[6] a) *E. Späth & N. Platzer*, Ber. deutsch. chem. Ges. *69*, 255 (1936); b) *W. Reppe et al.* Liebigs Ann. Chem. *596*, 164 (1955); c) *J. E. Livak, E. C. Britton, J. C. van der Weele & M. F. Murray*, J. Amer. chem. Soc. *67*, 2218 (1945); d) *R. Sudo*, Nippon Kagaku Zasshi *80*, 924, 929 (1959), ref. C.A. *55*, 4529 (1961); e) *C. Daremon, R. Rambaud, M. Verniette*, C.r. hebd. Séances Acad. Sci. *272*, 503 (1971).

[7] a) *L. Fowden, P. M. Scopes & R. N. Thomas*, J. chem. Soc. (C) *1971*, 833; b) *M. Legrand & R. Viennet*, Bull. Soc. chim. France *1965*, 679; *1966*, 2798; c) *L. I. Katzin & E. Gulyas*, J. Amer. chem. Soc. *90*, 247 (1968).

[8] a) *P. Crabbé*, Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry, Holden-Day 1965, pag. 267; b) *B. Witkop*, Experientia *12*, 372 (1956); c) *J. Kollonitsch, B. Witkop & Y. Fujita*, J. Amer. chem. Soc. *87*, 2030 (1965); d) *W. Klyne, P. M. Scopes & A. Williams*, J. chem. Soc. *1965*, 7237; e) *G. Fodor & F. Soti*, Tetrahedron Letters *1964*, 1917.

[9] *T. Okuda, S. Harigaya & A. Kiyomoto*, Chem. Pharm. Bull. (Tokyo) *12*, 504 (1964).

[10] *E. C. Jorgensen*, Tetrahedron Letters *1971*, 863.

[11] *B. W. Bycroft*, Nature *224*, 595 (1969).

[12] *L. Fowden*, Nature *209*, 807 (1966).

[13] *L. Fowden & P. M. Dunnill*, Phytochemistry *6*, 1659 (1967).

[14] *Th. Wieland*, Helv. *44*, 919 (1961).

[15] *Th. Wieland, M. Hasan & P. Pfaender*, Liebigs Ann. Chem. *717*, 205 (1968).

[16] *G. B. Barlow & A. J. MacLeod*, J. chem. Soc. *1964*, 141.

[17] *E. Fischer & H. Leuchs*, Ber. deutsch. chem. Ges. *35*, 3797 (1902).

[18] *H. L. Goering, S. J. Cristol & K. Dittmer*, J. Amer. chem. Soc. *70*, 3310 (1948).

[19] *J. Zellner & L. Bard*, Mh. Chem. *44*, 9 (1923).

[20] *J. L. Bonnet*, Bull. Soc. mycol. France *25*, 215 (1959).

[21] *S. Hatanaka & H. Terakawa*, Botan. Mag. (Tokyo) *81*, 261 (1968).

[22] *F. A. Wolf & F. T. Wolf*, The Fungi, Wiley, N.Y. (1947), Vol. II, pag. 35.

[23] *O. Gessner*, Die Gift- und Arzneipflanzen von Mitteleuropa. Winter, Heidelberg (1953).

[24] *Utz*, Apotheker-Zeitung *20*, 993 (1905).

[25] *W. W. Ford*, Poisonous Mushrooms, in Peterson-Haines, Textbook of legal medicine, Saunders NY. (1922), ref. nach *E. S. Faust*, Pilzgifte, in Handbuch der exp. Pharmakologie, A. Heffter Ed. Vol. 2, Berlin (1924).

[26] *C. H. Eugster*, Fortschr. Chem. Org. Naturst. (Ed. *L. Zechmeister*), *27*, 288 (1969).

[27] *W. A. Cowdrey, E. D. Hughes & C. K. Ingold*, J. chem. Soc. *1937*, 1228.

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147. The π-Orbital Sequence in Norbornadiene and Related Hydrocarbons[1])

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(6. III. 72)

Summary. A method outlined previously [1] is used to show that in norbornadiene (**3**) the $b_2(\pi)$ orbital lies above $a_1(\pi)$, as predicted by theory. This indicates that in **3** through-space interaction between the two basis π-orbitals π_a and π_b is more important than through-bond interaction.

