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13. The Interaction of π-Orbitals in Barrelene[1])

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(25. XI. 70)

Summary. The photoelectron spectrum (PE. spectrum) of barrelene (bicyclo[2.2.2]octatriene, **4**) is recorded and the first four bands are correlated with orbitals obtained with the MINDO/2-SCF procedure. The structural changes accompagnying the ionisation process **4** → **4**+ are qualitatively derived from the features of the top-occupied a'_2 (π) MO of **4**, which shows complete σ-π separation. The vibrational pattern of the corresponding PE. band ① as well as complete energy-minimisation of the geometries of **4** and **4**+ support the conclusion that **4** is a rather strained molecule. The interaction of the three π-bonds in **4** are discussed in terms of '*through-space*' and '*through-bond*' interaction with lower lying σ-orbitals. It is found that the latter is far from being negligible.

In a previous note of this series [2] we reported on the interaction of the π-orbitals π_1 and π_2 in bicyclo[2.2.2]octadiene (**3**), as determined by high-resolution photo-

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[1])   Part 20 of 'Application of Photoelectron-Spectroscopy', part 19 see ref. [1].
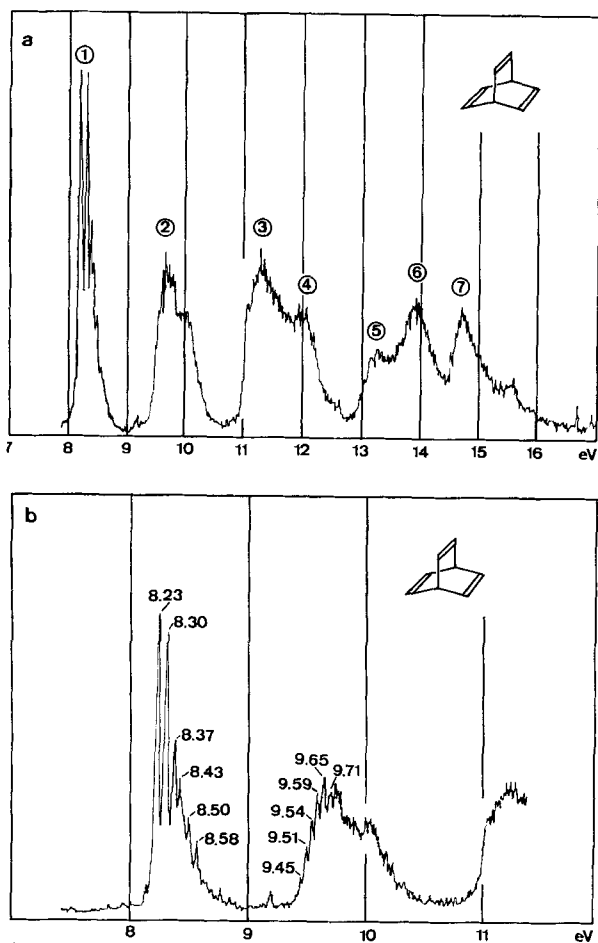
Fig. 1. *Photoelectron spectrum of barrelene* (**4**)

Table 1. *Photoelectron Spectrum of Barrelene (bicyclo[2.2.2]octatriene)* (**4**)

Adiabatic (I_a) and vertical (I_v) ionisation potentials in eV. I_G = values (in eV) obtained with a grid type spectrometer [4]. $\Delta\tilde{\nu}$ = spacing of vibrational fine structure

Band Assignment	① $\mathbf{a'_2}\,(\pi)$	② $\mathbf{e'}\,(\pi)$		③ $(\mathbf{e''}\,(\sigma))$?	④ $(\mathbf{a'}\,(\sigma))$?	⑤	⑥	⑦
I_a	8.23[a]	9.45		10.96		13.0		14.5
I_v	8.23[a]	9.65[b]	10.02[b]	11.25	11.9–12.0	13.2	13.9	14.7
I_G	8.24	9.63		11.11		13.1		14.5
$\Delta\tilde{\nu}$ eV	0.07	0.05₂						
cm⁻¹	570	420						

