78. Photoelectron-Spectroscopic Evidence for the Orbital Sequence in Fulvene and 3,4-Dimethylene-cyclobutene[1])

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(21. I. 71)

Summary. The photoelectron spectra of fulvene (II) and of 3,4-dimethylene-cyclobutene (III) have been recorded. The PE. bands are correlated, in order of increasing ionisation potentials, with the following orbitals: II: $1a_2(\pi)$, $2b_1(\pi)$, $7b_2(\sigma)$, $1b_1(\pi)$; III: $2b_1(\pi)$, $1a_2(\pi)$, $10a_1(\sigma)$, $8b_2(\sigma)$, $1b_1(\pi)$. This assignment is based on a semi-quantitative perturbation MO-model and on the SCF-LCAO-MO calculations reported by *Praud, Millie & Berthier* [5] for benzene, II and III.

There are four ways in which an ethylene moiety can be formally connected with a *s-cis*-butadiene part to yield a planar, monocyclic σ, π-system containing at least one additional plane of symmetry perpendicular to the σ-framework: benzene (I), fulvene (II), 3,4-dimethylene-cyclobutene (III) and trismethylene-cyclopropane ≡ [3]radialene (IV). Of these, II [2] and III [3] are the two isoelectronic isomers of I, which in the past have attracted the greatest interest. Like benzene they are planar and possess a conjugated π-system containing six electrons, II being a non-alternant and III an alternant cross-conjugated hydrocarbon. As a consequence, they are ideal test cases for π-theories, and numerous calculations on all levels of sophistication have been performed to explain their physical and chemical properties [4] [5].

	I	II	III	IV
Symm.:	D_{6h}	C_{2v}	C_{2v}	D_{3h}
E_π–6 α	8.00 β	7.47 β	7.21 β	7.30 β

(E_π is the total π-electron energy according to a standard HMO-calculation)

The photoelectron spectra (PE. spectra) of II and III are shown in Fig. 1 and the corresponding vertical ionisation potentials I_v are collected in Table 1.

The spectra have been recorded on a modified PS 15 photoelectron *Turner*-type spectrometer [6] of *Perkin-Elmer Ltd.* (Beaconsfield, England). For experimental details the reader is referred to previous communications of this series, *e.g.* [7].

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An assignment of the PE. spectra can be obtained by labelling each band according to the molecular orbital ψ_J from which the electron is thought to be ejected when the molecule M is ionised:

$$M + h\nu \rightarrow M^+(\mathbf{\Psi}) + e \qquad (1)$$

Table 1. *Photoelectron spectra of benzene (I), fulvene (II) and 3,4-dimethylene-cyclobutene (III)*
All values (in eV) refer to vertical ionisation potentials I_v. The numbering corresponds to the one given in Fig. 1. Values in brackets refer to prominent fine-structure components of lower intensity

	I: ⬡		[10]	II:			III:		
No.	I_v	Orb.	Char.	I_v	Orb.	Char.	I_v	Orb.	Char.
1	9.24	$1e_{1g}$	π	(8.36) 8.55 (8.71)	$1a_2$	π	8.80 (8.96) (9.10)	$2b_1$	π
2	11.7	$2e_{2g}$	σ	9.54 (9.66) (9.75)	$2b_1$	π	9.44	$1a_2$	π
3	12.2	$1a_{2u}$	π	12.1	$7b_2$	σ	11.5	$10a_1$	σ
4	13.9	$2e_{1u}$	σ	12.8	$1b_1$ ($11a_1$)?	π (σ)?	12.3	$8b_2$	σ
5	14.7	$1b_{2u}$	σ	13.6		σ	13.3	$1b_1$	π
6	15.4	$1b_{1u}$	σ	14.6[a]		σ	14.1		σ

[a]) shoulder

($\mathbf{\Psi}$ stands for the doublet electronic configuration $(\psi_1)^2 (\psi_2)^2 \ldots (\psi_J)^1 \ldots (\psi_N)^2$ of the radical cation M^+, *i.e.* with ψ_J singly occupied). Such a correlation, which subsumes that *Koopmans'* theorem [8] applies, will of course depend on the particular MO-model chosen. A criterion for the validity of the assignment will be its compatibility with the assignments of PE. spectra of other similar molecules, based on the same MO-model. Unfortunately the vibrational pattern of the individual PE. bands in the spectra of II and III, shown in Fig. 1, is not sufficiently well resolved to provide an additional check of the assignment, through an analysis of the spacing and intensity of the individual progression components [9] (see [10] in the case of I).

To begin with, we shall first establish which of the bands in the PE. spectra of II and III are π-bands, using a naive HMO-model, calibrated on reference spectra of known assignment. The results of this treatment will then be compared to those of an *ab initio*, all-valence electron calculation.