Analysis of the PE.-spectra of 8-isopropylidene-tricyclo[3.2.1.0²,⁴]-octane (**13**) and the corresponding octene (**15**) confirms that the π-orbital π_c of the exocyclic double bond conjugates more

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[1]) Part 34 of 'Applications of Photoelectron-Spectroscopy'; Part 33: [1].

strongly with the symmetric *Walsh*-orbital $\mathbf{e}_S$ of the cyclopropano moiety than with the π-orbital π_a of a double bond in the same position.

Some time ago [2] we have shown that the two highest occupied molecular orbitals in norbornadiene (**3**) are the π-orbitals $\mathbf{a}_1(\pi)$ and $\mathbf{b}_2(\pi)$ (symmetry C_{2v}) and that their orbital energies differ by $|\varepsilon(\mathbf{a}_1(\pi)) - \varepsilon(\mathbf{b}_2(\pi))| = 0.8_5$ eV. According to theory [3], $\mathbf{b}_2(\pi)$ lies above $\mathbf{a}_1(\pi)$ and the two basis orbitals π_a, π_b interact mainly by a through-space mechanism [4]. Applying the method described in the previous com-
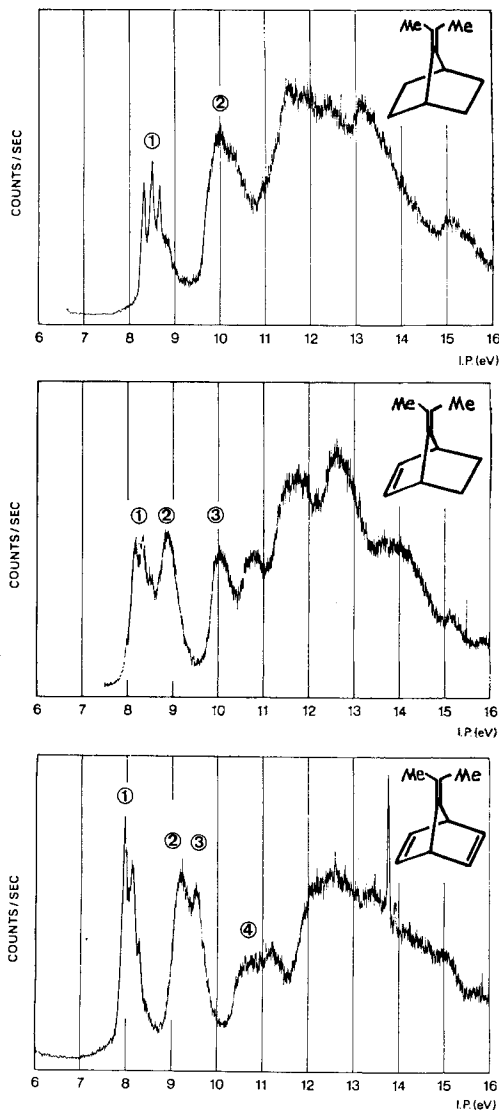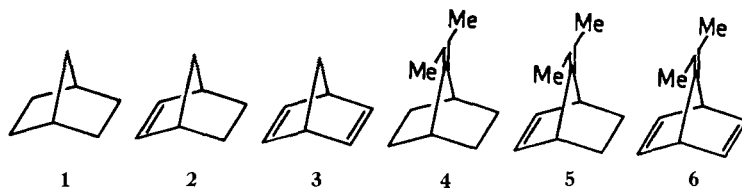

Fig. 1. *Photoelectron spectra of 7-isopropylidenenorbornane* (**4**), *7-isopropylidenenorbornene* (**5**) *and 7-isopropylidenenorbornadiene* (**6**).

munication [1] we wish to prove that this is indeed the case. A preliminary account
has been given [5].

The PE.-spectra of norbornane (**1**), norbornene (**2**) and norbonadiene (**3**) have
been described previously [2]. Those of 7-isopropylidenenorbornane (**4**), 7-isopropyl-
idenenorbornene (**5**) and 7-isopropylidenenorbornadiene (**6**) [6] are shown in Fig. 1
and in Tab. 1.