[a]) First vibrational fine-structure band of highest intensity.
[b]) *Jahn-Teller* split of 0.3 eV.

electron spectroscopy (PE.-spectroscopy). It was found that the orbital energies of the two top occupied π-orbitals $\mathbf{b}_2(\pi)$ and $\mathbf{a}_1(\pi)$ of **3** (assumed symmetry C_{2v}) are separated by a gap of $\varepsilon(\mathbf{b}_2(\pi)) - \varepsilon(\mathbf{a}_1(\pi)) = 0.58$ eV. The electronic mechanism responsible for this split has been discussed in terms of *'through-space'* and *'through-bond'* interactions ([3], see also [4]). Further evidence in support of such a mechanism was obtained through photoelectron spectroscopic investigations of *cis, cis, cis*-1,4,7-cyclononatriene [5], bullvalene [6] and other unsaturated cyclic hydrocarbons [7]. (For the theoretical aspects involved, the reader is referred to a review by *Hoffmann* [8]). With respect to the problem of the interaction of non-conjugated π-orbitals, barrelene (bicyclo[2.2.2]octatriene, **4** [9]) is obviously a key compound.

1   **2**   **3**   **4**
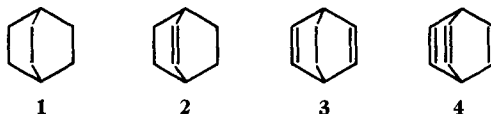
High-resolution PE. spectra of the hydrocarbons bicyclo[2.2.2]octane (**1**), bicyclo[2.2.2]octene (**2**) and bicyclo[2.2.2]octadiene (**3**) have been published (see fig. 3 of ref. [2]). On the other hand, the ionisation potentials of barrelene (**4**) measured by *Bodor, Dewar & Worley* [4], were obtained with a grid-type PE. spectrometer [10] and do not allow a uniquely defined assignment to particular orbitals. Furthermore the sample of **4** used at the time was contaminated with benzene (ionisation potentials at 9.22, 11.49, 13.79 and 16.89 eV [4]). Fig.1,a shows the high-resolution PE. spectrum of a pure sample of **4**, which has been recorded on a *Perkin-Elmer PS-16* spectrometer [11]. (The corresponding characteristic values are listed in tab.1.)

As shown in the correlation diagram of fig.2, the ionisation potentials corresponding to the onset of the σ-bands in the PE. spectra of **1**, **2** and **3** (**1**:9.7 eV; **2**:10.0 eV; **3**:10.4 eV [2]) extrapolate linearly to a value of about 10.8 eV for **4** (see fig.2). This shift towards higher ionisation potentials of the onset of the σ-band system, which occurs when the number of double bonds in a given hydrocarbon is increased, has also been observed in other cases [2] [5] [6]. A rationale for this effect is that the 2s-character of the σ-frame increases with the number of π-bonds in the system. To a first crude approximation the correlation between the magnitude of the shift and the number of π-bonds has proved to be linear in the cases studied so far. As a result the orbital energy $\varepsilon(\sigma)$ of the top occupied σ-orbital of **4** must lie at, or lower than – 10.8 eV. Consequently the first two bands (① and ②) in the PE. spectrum of **4** (see fig.1,a) must be classified as π-bands, *i.e.* they belong to ionisation processes in which the photoelectron vacates a π-orbital.

The first π-band (band ① in the PE. spectrum of **4** (see fig.1,b) is sharp, single and fine-structured. This is in agreement with the theoretical prediction, that the top occupied π-orbital $\mathbf{a}'_2(\pi)$ of **4** is not degenerate and belongs to the irreducible representation A'_2 of D_{3h}.