The three molecules I, II and III are planar, so that the principle of σ–π-separation applies. (X-ray diffraction of dimethylfulvene: [11]; Electron diffraction of III: [12].) We shall therefore use standard HMO-basis functions for the π-systems as a start (all α_μ and all $\beta_{\mu\nu}$ between bonded centers μ, ν equal), even though it is known that the σ-systems of II and III possess an uneven charge distribution (see for example [13]).
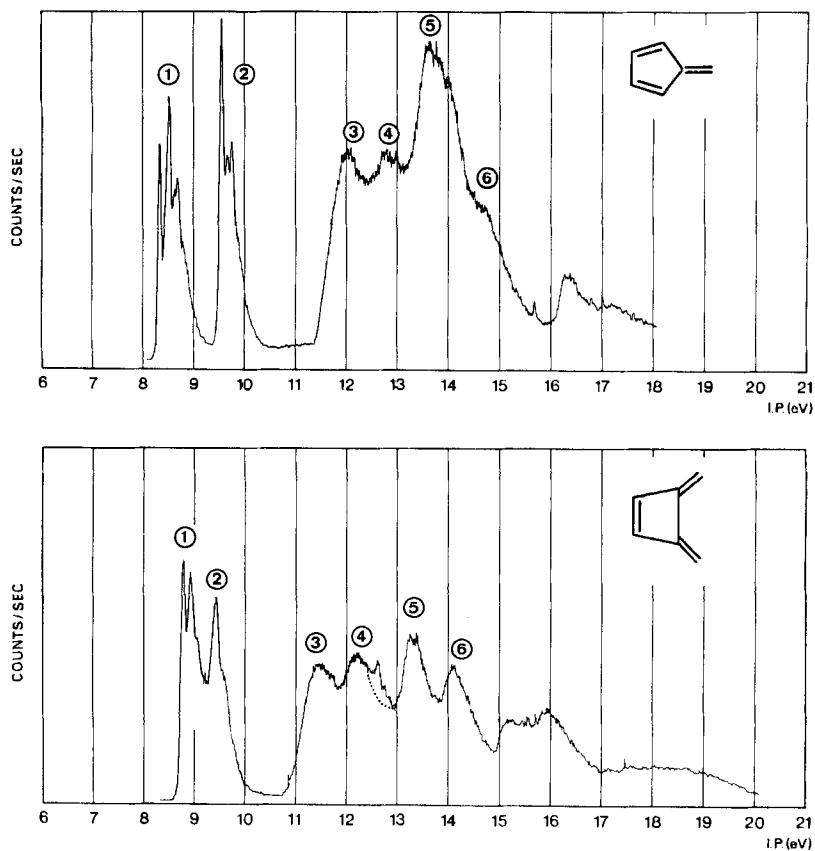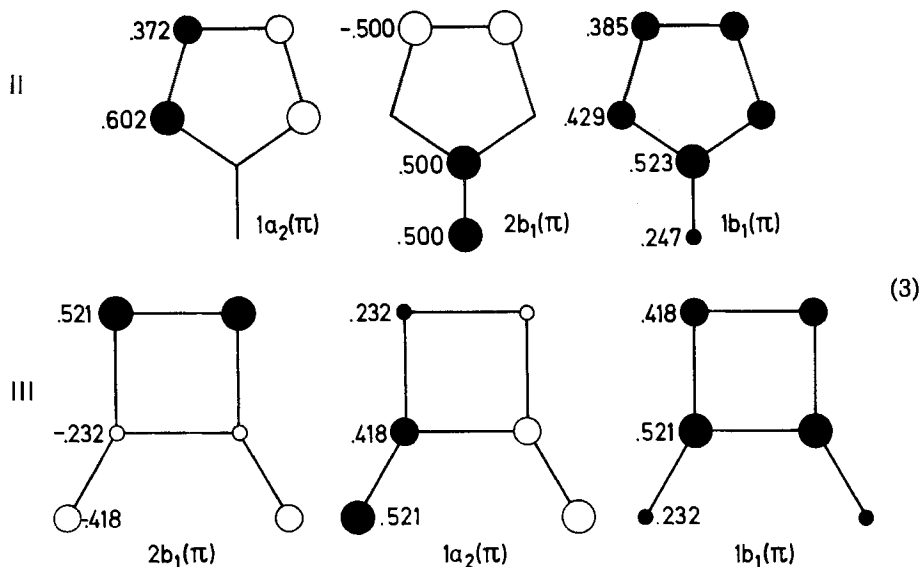
Fig. 1. *Photoelectron spectra of fulvene (II) and 3,4-dimethylene-cyclobutene (III)*

In all three cases there are 36 molecular orbitals (including those extending over the 1s-basis functions), 21 of which are bonding. The latter are distributed as follows over the irreducible representations of the respective symmetry groups:

I			II			III			
D_{6h}			C_{2v}			C_{2v}			
A_{1u}	3	σ	A_1	11	σ	A_1	10	σ	(2)
A_{2u}	1	π	A_2	1	π	A_2	1	π	
B_{1u}	2	σ	B_1	2	π	B_1	2	π	
B_{2u}	1	σ	B_2	7	σ	B_2	8	σ	
E_{1g}	1×2	π							
E_{1u}	3×2	σ							
E_{2g}	3×2	σ							

50

According to standard HMO-theory the three bonding π-molecular orbitals of II and III [14] are, in order of decreasing energy:

II

.372 ─ ○
.602

$1a_2(\pi)$

-.500 ○ ─ ○
.500
.500

$2b_1(\pi)$

.385 ● ─ ●
.429
.523
.247

$1b_1(\pi)$

(3)

III

.521 ● ─ ●
-.232 ○ ─ ○
○ -.418 ○

$2b_1(\pi)$

.232 ● ─ ○
.418 ─ ○
● .521

$1a_2(\pi)$

.418 ● ─ ●
.521
● .232

$1b_1(\pi)$

Even though such a treatment grossly exaggerates the electron delocalisation between the strongly localised π-bonds, it nevertheless suggests that an adequate description can be obtained through a linear combination of the semi-localised molecular π-orbitals
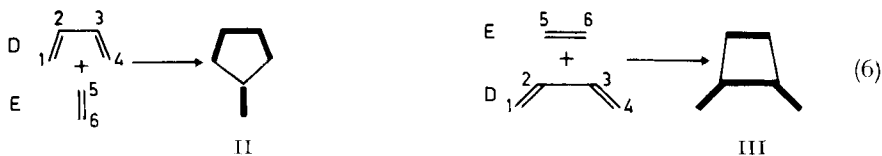
$$\varphi_2(B_1) = 0.372\,(2\mathbf{p}_1 + 2\mathbf{p}_4) + 0.602\,(2\mathbf{p}_2 + 2\mathbf{p}_3)$$

$$\varphi_1(A_2) = 0.602\,(2\mathbf{p}_1 - 2\mathbf{p}_4) + 0.372\,(2\mathbf{p}_2 - 2\mathbf{p}_3)$$

(4)

of the s-cis-diene moieties (D) and of the π-orbitals

$$\varphi_3 = (1/\sqrt{2})\,(2\mathbf{p}_5 + 2\mathbf{p}_6)\,, \quad \varphi_4 = (1/\sqrt{2})\,(2\mathbf{p}_5 - 2\mathbf{p}_6)$$

(5)

of the ethylenic double bond (E) of II and III:

D
E

$\longrightarrow$

II

E
D

$\longrightarrow$

III

(6)

For a derivation of the $\mathbf{b}_1(\pi)$ orbitals of II and III, only the bonding π-orbital φ_3 of E is needed, while the $1a_2(\pi)$ orbital of III demands the admixture of the anti-bonding π-orbital φ_4 of E (see further below). The advantage of such a model, based on second order perturbation theory, is that it allows the assignment of orbital energies $\varepsilon(\varphi_j)$ to the basis orbitals φ_j, which have been calibrated on experimental

data. Such a calibration can be achieved through the use of *Koopmans'* theorem [8], by setting $\varepsilon(\boldsymbol{\varphi}_j) = -I_{vj}$, where I_{vj} is the vertical ionisation potential corresponding to the ejection of an electron from the orbital $\boldsymbol{\varphi}_j$ in a reference compound.

The vertical π-ionisation potential of ethylene is $I_v = 10.51$ eV [15]. The π-ionisation of *s-trans*-butadiene (V(*tr*)) (C_{2h}) yields $I_{v1}(\pi) = 9.06$ eV and $I_{v2}(\pi) = 11.47$ eV [15] [16], which correspond to processes where the photoelectron vacates the orbitals $\mathbf{1b}_g(\pi)$ and $\mathbf{1a}_u(\pi)$ respectively. (Recently it has been suggested [17] that the second π-ionisation potential of *s-trans*-butadiene is $I_{v2} = 12.23$ eV, the PE. band at 11.5 eV being assigned to a σ-ionisation process. However, the evidence is not conclusive and the π-orbital gap of $12.23 - 9.06 = 3.17$ eV resulting from this reinterpretation of the PE. spectrum seems rather too large in comparison to the values obtained for other hydrocarbons containing conjugated double-bonds [18].) In the following we shall use $\varepsilon(\mathbf{b}_g(\pi)) = -9.06$ and $\varepsilon(\mathbf{a}_u(\pi)) = -11.47$ eV as representative π-orbital energies for a *s-trans*-butadiene system. The mean orbital energy $(\varepsilon(\mathbf{b}_g(\pi)) + \varepsilon(\mathbf{a}_u(\pi))/2 = -10.27$ eV must therefore correspond to the orbital energy $\varepsilon(\boldsymbol{\pi}) = \langle \boldsymbol{\pi} \,|\, \mathcal{H} \,|\, \boldsymbol{\pi} \rangle$ of the basis π-orbitals of a single non-conjugating double bond in V(*tr*). (This value is also equal to the mean of the orbital energies of the bonding π-orbitals of benzene (I), as derived from its PE. spectrum [10]: $\varepsilon(\mathbf{e}_{1g}(\pi)) = -9.24$ eV; $\varepsilon(\mathbf{a}_{2u}(\pi)) = -12.2$ eV; $\varepsilon(\boldsymbol{\pi}) = (2 \cdot (-9.24) + (-12.2))/3 = -10.2_3$ eV). We conclude that replacing a C–H bond in ethylene ($I_v = 10.51$ eV) by a C–C(sp^2) σ-bond shifts the orbital energy $\varepsilon(\boldsymbol{\pi})$ of the π-orbital by approximately 0.2 eV towards higher energies. The energy gap $\varepsilon(\mathbf{1a}_u(\pi)) - \varepsilon(\mathbf{1b}_g(\pi)) = 2 \langle \boldsymbol{\pi}_{12} \,|\, \mathcal{H} \,|\, \boldsymbol{\pi}_{34} \rangle = -2.41$ eV in V(*tr*) is equal to the resonance integral $\beta_{23} = \langle 2\mathbf{p}_2 \,|\, \mathcal{H} \,|\, 2\mathbf{p}_3 \rangle = -2.41$ eV between the $2p$ atomic orbitals $2\mathbf{p}_2$, $2\mathbf{p}_3$, which are those connected by the non-essential π-bond in the *s-trans*-butadiene molecule.