In assigning C_{2v} symmetry to **4** and **6** and C_s to **5** we have implicitly assumed that
the methyl groups are in conformations which satisfy these symmetry requirements.

Table 1. *Vertical* ($I_{v,J}$) *and adiabatic* ($I_{a,J}$) *ionization potentials corresponding to ejection from orbital*
ψ_J.
All values in eV. σ-Ons. = Onset of the σ-band system. The numbering ⓙ of the bands refers to
Fig. 1.

	①			②			③			④	
Cpd.	$I_{a,1}$	$I_{v,1}$	ψ_1	$I_{a,2}$	$I_{v,2}$	ψ_2	$I_{a,3}$	$I_{v,3}$	ψ_3	$I_{a,4}$	ψ_4
1		10.2	σ-Ons.								
2		8.97	$\mathbf{a'}(\pi)$		10.6	σ-Ons.					
3		8.69	$\mathbf{b_2}(\pi)$		9.55	$\mathbf{a_1}(\pi)$		11.3	σ-Ons.		
4	8.30	8.49	$\mathbf{b_2}(\pi)$	9.6	10.0	σ-Ons.					
5	8.27	8.43	$\mathbf{a'}(\pi)$		8.9_5	$\mathbf{a'}(\pi)$	9.9	10.15	σ-Ons.		
6	7.97	7.97	$\mathbf{b_2}(\pi)$	8.9	9.25	$\mathbf{b_2}(\pi)$		9.54	$\mathbf{a_1}(\pi)$	10.4	σ-Ons.

Basis-Orbitals

In the following discussions we shall make use of *Koopmans'* theorem [7] by
postulating that

$$\varepsilon_J = -I_{v,J}, \qquad (1)$$

where ε_J is the orbital energy assigned to the molecular orbital ψ_J from which the
photoelectron is ejected in the ionization process yielding a PE.-band in position
$I_{v,J}$ (= vertical ionization potential).

It is an empirical fact that introduction of a second π-bond into a monoene lowers
    a) the orbital energies of the σ-orbitals which determine the onset of the σ-band
system, and
    b) the mean of the π-orbital energies relative to the value observed for the monoene
[2] [8], e.g.:

$$\text{a)} \quad \begin{matrix} \mathbf{1}: \varepsilon(\sigma\text{-Ons.}) = -10.2 \text{ eV} \\ \mathbf{2}: \varepsilon(\sigma\text{-Ons.}) = -10.6 \text{ eV} \\ \mathbf{3}: \varepsilon(\sigma\text{-Ons.}) = -11.3 \text{ eV} \end{matrix} \begin{matrix} \Delta = -0.4 \text{ eV} \\ \Delta = -0.7 \text{ eV} \end{matrix}$$

$$\text{b)} \quad \begin{matrix} \mathbf{2}: \qquad\qquad \varepsilon(\mathbf{a'}(\pi)) = -8.97 \text{ eV} \\ \mathbf{3}: [\varepsilon(\mathbf{b_2}(\pi)) + \varepsilon(\mathbf{a_1}(\pi))]/2 = -9.12 \text{ eV} \end{matrix} \Delta = -0.15 \text{ eV}$$

(2)

Substitution of **1**, **2** and **3** by an isopropylidene group in position 7 has two opposing effects on the σ-orbital energies:

a) It induces an upward shift of the orbital energies of the highest occupied σ-orbitals, due to the enlargement of the σ-frame, and

b) it adds a π-bond to the system, which, according to previous experience, should result in a lowering (negative shift) of these orbital energies. The data given in Tab. 1 indicate that the two effects almost cancel in **4** and result in a positive shift in **5** and **6**:

$$\left.\begin{array}{l} \textbf{1}: \varepsilon(\sigma\text{-Ons.}) = -10.2 \ \text{eV} \\ \textbf{4}: \varepsilon(\sigma\text{-Ons.}) = -10.0 \ \text{eV} \end{array}\right\} \varDelta = +0.2 \ \text{eV}$$

$$\left.\begin{array}{l} \textbf{2}: \varepsilon(\sigma\text{-Ons.}) = -10.6 \ \text{eV} \\ \textbf{5}: \varepsilon(\sigma\text{-Ons.}) = -10.1_5 \ \text{eV} \end{array}\right\} \varDelta = +0.4_5 \ \text{eV} \qquad (3)$$

$$\left.\begin{array}{l} \textbf{3}: \varepsilon(\sigma\text{-Ons.}) = -11.3 \ \text{eV} \\ \textbf{6}: \varepsilon(\sigma\text{-Ons.}) = -10.7 \ \text{eV} \end{array}\right\} \varDelta = +0.6 \ \text{eV}$$