On the other hand the complex structure of the second band (band ②, see fig.1,b) and in particular the fact that it is split into two components separated by about 0.3 eV can be easily understood: Indeed all theoretical treatments agree [3] [8] that the second π-orbital $\mathbf{e}'(\pi)$ of **4** is degenerate, belonging to the irreducible representation E' of D_{3h}. Therefore the radical cation 4^+ of electron configuration... $(\mathbf{e}'(\pi))^3$ $(\mathbf{a}'_2(\pi))^2$, that is in its electronically excited $^2E'$ state, undergoes a *Jahn-Teller* distortion.
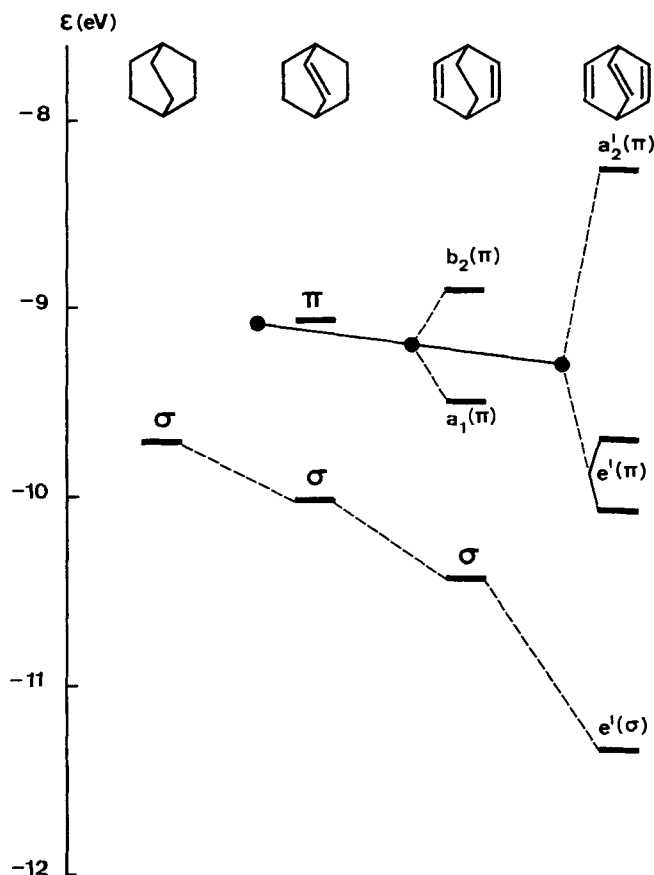
Fig. 2. *Correlation diagram for the π- and σ-orbitals of bicyclo [2.2.2] octane* (**1**), *bicyclo[2.2.2] octene* (**2**), *bicyclo[2.2.2]octadiene* (**3**), *and barrelene* (**4**)

The orbital energies of the π-orbitals correspond to the negative, vertical ionisation potentials, those of the σ-orbitals to the onset of the σ-band system

A simple group-theoretical analysis will show that the 48 basis atomic orbitals of **4** (including the 1s atomic orbitals of the carbon atoms) yield 48 bonding and anti-bonding molecular orbitals belonging to the following irreducible representations of the group D_{3h}: 9 to A_1, 9 to A''_2, 7 pairs to E', 7 pairs to E'' and only one single orbital belonging to A'_2 and A''_1, respectively. Of these $\mathbf{a}'_2(\pi)$ is bonding and $\mathbf{a}''_1(\pi)$ anti-bonding. These two orbitals are rather remarkable: Even though **4** has a π-system as far from coplanarity as one could wish, both $\mathbf{a}'_2(\pi)$ and $\mathbf{a}''_1(\pi)$ are strictly orthogonal to all other molecular orbitals and thus pure π-orbitals. The differences of their orbital energies $\varepsilon(\mathbf{a}'_2(\pi))$ and $\varepsilon(\mathbf{a}''_1(\pi))$, relative to the energies $\varepsilon(\pi_j)$ and $\varepsilon^*(\pi_j)$ of the basis orbitals π_j $(j = 1, 2, 3)$ are therefore due only to the *'through space'* interaction among the π_j's. If reliable estimates of $\varepsilon(\pi_j)$ were available, one could determine the inter-action matrix element $\beta_{ij} = \langle \pi_i | \mathcal{H} | \pi_j \rangle$ directly from the observed first ionisation potential of **4**. Unfortunately this does not seem possible for the moment.