In comparison, one may refer to the split of $-9.2 - (-12.2) = 3.0$ eV between the $1\mathbf{e}_{1g}(\pi)$ and $1\mathbf{a}_{2u}(\pi)$ orbitals of benzene, which corresponds to a resonance integral $\beta_{\mu\mu\pm1} = \langle 2\mathbf{p}_\mu \,|\, \mathcal{H} \,|\, 2\mathbf{p}_{\mu\pm1} \rangle = -3.0$ eV between neighbouring $2p$ atomic orbitals separated by 1.39 Å. Note that this larger value of the resonance integral is also the one predicted from $\beta_{23} = -2.4$ eV and from the ratio of the overlap integrals $S(R) = \langle 2\mathbf{p}_\mu \,|\, 2\mathbf{p}_{\mu\pm1} \rangle$ for $R = 1.39$ Å and $R = 1.48$ Å.

If *s-trans*-butadiene (V(*tr*), C_{2h}) is converted to the *s-cis* conformer (V(*c*), C_{2v}), then the orbitals $\mathbf{1b}_g(\pi)$ and $\mathbf{1a}_u(\pi)$ of V(*tr*) become $\mathbf{1a}_2(\pi) \equiv \boldsymbol{\varphi}_1(A_2)$ and $\mathbf{1b}_1(\pi) \equiv \boldsymbol{\varphi}_2(B_1)$ (see (4)) of V(*c*), respectively. We shall assume that the change in orbital energies which accompanies this change in conformation is due to the added interaction between the centers 1 and 4 in the V(*c*) moiety of II and III (cf. (6)). Making the usual assumption that $\beta_{23}/\beta_{14} = S_{23}/S_{14}$, where $S_{\mu\nu} = \langle 2\mathbf{p}_\mu \,|\, 2\mathbf{p}_\nu \rangle$ is the overlap integral, we find that $\beta_{14} = -0.35$ eV in II and $\beta_{14} = -0.05$ eV in III ($R_{14} = 2.4$ Å in II [11], $R_{14} = 3.4$ Å in III [12]). While the interaction in III is quite negligible, the one in II will tend to raise the energy of $\boldsymbol{\varphi}_1(A_2)$ by $2(0.602)^2 \cdot 0.35 = 0.25$ eV and to lower the one of $\boldsymbol{\varphi}_2(B_1)$ by $-2(0.372)^2 \cdot 0.35 = -0.10$ eV.

A check of the value $\varepsilon_1 = \varepsilon(\boldsymbol{\varphi}_1) = -8.8$ eV is provided by the ionisation potential $I_{v1} = 8.52$ eV of cyclopentadiene. This is smaller by 0.3 eV than $-\varepsilon_1$, *i.e.* by just the amount expected for the polar effect of the bridging methylene group. Note that for symmetry reasons there is no hyperconjugative effect between the linear combination of the C–H σ-orbitals and the π-orbital $\mathbf{a}_2$. In contrast, the second ionisation potential $I_{v2} = 10.7$ eV of cyclopentadiene is ~ 1 eV smaller than $-\varepsilon_2 = 11.6$, due to the second

order interaction between the π-orbital $\mathbf{b_1}$ and the C–H σ-orbital combination of same symmetry.

Accordingly we shall use for the perturbation scheme suggested in (6) the following set of rounded energy parameters (in eV):

	D		E		
	$\varphi_1(A_2)$	$\varphi_2(B_1)$	$\pi(B_1)$		
II	– 8.8	– 11.6	– 10.3	; $\beta = -2.4$ eV	(7)
III	– 9.1	– 11.5			

These parameters, together with the basis orbitals given in (4), yield the following secular determinants for the orbital energies of the π-orbitals of B_1 symmetry in the molecules II and III. (The cross terms $H_{23} = \langle \varphi_2(B_1) | \mathcal{H} | \varphi_3 \rangle$ are $H_{23} = 2 \cdot 0.372 \cdot (1/\sqrt{2}) \cdot (-2.4) = -1.3$ eV in II and $H_{23} = 2 \cdot 0.602 \cdot (1/\sqrt{2}) \cdot (-2.4) = -2.0$ eV in III, respectively.)