For the π-orbitals one finds:

$$\begin{array}{l} \textbf{2}: \ \varepsilon(\mathbf{a}'(\pi)) = -8.97 \ \text{eV} \\ \textbf{4}: \ \varepsilon(\mathbf{b}_2(\pi)) = -8.49 \ \text{eV} \end{array}\left.\begin{array}{l} \\ \end{array}\right\} \text{Mean } \bar{\varepsilon} \quad\quad = \ 8.73 \ \text{eV} \left.\begin{array}{l} \\ \\ \end{array}\right\} \varDelta = +0.04 \ \text{eV}$$

$$\begin{array}{l} \textbf{5}: [\varepsilon(\mathbf{a}'(\pi))_1 + \varepsilon(\mathbf{a}'(\pi))_2]/2 \quad\quad\quad = -8.69 \ \text{eV} \\ \textbf{6}: [\varepsilon(\mathbf{b}_2(\pi))_1 + \varepsilon(\mathbf{a}_1(\pi))_2 + \varepsilon(\mathbf{b}_2(\pi))_3]/3 = -8.92 \ \text{eV} \end{array}\left.\begin{array}{l} \\ \\ \end{array}\right\} \varDelta = -0.23 \ \text{eV} \qquad (4)$$

These results agree with those derived from the PE.-spectra of 7-methylene-norbornane **7** and 7-methylenenorbornadiene **8** [9].

7   8
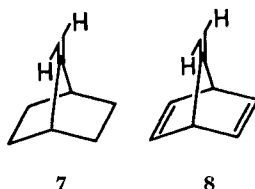
The mean of the π-ionization potentials of **2** and **7** is $(8.97 + 9.40)/2 = 9.19$ eV and of the three π-bands of **8** $(8.50 + 9.65 + 9.90)/3 = 9.35$ eV. Hence, the difference in mean π-orbital energies is -0.16 eV, as compared with $-0.23 + 0.04 = -0.19$ eV calculated from the shifts given in (4). The π-ionization potential difference of 0.9 eV in going from **4** to **7** is consistent with the shifts observed when ethylene is substituted by methyl groups: ethylene $I_{v,\pi} = 10.6$ eV, propene $I_{v,\pi} = 9.7$ eV, isobutene $I_{v,\pi} = 9.2$ eV, *cis*- and *trans*-butene $I_{v,\pi} = 9.1$ eV, 2-methyl-2-butene $I_{v,\pi} = 8.7$ eV, 2,3-dimethyl-2-butene $I_{v,\pi} = 8.3$ eV [10].

However, these data do not permit unambigous assignment of shifts to the individual basis orbitals in **5, 6** and **8**, because of the non-equivalence of the endocyclic and exocyclic π-bonds.

With reference to the nomenclature given in [1] we define our basis orbitals and their relative signs as follows:
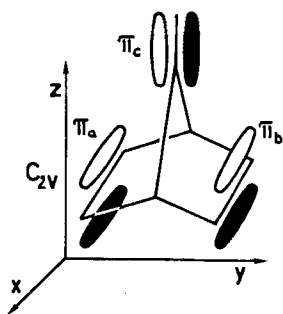
$$M \equiv 3: \varphi_a \equiv \pi_a; \; \varphi_b \equiv \pi_b$$

$$M' \equiv 6: \varphi_a \equiv \pi_a; \; \varphi_b \equiv \pi_b; \; \varphi_c \equiv \pi_c$$

The symmetry-adapted linear combinations (see formula (6) of [1]) are:

$$\pi_+ = (\pi_a + \pi_b)/\sqrt{2}$$
$$\pi_- = (\pi_a - \pi_b)/\sqrt{2} \tag{5}$$