An interesting consequence of this complete σ-π-separation valid for the top-occupied molecular orbital $\mathbf{a'_2}(\pi)$ of **4** is that removal of one of its electrons can influence the structure of the system only in two ways. (This can be deduced by inspection from the diagrammatic representation of orbital $\mathbf{a'_2}(\pi)$ given below.)

a) Since the three basis orbitals π_j of $\mathbf{a'_2}(\pi)$ are bonding, removal of an electron will weaken each of the three π-bonds.

b) Since the interaction between any two of the basis orbitals π_j in $\mathbf{a'_2}(\pi)$ is anti-bonding, removal of an electron will reduce the repulsion between all pairs of π-bonds.

Consequently the relaxation following an ionisation process which leaves $\mathbf{a'_2}(\pi)$ singly occupied will lead a) to a lengthening of the π-bonds and b) to a slimming of the radical cation **4**+ in its $^2A'_2$-state relative to the neutral molecule **4**. However, the π-bond lengthening will be only 1/3 of that of an isolated double bond as the linear combination $\mathbf{a'_2}(\pi)$ contains the three basis orbitals π_j with coefficients $3^{-1/2}$. On the other hand the reduced repulsion between the π-bonds will lead to a deformation of the molecular frame in which the apical methine groups move away from each other. The situation is rather similar to that observed in the case of 1,4-diazabicyclo[2.2.2]octane upon ejection of an electron from the $\mathbf{a''_1}(n)$ orbital [12], even though the electronic mechanism is quite different [13]. This deformation involving only the 'soft' bond angles will yield relatively large changes in the non-bonded distances. Such a process is associated with a rather shallow potential well. As a consequence one expects that the vibrational fine structure pattern of the first band in the PE. spectrum of **4** will be dominated by the totally symmetric mode (i.e. belonging to A'_1) which corresponds to the deformation of the molecular cage described above and not by the one associated with the C=C-stretching. Model normal co-ordinate calculations for **1** [14] which in a first crude approximation are also representative for **4**, yield such a normal mode with $\tilde{\nu} = 600$ cm^{-1}. This is in excellent qualitative agreement with the observed fine structure spacing of 570 cm^{-1} of the first band in the PE. spectrum of **4**. In contrast, the frequencies of C=C-stretching vibrations in radical cations of unsaturated hydrocarbons with singly occupied π-orbitals are of the order of 1400 cm^{-1} [15].

This interpretations of the vibrational pattern of band ① in the PE. spectrum of **4** can be confirmed by a detailed theoretical calculation of the changes in topography which accompany the ionisation process $\mathbf{4} + h\nu \rightarrow \mathbf{4}^+ + e$, both **4** and **4**+ being in their respective electronic ground state. The internal co-ordinates given in tab. 2 have been obtained by the complete minimisation of the structures **4** and **4**+ with respect to their total energies, using the MINDO/2-SCF-procedure [16]. (It was assumed that D_{3h}-symmetry is retained in **4**+). The major changes consist in a lengthening of the distance between the apical carbon atoms 1 and 4 by 0.13 Å and in a corresponding shortening of the separation between the axes of the three π-bonds by 0.07 Å. Furthermore, the C–C single bonds shorten by 0.02 Å, while the length of each double bond increases by only 0.03 Å. This value is about 1/3 of that calculated for trans 2-butene (0.08 Å, [17]), in agreement with the qualitative predictions made above.

From these data it can be deduced that removal of an electron from the top occupied bonding orbital $\mathbf{a'_2}(\pi)$ results in an overall contraction of the system, *i.e.* in a reduction of the molecular volume. This, in turn, indicates that there must be a fair amount of repulsive interaction between the non-bonded π-centers in the neutral

Table 2. *Predicted changes in interatomic distances which follow the ionisation process* **4** → **4+**