II
$$\begin{Vmatrix} -11.6 - \varepsilon & -1.3 \\ -1.3 & -10.3 - \varepsilon \end{Vmatrix} = 0 \qquad \begin{array}{l} \varepsilon(1\,\mathbf{b_1}(\pi)) = -12.4 \text{ eV} \\ \varepsilon(2\,\mathbf{b_1}(\pi)) = -9.5 \text{ eV} \end{array}$$

(8)

III
$$\begin{Vmatrix} -11.5 - \varepsilon & -2.0 \\ -2.0 & -10.3 - \varepsilon \end{Vmatrix} = 0 \qquad \begin{array}{l} \varepsilon(1\,\mathbf{b_1}(\pi)) = -13.0 \text{ eV} \\ \varepsilon(2\,\mathbf{b_1}(\pi)) = -8.8 \text{ eV} \end{array}$$

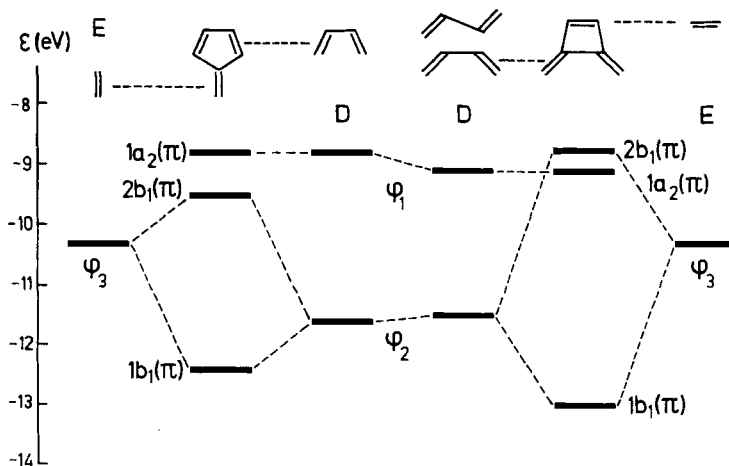The resulting orbital diagram is shown in Fig. 2.

Fig. 2. *Orbital diagram for the perturbation scheme (6)*

We have neglected those changes in the orbital energies $\varepsilon(\varphi_1)$ and $\varepsilon(\varphi_2)$ of the diene part D which are due to the replacement of the two C–H σ-bonds by C–C(sp^2) bonds. These changes are presumably smaller than that postulated for $\varepsilon(\varphi_3)$ of the single π-bond of the E moiety. On the other hand, two effects have to be considered:

For the $\mathbf{a}_2(\pi)$ orbital of II one has to include the influence of the excess negative charge of the five-membered ring, which will result in a decrease of the ionisation potential, *i.e.* in a shift towards higher energies of $\varepsilon(\mathbf{a}_2(\pi))$. In contrast, the mixing of the basis function $\varphi_1(A_2)$ in III with the antibonding orbital φ_4 of the endocyclic double bond will lower the computed value $\varepsilon(\mathbf{a}_2(\pi)) = -9.1$ eV (see (7)).

With these corrections in mind, the correlation with the observed band position yields the following identification of the π-bands in the PE. spectra of II and III, the arrows $\uparrow$ and $\downarrow$ indicating that the experimental value is predicted to lie above or below the orbital energy derived from our simple HMO-model:

	π-orbital	Predicted orbital energy	Nearest PE. band j	$\varepsilon_j = -I_{vj}$ (observed)	
	$\mathbf{1a}_2(\pi)$	$-\ 8.8$ $(\uparrow)$	①	$-\ 8.55$	
II	$\mathbf{2b}_1(\pi)$	$-\ 9.5$	②	$-\ 9.54$	
	$\mathbf{1b}_1(\pi)$	-12.4	④	-12.8	
					(9)
	$\mathbf{2b}_1(\pi)$	$-\ 8.8$	①	$-\ 8.80$	
III	$\mathbf{1a}_2(\pi)$	$-\ 9.1$ $(\downarrow)$	②	$-\ 9.44$	
	$\mathbf{1b}_1(\pi)$	-13.0	⑤	-13.3	

By elimination, the PE. band ③ at 12.1 eV of II and the bands ③, ④ at 11.5, 12.3 eV of III should be σ-bands, the photoelectron vacating a σ-orbital of either A_1 or B_2 symmetry.

This assignment receives convincing support from a non-empirical LCAO-MO-SCF calculation (IBMOL [19]) carried out by *Praud, Millie & Berthier* [5] for I, II and III. The basis functions used are contracted gaussians and the structural parameters adopted for II and III were the following: $R_{C-C} = 1.437$ Å, $R_{C=C} = 1.345$ Å, $R_{CH} = 1.086$ Å for II (see [11]); same distances, except $R_{C-C} = 1.48$ Å for III; (bond angles not given in ref. [5]). The top-occupied orbitals ψ_j together with the orbital energies ε_j (in eV) are given in Table 2. As usual for this type of calculation, the direct application of *Koopmans'* theorem yields vertical ionisation potentials which are too high, and it is necessary to introduce a scaling factor. In the particular case this can be done on the basis of the results obtained for benzene (I). There is complete agreement between the calculated [5] and experimentally determined [10] [20] sequence of orbitals in I, so that a valid calibration can be performed. A linear regression calculation based on the values of the top four occupied orbitals yields:

$$I_{vj} = (0.549 - 0.740\ \varepsilon_j) \text{ eV}. \tag{10}$$

The standard errors of the intercept at the origin (0.549 ± 0.790) and of the slope (-0.740 ± 0.049) are rather large, because of the low degree of freedom $(\phi = 2)$ for the residual variance $(V(I_v) = 0.049$ eV²). Note that the origin $I_v = 0$ is included in the range of the intercept at $\varepsilon_j = 0$.