These contribute with greatest weight to the following orbitals (see formula (8) of [1]):

In 3 ($\equiv$ M):
$$\psi_+ \equiv a_1(\pi_+); \; \psi_- \equiv b_2(\pi_-)$$
In 6 ($\equiv$ M'): $\tag{6}$
$$\psi_+ \equiv a_1(\pi_+); \; \psi_{-,1} \equiv b_2(\pi_c - \lambda\pi_-)$$
$$\psi_{-,2} \equiv b_2(\pi_- + \lambda\pi_c)$$

The parameter $\lambda (|\lambda| < 1)$ is positive (negative) if π_c lies above (below) π_-. (According to formula (8) of [1], the molecular orbitals ψ_+ and ψ_- include σ/π-mixing).

Consider first the hydrocarbon 3 $\equiv$ M, i.e. the molecule M for which we wish to derive the sequence of the π-orbitals $a_1(\pi_+)$, $b_2(\pi_-)$. From the experimental results given in [2] we obtain (formulae (11) and (13) of [1]):

$$A_a = -\overline{I_v} = -9.12 \text{ eV}$$

$$|B_{ab}| = \frac{\Delta I_v}{2} = -0.42_5 \text{ eV} \tag{7}$$

We assume that the dihedral angle ω between the two C–CH=CH–C moieties is the same in 6 (= M') as in 3, i.e. independent of the presence or absence of an exocyclic double bond in position 7. Consequently the overlap integral $S_{ab} = \langle \pi_a | \pi_b \rangle$ is also the same in 3 and 6, so that $B_{ab} = B'_{ab}$ (see formula (18) of [1]). On the other hand $A'_a = A_a + \delta A_a$. We estimate $\delta A_a \approx 0.1$ eV, which yields

$$A'_a \approx -9.0 \text{ eV} \tag{8}$$

The negative ionization potential $-I_{v,1} = \varepsilon(b_2(\pi)) = -8.49$ eV of 4 corresponds in our simplified model to the unperturbed orbital energy of π_c:

$$A_c^0 = -8.49 \text{ eV} \tag{9}$$

According to (2) the shift from A_c^0 to A_c' is presumably $\delta A_c \approx -0.15$ eV per double bond, which leads to

$$A_c' = A_c^0 + 2\,\delta A_c \approx -8.79 \text{ eV} \qquad (10)$$

Thus A_c' **is** almost degenerate with A_a'.

π-Orbital Sequence in Norbornadiene

With the above parameters for the basis orbitals we now investigate whether the order of the π-orbitals in **3** corresponds to
  case A), the natural sequence $\mathbf{b}_2(\pi_-)$ above $\mathbf{a}_1(\pi_+)$ (see Fig. 2), or to
  case B), the inverted sequence $\mathbf{a}_1(\pi_+)$ above $\mathbf{b}_2(\pi_-)$ (see Fig. 3).

To discriminate between these two cases we derive the corresponding band positions for the PE.-spectrum of **6** and compare them with the experimental results.
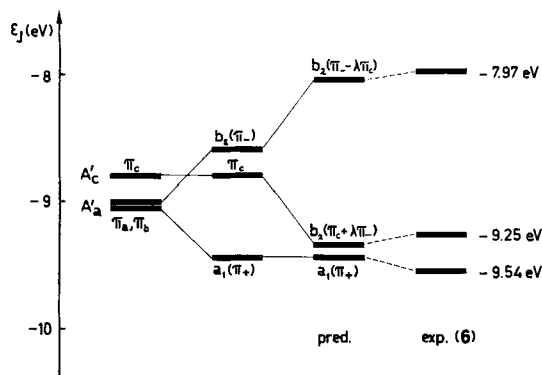
Case A

Fig. 2. *Predicted π-orbital sequence in* **6** *assuming the natural sequence* $\mathbf{b}_2(\pi)$ *above* $\mathbf{a}_1(\pi)$ *for norbornadiene* **3**