Both **4** and **4+** in their electronic ground state and of D_{3h}-symmetry
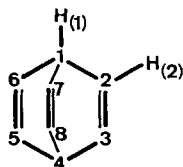
Bonds	Distances in Å for		Change in Å
	4	**4+**	
$C_{(1)}$—$C_{(2)}$	1.495	1.479	− 0.016
$C_{(2)}$—$C_{(3)}$	1.335	1.365	+ 0.030
$C_{(1)} \cdots C_{(4)}$	2.549	2.678	+ 0.129
$C_{(2)} \cdots C_{(6)}$	2.367	2.296	− 0.071
$C_{(1)}$—$H_{(1)}$	1.093[a]	1.093[a]	—
$C_{(2)}$—$H_{(2)}$	1.083[a]	1.083[a]	—

[a]   These values are assumed ones and are kept constant both for **4** and **4+**. The C—H distances actually used in the MINDO/2 computation are bigger by 0.100 Å for reasons explained in [16].

barrelene molecule, which has therefore to be considered as a strained system. Such a conclusion is strongly supported by the enthalpies of hydrogenation (ΔHh) of **3** and **4** [18]: **3** + 2 H_2 → **1**, ΔHh = −56.21 kcal mol^{-1}; **4** + 3 H_2 → **1**, ΔHh = −93.78 kcal mol^{-1} (all values measured at 25°). From these values one calculates that the enthalpy of hydrogenation for the first double bond in barrelene (**4** + H_2 → **3**) is ΔHh = −37.6 kcal mol^{-1}, which seems to be the largest ΔHh-value ever observed for the hydrogenation of a single double bond. (For comparison: 2,2,5,5-tetramethyl-*cis*-3-hexene, ΔHh = −36.2 kcal mol^{-1}; cyclohexene, ΔHh = −27.1 kcal mol^{-1} [18].) The obvious interpretation is that barrelene (**4**) is a strained molecule and that this strain is relieved in **3**. This is in agreement with the conclusions derived from the analysis of the first band in the PE. spectrum of **4** and from the theoretical considerations.

As far as the second band in the PE. spectrum of **4** is concerned, the situation is much more complicated, due to the presence of a *Jahn-Teller* split. However, the first component of this band exhibits a dominant progression of 420 cm^{-1} spacing *i.e.* of the same order as the spacing observed in the first band. It could be related to a similar deformation vibration of the distorted molecular frame.

The assignment of the first two bands in the PE. spectrum of **4** to the orbitals $a'_2(\pi)$ and $e'(\pi)$ is quite unambiguous. However, some difficulties arise when one tries to correlate the bands which follow at higher ionisation potentials with molecular orbitals derived from theoretical models. The reason for this situation is exemplified in tab. 3 and fig. 3, which summarise the results obtained by the MINDO/2 procedure [16]. The orbital energies of the four top occupied molecular orbitals and the enthalpy of formation ΔHf°_{298} of barrelene (**4**) have been computed as a function of the angle θ between the axial C–H- and the C–C-single bonds under the simplifying assumption that all bond lengths remain constant and that D_{3h}-symmetry is conserved.

Table 3. *Orbital energies (ε in eV) of the four top occupied orbitals and enthalpy of formation (ΔHf°_{298} in kcal mol^{-1}) of barrelene* (**4**), *calculated by the MINDO/2 procedure as a function of the angle θ*

Parameters used: R (H–C(sp^2)) = 1.083 Å, R (H–C(sp^3)) = 1.093 Å, R (C=C) = 1.337 Å, R (C–C) = 1.520 Å. D_{3h}-symmetry

θ	109.5°	113.0°	116.5°	120.0°	a)
$\mathbf{a'}_2$ (π)	− 9.52	− 9.38	− 9.22	− 9.03	− 8.88 (1)
$\mathbf{e'}$ (π)	− 9.78	− 9.72	− 9.63	− 9.50	− 9.37 (2)
$\mathbf{a'}_1$ (σ)	− 9.65	− 9.83	−10.06	−10.33	−10.36 (1)
$\mathbf{e''}$ (σ)	−10.33	−10.25	−10.13	− 9.98	−10.13 (2)
ΔHf°_{298}	53.9	48.0	49.5	58.5	

a) Orbital energies taken from [4]. (1) = non degenerate level, (2) = degenerate level.