The I_{vj} values calculated from (10) are given in Table 2. (They are affected with confidence limits of $+\ 0.25$ eV near $\varepsilon_j = -15$ eV and $+\ 0.30$ eV at the edges of the interval 10 eV $< \varepsilon_j < 18$ eV, for a probability $P \sim 2/3$ of the true value I_v lying inside these limits.) It is found that the agreement with the observed band positions of II and III is even better than was to be expected and that in particular the predicted

Table 2. *Comparison between predicted and observed PE. band positions for benzene (I), fulvene (II) and 3,4-dimethylene-cyclobutene (III)*

a: Orbitals and orbital energies according to *Praud, Millie & Berthier* [5]. b: Predicted vertical ionisation potentials from regression (10) calibrated on benzene (I). c: Lower and upper 90 percent confidence limits for vertical ionisation potentials from (12). d: Experimental values (for I from [10])

|	(a)		(b)	(c)	(d)
Compound	ψ_j	ε_j (eV)	I_{vj} : (10), eV	I_{vj} : (12), eV	I_v (exp), eV
I	$1e_{1g}(\pi)$	-11.62	9.15	8.90– 9.49	9.24
	$2e_{2g}(\sigma)$	-15.19	11.79	11.62–12.41	11.7
	$1a_{2u}(\pi)$	-16.03	12.41	12.26–13.10	12.2
	$2e_{1u}(\sigma)$	-17.78	13.71	13.60–14.53	13.9
II	$1a_2(\pi)$	-10.74	8.50	8.22– 8.77	8.55
	$2b_1(\pi)$	-11.83	9.30	9.05– 9.67	9.54
	$7b_2(\sigma)$	-15.26	11.84	11.67–12.47	12.1
	$11a_1(\sigma)$	-16.01	12.40	12.24–13.08	(12.8 ?)
	$1b_1(\pi)$	-16.31	12.62	12.48–13.32	12.8
III	$2b_1(\pi)$	-11.02	8.70	8.43– 9.00	8.80
	$1a_2(\pi)$	-11.66	9.18	8.92– 9.53	9.44
	$10a_1(\sigma)$	-14.86	11.55	11.37–12.14	11.5
	$8b_2(\sigma)$	-15.56	12.06	11.90–12.71	12.3
	$1b_1(\pi)$	-16.41	12.69	12.55–13.41	13.3
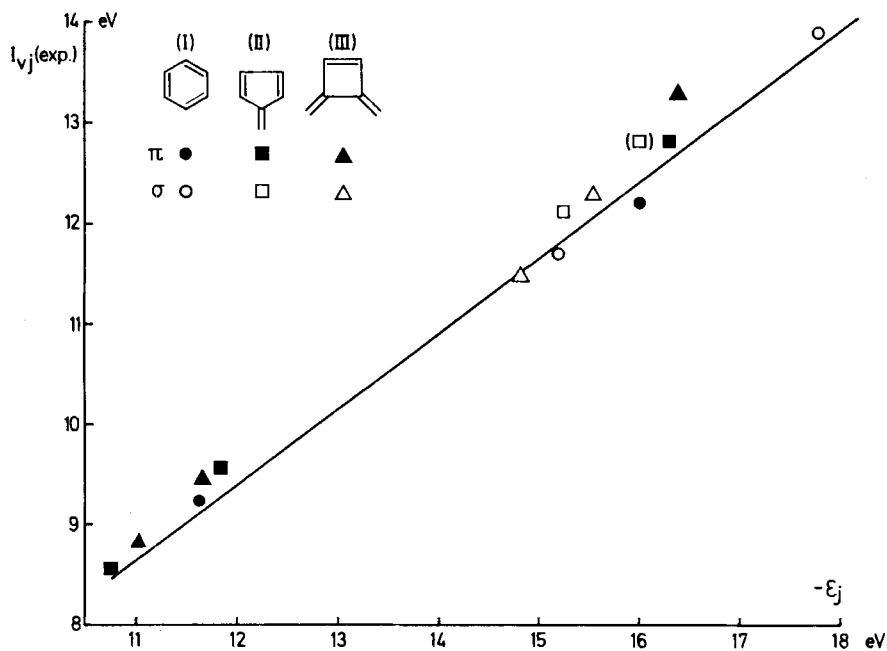
Fig. 3. *Linear regression (11) of the vertical ionisation potentials I_{vj} on the LCAO-MO-SCF orbital energies ε_j obtained by* Praud, Millie & Berthier [5]

positions of the π-bands agree very well with those derived on the basis of our simple semi-quantitative considerations (see however comment 1) below.

