx \pi_a - \pi_c$ and $\pi_3 = \pi_a - 2\pi_b + \pi_c$ are shown qualitatively together with the σ orbitals of the same symmetry. The interaction between these orbitals has been partitioned into a through space part ($\beta_{ab} = \beta_{bc} = -0.15 \text{ eV}$) and a through bond part ($\delta(\pi_1) = 0.9 \text{ eV}$; $\delta(\pi_2) = 0.5 \text{ eV}$).

orbitals to the first two or three PE. bands of 2 or 3 is largely guesswork and should at best be considered only as a working hypothesis. However, this hypothesis is compatible with the results of an analysis of the PE. spectra of other polycyclic polyenes,⁸⁻¹⁰ where the interpretation is more clear-cut.

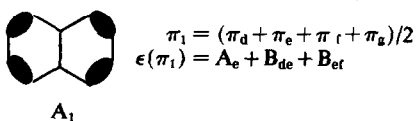
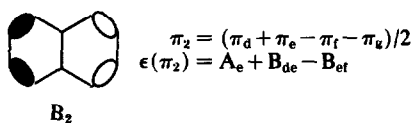
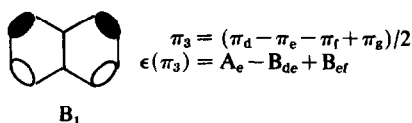
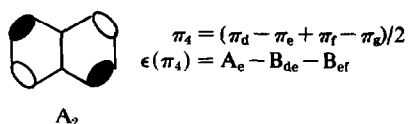
The main purpose of having presented this hypothesis in such detail is to show how complex the analysis of a seemingly simple PE. spectrum can be and to drive home the message that the interpretation of such spectra is not always as straightforward as sometimes assumed.

Correlation 4-----5-----6

With the above reservation in mind we shall now examine the PE. spectroscopic data of 4, 5 and 6 (Fig 2).

In one respect these data are much simpler to interpret, because of the presence of the *s-cis* diene moieties, whose π -orbital energies can be estimated with some confidence. Furthermore, electron ejection from these orbitals yields bands in the PE. spectra, which are well detached from those at higher ionization potentials and therefore easy to identify. This is a result of the fact that direct conjugative interaction of π_d with π_e and

π_f with π_g is governed by a resonance integral $B_{de} = B_{fg} = -1.2$ eV, as derived from the PE spectra of, e.g., butadiene¹³ or cyclohexa-1,3-diene.¹¹ Furthermore the homoconjugative interaction of π_d with π_g and of π_e with π_f is presumably through space dominated, i.e., describable by a resonance integral $B_{ef} = B_{dg}$. This leads to the following four symmetry adapted linear combinations for **6**, which belong to four different irreducible representations of the group C_{2v} :



The orbital scheme given in Fig 2 for **6** is self-explanatory. Because of the relationship $B_{de} \gg B_{ef}$, the first two bands must correspond to an ionization process in which the electron vacates $a_2(\pi_4)$ or $b_1(\pi_3)$, orbitals, which are essentially π_4 or π_3 in character. From $\epsilon(a_2(\pi_4)) - \epsilon(b_1(\pi_3)) = 0.4$ eV, we deduce $B_{ef} = -0.2$ eV, which corresponds to a resonance integral between the homoconjugating 2p-atomic orbitals of $\beta_{h.c.} = -0.4$ eV. This agrees with what has been observed for the homoconjugative interaction of two 2p atomic orbitals in e.g. norbornadiene⁶ ($\beta_{h.c.} = -0.4$ eV), bicyclo[2.2.2]octadiene ($\beta_{h.c.} = -0.3$ eV) or cis-cis-cis-1,4,7-nonatriene¹⁴ ($\beta_{h.c.} = -0.6$ eV). The mean value of $\epsilon(a_2(\pi_4))$, $\epsilon(b_1(\pi_3))$, $\epsilon(b_2(\pi_2))$ and $\epsilon(a_1(\pi_1))$ is $\overline{\epsilon(\pi)} = A_e = -9.4$ eV. This value is rather uncertain, because the two bands associated with electron ejection from $b_2(\pi_2)$ and $a_1(\pi_1)$ are strongly overlapped by the band system due to ionization from σ -orbitals. Nevertheless the value is reasonable. The interaction described by B_{de} is obtained

according to $[\epsilon(a_2(\pi_4)) + \epsilon(b_1(\pi_3)) - \epsilon(b_2(\pi_2)) - \epsilon(a_1(\pi_1))]/4 = -1.15$ eV = B_{de} , which is in good agreement with the value -1.2 eV quoted above. This leaves $b_2(\pi_2)$ with $\epsilon(b_2(\pi_2)) = -9.2$ eV.

The correlation with the orbitals of **4** and **5**, which is indicated in Fig 2, is straightforward. Small deviations are probably due to changes in bond angles and twist angles, which are difficult to assess from molecular models.

The preceding discussion emphasises the fact that whenever π -orbital interactions in non-planar systems are discussed, σ/π -interaction has to be considered explicitly. In the case of the propellanes **1**, **2**, **3**, through bond interaction overrules the inductive effect, which the alkyl moieties exert on the basis π -orbital energies. In contrast, the positions of the π -bands in the PE spectrum of **6**, and to a lesser degree of **4** and **5**, are mainly determined by through space conjugation of the classical and/or hyperconjugative type.

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