The character of the four top orbitals $\mathbf{a'}_2(\pi)$, $\mathbf{e'}(\pi)$, $\mathbf{a'}_1(\sigma)$ and $\mathbf{e''}(\sigma)$ can be symbolically represented as follows:
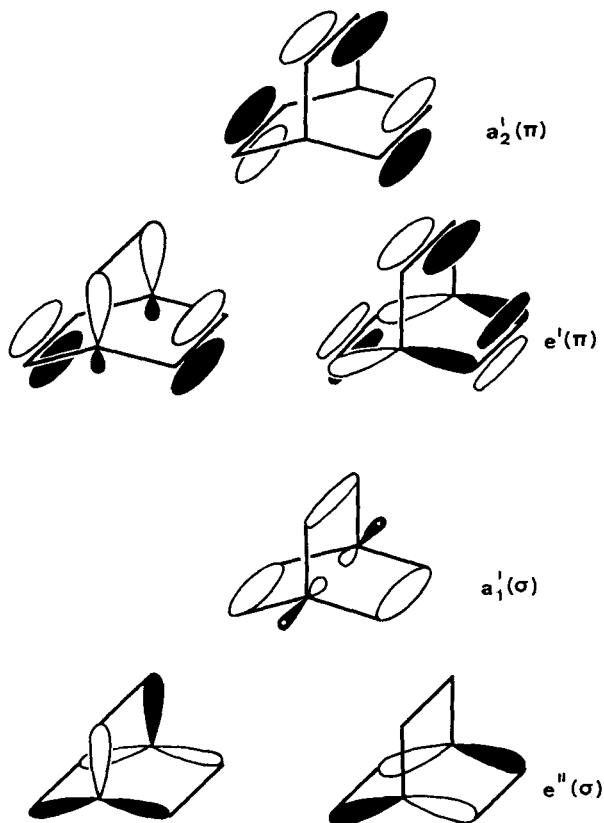
As seen from fig. 3 the orbital energies and thus the order of the orbitals $\mathbf{a'_2}(\pi)$, $\mathbf{e'}(\pi)$, $\mathbf{a'_1}(\sigma)$ and $\mathbf{e''}(\sigma)$ are strongly dependent on the assumed geometry. The computed enthalpy of formation $\Delta H f^{\circ}_{298}$ goes through a minimum at $\theta \approx 114°$. The same is true if θ is obtained by complete minimisation of $\Delta H f^{\circ}_{298}$ without any restrictive conditions. In view of the strong dependence of the sequence of the orbitals on the structure of **4** and of the uncertainty with which this structure can be predicted, the order of the orbitals $\mathbf{a'_1}(\sigma)$ and $\mathbf{e''}(\sigma)$ is open to dispute. All we can say is that their orbital energies must be rather close to each other. Consequently the overlapping PE. bands (labeled ③, ④) in the region of 11 to 12.4 eV (see fig. 1) must correspond to ionisation processes where the photoelectron is ejected from either $\mathbf{a'_1}(\sigma)$ or $\mathbf{e''}(\sigma)$ if our model is reasonable.
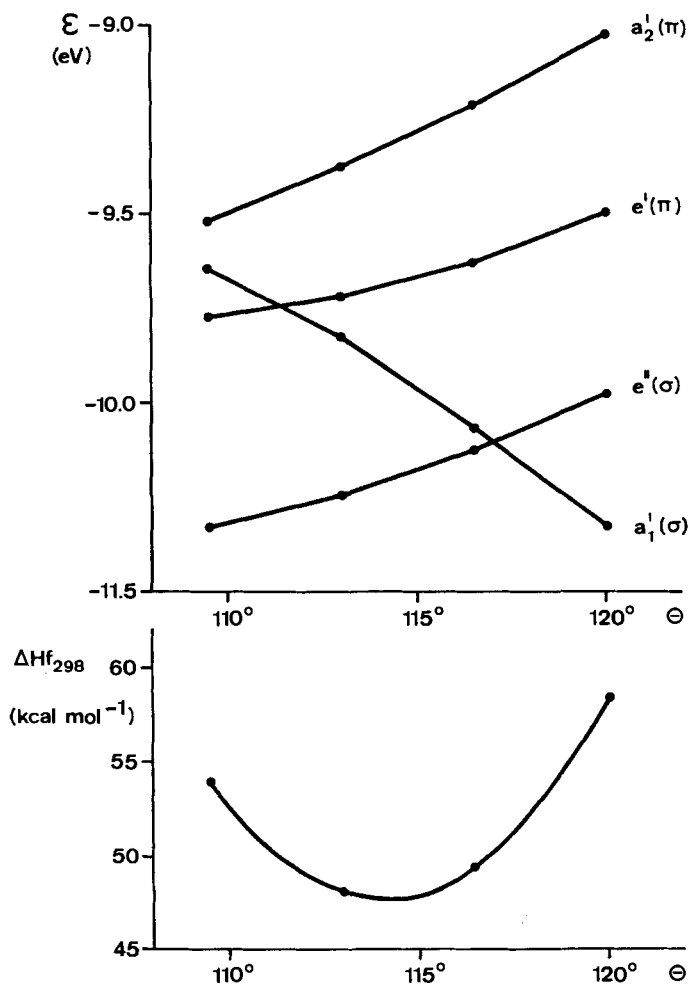