The quality of the over-all linear correlation between the computed and the experimentally determined ionisation potentials for the three compounds I, II, III is evident from Fig. 3. The relatively small amount of scatter is quite remarkable in view of the fact that the regression covers three rather different systems I, II, III and both σ- and π-ionisation processes. In addition it should be remembered that the structural parameters underlying the calculations for II and III deviate somewhat from those of the true ground state geometries [11].

If all 14 points shown in Fig. 3 (cf. Table 2) are included in a regression calculation, then the following least-squares line is obtained:

$$I_{vj} = (0.509 - 0.7541 \; \varepsilon_j) \; eV \; . \tag{11}$$

The standard errors (for a degree of freedom $\phi = 12$) of the intercept at the origin and for the slope are: 0.509 ± 0.416; -0.754 ± 0.0247. The standard error for a single point is $SE(I_{vj}) = 0.212$.

A statistical test will show that, even on a security level as low as 75 percent, the intercept $I_v \, (\varepsilon_j = 0) = 0.509$ eV does not differ significantly from zero. This means that for all practical purposes the regression line (11) passes through the origin and, consequently, that the orbital energies ε_j obtained by *Praud, Millie & Berthier* [5] can be converted directly into vertical ionisation potentials I_{vj} by multiplication with a scaling factor:

$$I_{vj} = - (0.791 \pm 0.026) \; \varepsilon_j \; eV \; . \tag{12}$$

Formula (12) yields the upper and lower 90 percent confidence limits for the predicted vertical ionisation potentials (standard error for the scale factor 0.0145; *Student's* $t(0.9; \phi = 13) = 1.771$). The values so obtained are included in Table 2.

Before summarising the results, we wish to draw attention to the following difficulties which make the assignment of the PE. bands at higher ionisation potentials for II and III somewhat uncertain:

1. For the time being, we have assumed that the band ④ of II is the third π-band, corresponding to ejection of an electron from $1\mathbf{b}_1(\pi)$. This assignment is based on our semi-quantitative perturbation treatment (see Fig. 2) and on the *ab-initio* results of *Praud, Millie & Berthier* [5]. The latter treatment is expected to yield more reliable results for the orbital energies of the π-orbitals than for the σ-orbital energies, which depend more markedly on small deviations of the structural parameters from the true values. According to the calculation reported in [5], the ionisation process whereby the photoelectron vacates the σ-orbital $11\mathbf{a}_1(\sigma)$ should give rise to a PE. band located near 12.4 to 12.7 eV, *i.e.* in the region between the maxima labelled ③ and ④ in the PE. spectrum of II. This could be indeed the case. The integrated intensity from 11.5 to 13.3 eV is not necessarily in contradiction with the presence of three overlapping PE. bands. On the other hand it might also be postulated that the ionisation from $11\mathbf{a}_1(\sigma)$ occurs at a potential near 13.6 eV, in which case the band would be part of the prominent feature of the PE. spectrum in that range. Even though it cannot be excluded that the third π-band (ionisation from $1\mathbf{b}_1(\pi)$) is part of the big maximum ⑤, we have assumed, on theoretical grounds, that this is not the case. In Tables 1 and

2, as well as in Fig. 3, ionisation from $11a_1(\sigma)$ has been assigned the same ionisation potential as that from $1b_1(\pi)$.

2. The sample of III, which is a very labile compound, contained traces of water, characterized by its typical fine-structured feature at 12.6 to 13.0 eV. If this is substracted from the PE. spectrum, then three clearly separated bands ③, ④, ⑤ are obtained, as shown in Fig. 1. However, there remains still the possibility that the water maxima overlap with a band which would give rise to a shoulder near 12.8 eV. If this were the case, then this shoulder could be due to the π-band corresponding to ionisation from $1b_1(\pi)$.

Bearing the above reservations in mind, we believe that the following assignment of the PE. bands of II and III is reasonable. It is essentially the one predicted by theory and it has, at least, the merit to be consistent with the well established assignments of other unsaturated hydrocarbons, especially that of benzene (I).

	①	②	③	④	⑤	
II:	$1a_2(\pi)$	$2b_1(\pi)$	$7b_2(\sigma)$	$1b_1(\pi)$		(13)
III:	$2b_1(\pi)$	$1a_2(\pi)$	$10a_1(\sigma)$	$8b_2(\sigma)$	$1b_1(\pi)$	

To conclude, we add the following two comments:

1. The π-band position in the spectra of I, II and III can be nicely accounted for by a naive HMO calculation. As pointed out above, the HMO's (3) exaggerate the delocalisation between the semi-localised π-bonds in II and III and they underestimate the resonance integral β inside these π-bonds, if β is appropriate for I. To correct this, we change the resonance integrals as follows: $\beta_d = \beta + \delta\beta$ for the localised double bonds, and $\beta_s = \beta - \delta\beta$ for the non-essential π-bonds connecting the double bonds. A simple first-order perturbation calculation will yield the following orbital energies:

$$\varepsilon_J' = \alpha + X_J \beta + 2\sum_{\mu,\nu} C_{J\mu} C_{J\nu} \delta\beta_{\mu\nu} . \tag{14}$$