Interaction of π_a and π_b ($A_a' = -9.00$ eV; $B_{ab}' = -0.43$ eV) yields $\varepsilon(\mathbf{a}_1(\pi_+)) = -9.43$ eV and $\varepsilon(\mathbf{b}_2(\pi_-)) = -8.58$ eV. The mean value $(\varepsilon(\pi_-) + A_c')/2 = -8.69$ eV agrees quite well with the observed mean $-(I_{v,1} + I_{v,2})/2 = -8.61$ eV derived from the positions of the first two π-bands in the PE.-spectrum of **6**. For symmetry reasons π_c can interact only with $\mathbf{b}_2(\pi_-)$. To a first approximation, i.e. neglecting the contribution of σ-orbitals, the interaction matrix element is

$$\langle \pi_c | \mathcal{H} | \mathbf{b}_2(\pi_-) \rangle = \sqrt{2}\, B_{ac}' \qquad (11)$$

(see (17) of [1]). The orbital energies associated with $\mathbf{b}_2(\pi_c - \lambda\pi_-)$ and $\mathbf{b}_2(\pi_- + \lambda\pi_c)$ (c.f. (6)) are calculated according to

$$\varepsilon = -8.68_5 \pm \sqrt{0.011025 + 2\,B_{ac}'^2} \qquad (12)$$

From the observed gap $I_{v,2} - I_{v,1} = 1.28$ eV one obtains $B_{ac}' = -0.45$ eV, the negative sign corresponding to the assumption of through-space interaction. The result $B_{ac}' \approx B_{ab}'$ is reasonable.
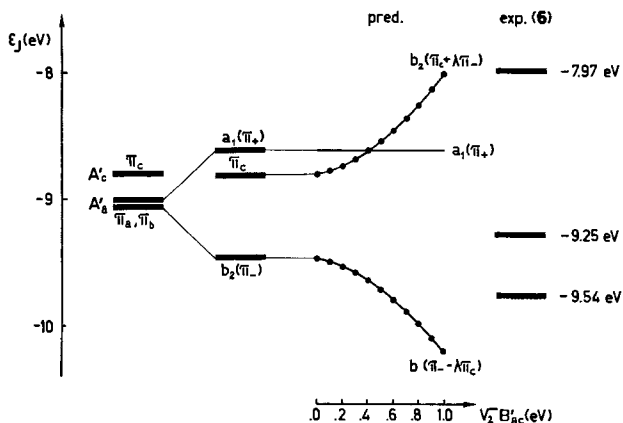
Case B

Fig. 3. *Predicted π-orbital sequence in* **6** *assuming the inverted sequence* $a_1(\pi)$ *above* $b_2(\pi)$ *for norbornadiene* **3**

Interaction of π_a and $\pi_b(A'_a = -9.00$ eV, $B'_{ab} = +0.43$ V) yields $\varepsilon(a_1(\pi_+)) = -8.58$ eV and $\varepsilon(b_2(\pi_-)) = -9.43$ eV. Consequently we should expect a π-band in the PE.-spectrum of **6** near 8.6 eV, corresponding to ejection of an electron from the orbital $a_1(\pi_+)$, but no such band is present. In addition the first and third π-ionization potentials $I_{v,1} = 7.97$ eV and $I_{v,3} = 9.54$ eV of **6** would have to be assigned to ejection from $b_2(\pi_c - \lambda\pi_-)$ and $b_2(\pi_- + \lambda\pi_c)$ (cf. (6)), the orbital energies of which are given by