Fig. 3. *Orbital energies of the upper four occupied orbitals and enthalpy of formation of barrelene computed by the MINDO/2 SCF method*

(Definitions of parameters and symbols, see tab. 3)

In view of the higher intensity of the band at $I_v = 11.3$ eV, relative to the one at $I_v \approx 11.9$ eV, one could perhaps advance the following arguments: On the one hand the first band could be correlated with the $\mathbf{e}''(\sigma)$ level which accomodates four electrons and the second with the $\mathbf{a}'(\sigma)$ level containing only two. This would imply $\theta > 117°$ in the model used for the calculation of the data on which fig. 3 is based. On the other hand, if ejection of an electron from $\mathbf{e}''(\sigma)$ results in a large *Jahn-Teller* split (≈ 0.6 eV), the first band at 11.3 eV could correspond to the superposition of the $\mathbf{a}'(\sigma)$ band with one of the $\mathbf{e}''(\sigma)$ band components. The latter interpretation is the one favoured by the calculation summarised in fig. 3, provided that *Koopmans'* theorem holds.

In this connection we wish to draw attention to a serious difficulty which arises when the MINDO/2 model is used for predicting absolute values of higher ionisation potentials. According to the theoretical data published by *Bodor, Dewar & Worley* [4] for **1** to **4** the onset of the σ-band systems in the PE. spectra is predicted as follows: I (onset σ): **1**:9.68 eV; **2**:9.35 eV; **3**:9.49 eV; **4**:10.13 eV. In other words, the onset of **2** and **3** should occur at lower potentials than for **1** and there should be a sharp drop going from **3** to **4**. This is in contradiction to the observation summarised in the correlation diagram of Fig. 2.

Finally we wish to comment on the relative size of the interaction among the π-orbitals π_1 and π_2 in **3**, and of π_1, π_2 and π_3 in **4**. The splits $\varepsilon(\mathbf{b}_2(\pi)) - \varepsilon(\mathbf{a}_1(\pi)) = 0.58$ eV in **3** and $\varepsilon(\mathbf{a}'(\pi)) - \varepsilon(\mathbf{e}'(\pi)) = 1.64$ eV in **4** are the resultants of two effects: *'Through-space'* interaction, to be described by a resonance integral $\beta_{ij} = \langle \pi_i | \mathcal{H} | \pi_j \rangle$, and *'through-bond'* interaction, mainly with lower lying σ-orbitals. It has been shown [5] that in the hydrocarbon **3** $\mathbf{a}_1(\pi)$ interacts strongly, $\mathbf{b}_2(\pi)$ only weakly with bonding σ-orbitals. This leads to a sizeable decrease of the gap which would occur between these π-orbitals if they interacted only *'through-space'*. On the other hand, as mentioned above, the orbital $\mathbf{a}'_2(\pi)$ of **4** cannot interact with any other orbital of this molecule while $\mathbf{e}'(\pi)$ will mix with the $\mathbf{e}'(\sigma)$ orbitals.