In (14), X_J is the orbital energy coefficient obtained according to the standard HMO procedure and the summation extends over all bonded pairs μ, ν of $2p$-orbitals. As specified above, the perturbation $\delta\beta_{\mu\nu}$ is either $+\delta\beta$ or $-\delta\beta$, depending on the type of bond μ, ν. The values of X_J and of the perturbation factor $Z_J = \sum_{\mu,\nu} C_{J\mu} C_{J\nu} (\delta\beta_{\mu\nu}/\delta\beta)$ are given in Table 3, columns 3 and 4. A least-squares treatment yields the regression plane

$$\varepsilon_J' = (-6.392 - 3.079 \, X_J - 1.001 \, Z_J) \text{ eV} , \tag{15}$$

from which the 'predicted' ε_J-values in Table 3, column 6, are calculated. A comparison of ε_J' and ε_J shows that (15) is an excellent parametrisation of our results. Attention should be drawn to the fact that the residual variance for the regression (15) $(V(\varepsilon_J) = 0.0624 \text{ eV}^2; s(\varepsilon_J') = 0.25 \text{ eV})$ is *not* significantly smaller than the one obtained for the linear regression $\varepsilon_J = -6.973 - 2.717 \, X_J$ $(V(\varepsilon_J) = 0.0865 \text{ eV}^2; s(\varepsilon_J) = 0.29 \text{ eV})$, *i.e.* for a model without the bond localisation correction $\delta\beta$. This means that inclusion of the perturbation $\delta\beta$ is *not* strictly necessary for predictive purposes. However, the model underlying (14) and (15) is certainly a more realistic one.

2. A vibrational analysis of the bands ① and ② of II and of band ① of III will have to wait until better resolved spectra are available.

Table 3. *HMO-parametrisation of the π-ionisation potentials*

X_J = Orbital energy coefficients [13]. The coefficients $C_{J\mu}$ are given in the diagrams (3). ε'_J and ε_J in eV. $Z_J = \sum\limits_{\mu,\nu} C_{J\mu} C_{J\nu} (\delta\beta_{\mu\nu}/\delta\beta)$

Compound	Orbital	X_J	Z_J	Experim. $-I_{vJ} = \varepsilon_J$	ε'_J from (15)
I	$1e_{1g}(\pi)$	1.000	0.000	− 9.24	− 9.47
	$1a_{2u}(\pi)$	2.000	0.000	−12.20	−12.55
II	$1a_2(\pi)$	0.618	0.310	− 8.55	− 8.61
	$2b_1(\pi)$	1.000	0.000	− 9.54	− 9.47
	$1b_1(\pi)$	2.115	− 0.137	−12.80	−12.77
III	$2b_1(\pi)$	0.555	0.653	− 8.80	− 8.76
	$1a_2(\pi)$	0.802	0.363	− 9.44	− 9.23
	$1b_1(\pi)$	2.247	− 0.291	−13.30	−13.02

From the PE. spectrum of II shown in Fig. 1 it seems that the first two bands are dominated by two progressions each: ①: 1400 and 1200 cm⁻¹; ②: 1700 and 1000 cm⁻¹. (The progression with the rather high value of 1700 cm⁻¹ could be an artefact, due to overlapping components of two progressions with fractional spacings, say ∼600 and ∼900 cm⁻¹.) These values are in the proper range, if compared to the wavenumbers reported by *Brown, Domaille & Kent* [21] for the totally symmetric vibrational modes of II in its electronic ground state (C–H (bending) 1324, 1440 (?), 1486; C=C (stretch, exocyclic) 1670; C=C (stretch, ring modes) 986, 1100 (?), 1520, 1670 cm⁻¹).

The samples of II and III were prepared according to the literature procedures given in [2] and [3].

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79. Berechnung von freien Hydratationsenthalpien und Koordinationszahlen für Kationen aus leicht zugänglichen Parametern

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Summary. A model for the computation of free energies of hydration and coordination numbers of cations using easily available parameters is described. For 27 mono-, di- and trivalent cations the mean deviation of the calculated from the experimental ΔG_H^0 values is 3.9%. All the computed coordination numbers agree with experimental ones.

1. Einleitung. – Im Rahmen von Untersuchungen an ionenselektiven Systemen [1] ist die Kenntnis der freien Solvatationsenthalpien von Ionen für eine Reihe von elektrisch neutralen Liganden notwendig geworden. Da sich derartige Behandlungen der Solvatation bisher auf nur wenige nichtwässerige Lösungsmittel wie z.B. Formamid [2] beschränkten, wurde ein Modell geschaffen, welches allgemein die Berechnung der freien Solvatationsenthalpien und Koordinationszahlen von Kationen aus einer besonders kleinen Zahl bekannter Daten ermöglicht. In der vorliegenden Arbeit wird einerseits über ein derartiges Modell berichtet und andererseits werden Resultate diskutiert, die damit für die Hydratation als besonders ausgiebig untersuchtem Fall der Solvatation erzielt wurden.

Die bisher bekannten Theorien zur Berechnung freier Hydratationsenthalpien von Kationen lassen sich im wesentlichen in zwei Gruppen aufteilen. Die empirischen Korrelationen, welche aus dem Modell von *Born* [3] mit Behandlung des Lösungs-