From the correlation diagram of fig. 2 it follows that the 'center of gravity' of the π-orbitals shifts only 0.3 eV going from **2** to **4**. This 'center of gravity' cannot represent the true value of the orbitals energy $\varepsilon(\pi_j)$ of the basis orbitals π_j in **3** and **4**, because the *'through-bond'* interaction will tend to raise the observed value of this center above $\varepsilon(\pi_j)$.

As a result the problem at hand can be discussed in two ways, both crudely approximate but containing hopefully a grain of truth.

A) If $\mathbf{b}_2(\pi)$ of **3** and $\mathbf{a}'_2(\pi)$ of **4** are assumed not be affected by *'through-bond'* interaction and if we postulate that the energy $\varepsilon(\pi_j)$ of the basis orbitals π_j is the same in **3** and **4**, then the difference $\varepsilon(\mathbf{b}_2(\pi)) - \varepsilon(\mathbf{a}'_2(\pi)) = 8.87 - (-8.23) = -0.64$ eV would be equal to the resonance integral β_{ij}. However, this can be at best a lower limit for β_{ij}, as it is known from previous experimental work that the energy $\varepsilon(\pi_j)$ of the basis orbitals π_j is in fact not constant, but shifted towards lower values with increasing number of π-bonds in the molecule. (In this connection it is noteworthy that this feature is again in contrast to the predictions derived from some of the many-electron treatments if *Koopmans'* theorem is used.) A simple calculation will show that the observed splits $\varepsilon(\mathbf{b}_2(\pi)) - \varepsilon(\mathbf{a}_1(\pi)) = 0.58$ eV in **3** and of $\varepsilon(\mathbf{a}'_2(\pi)) - \varepsilon(\mathbf{e}'(\pi)) = 1.64$ eV in **4** imply a shift towards higher orbital energies due to *'through-bond'* interaction of 0.70 eV for orbital $\mathbf{a}_1(\pi)$ in **3** and 0.28 eV for orbital $\mathbf{e}'(\pi)$ in **4**.

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B) Another approach would be to postulate that *'through-bond'* interaction will influence the orbitals $\mathbf{a_1}(\pi)$ of **3** and $\mathbf{e'}(\pi)$ of **4** to the same extend, *i.e.* that it will shift the energies of these two orbitals by the same positive amount $\varkappa$. In this case we shall obtain for the molecule **3** that $\varepsilon(\mathbf{b_2}(\pi)) - \varepsilon(\mathbf{a_1}(\pi)) = 2\beta_{ij} + \varkappa = 0.58$ eV and for **4** that $\varepsilon(\mathbf{a'_2}(\pi)) - \varepsilon(\mathbf{e'}(\pi)) = 3\beta_{ij} + \varkappa = 1.64$ eV. From this we calculate the values $\beta_{ij} = -1.06$ eV and $\varkappa = 1.54$ eV. These are upper limits for both quantities which is obvious from the fact that they yield unreasonable energies for the basis orbitals: $\varepsilon(\boldsymbol{\pi}_j) = -9.93$ eV in **3** and $\varepsilon(\boldsymbol{\pi}_j) = -10.35$ eV in **4**. (For comparison: $\varepsilon(\boldsymbol{\pi}) = -10.4$ eV in ethylene, $\varepsilon(\boldsymbol{\pi}_j) = -9.2$ eV in *cis, cis, cis*-1, 4, 7-cyclononatriene.)

However, we may safely conclude that *'through-bond'* interaction of $\boldsymbol{\pi}_1$ and $\boldsymbol{\pi}_2$ in **3** and of $\boldsymbol{\pi}_1$, $\boldsymbol{\pi}_2$ and $\boldsymbol{\pi}_3$ in **4** is far from being negligible.

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