$$\varepsilon = -9.11 \pm \sqrt{0.1024 + 2\,B'^2_{ac}} \qquad (13)$$

As can be seen from Fig. 3 it is impossible to obtain even rough agreement with the observed PE.-spectrum of **6**, independent of the choice of B'_{ac}. Indeed, setting $\varepsilon = \varepsilon(b_2(\pi_- - \lambda\pi_c)) = -7.97$ eV we calculate from (13) $B'_{ac} = -0.77$ eV, a value much too large to be acceptable. Also, this would lead to a value $\varepsilon(b_2(\pi_- + \lambda\pi_c)) = -10.25$ eV, too low by 0.7 eV.
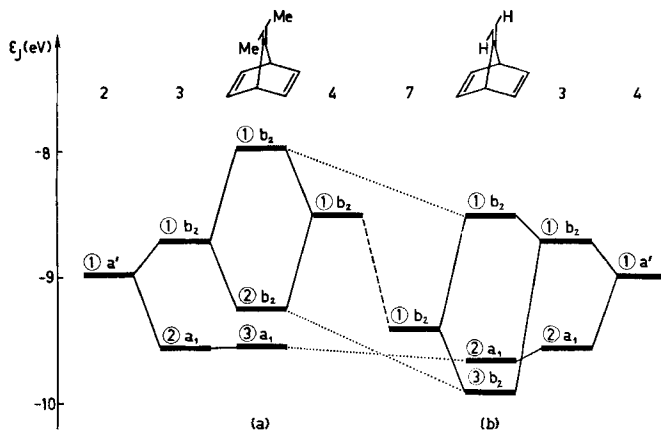

Fig. 4. *Comparison of the π-orbital energies for (b) 7-methylenenorbornane* **7** *and 7-methylenenorbornadiene* **8** [9] *with those of the corresponding 7-isopropylidene derivatives* **4** *and* **6** *(a)*. The levels correspond, according to (1), to the observed vertical ionization potentials.

We conclude: *The analysis of the PE.-spectrum of* **6** *proves that the order of the π-orbitals in* **3** *corresponds to case A, the natural sequence of* **b₂**(π₋) *above* **a₁**(π₊). *Consequently the interaction of* πₐ *and* π_b *in* **3** *is through-space dominated.*

This is summarized in the correlation diagram (a) of Fig. 4 (see also [5]). Lately the analogous correlation was proposed for **7** and **8** by *Hoffmann, Schüttler, Schäfer & Schweig* [9] (see correlation diagram (b) of Fig. 4), thus providing a welcome verification of our previous results [5]. The orbital energies ε_J given in Fig. 4 are those deduced according to (1) from the measured band positions $I_{v,J}$. The influence of the two additional methyl groups in **6**, relative to **8**, results in a reversal of the symmetry labels for the bands ② and ③, because of the positive displacement by 0.9 eV in the energy of the orbital π_c in **4** relative to **7**, and thus in the basis orbital energy A_c' of **6** relative to **8**.

Comments

1) In the case of **7** and **8** the parameters A_a and B_{ab} given in (7) remain unchanged. On the other hand, the perturbation δA_a is presumably negative because of the loss of two methyl groups in going from **6** to **8**. Assuming $\delta A_a = -0.1$ eV yields $A_a' = -9.2$ eV. On the basis of $I_{v,1} = 9.40$ eV from the PE.-spectrum of **7**, we calculate in analogy to (10) that $A_c' = A_c^0 + 2\,\delta A_c = -9.40 - 0.30 = -9.70$ eV. With these parameters, relation (12) becomes

$$\varepsilon = -9.24 \pm \sqrt{0.2116 + 2\,B_{ac}'^2} \tag{14}$$

From the gap $I_{v,3} - I_{v,1} = 1.40$ eV between bands ① and ③ in the PE.-spectrum of **8** (cf. Fig. 4) one obtains $B_{ac}' = -0.37$ eV, in agreement with $B_{ac}' = -0.45$ eV derived above for **6**.

2) Further confirmation is obtained from an analysis of the PE.-spectrum of **5**. The energy A_a of the basis π-orbital π_a is estimated to be $A_a' \approx -8.8$ to -8.8_5 eV, i.e. higher by $\delta A_a \approx 0.15$ to 0.10 eV than the observed π-orbital energy in **2** (cf. (4)). The introduction of a double bond in **4** should lower A_c^0 by $\delta A_c \approx -0.1$ to -0.15 eV relative to the observed value $A_c^0 = -8.49$ eV. This places the center $(A_a' + A_c')/2$ at -8.7 to 8.75 eV, in agreement with the observed value $-(I_{v,1} + I_{v,2})/2 = -8.69$ eV (see PE.-spectrum of **5**). With $A_a' = -8.8$ eV and $A'_c = -8.6$ eV, the observed split $I_{v,2} - I_{v,1} = 0.52$ eV leads to $B_{ac}' = -0.24$ eV. This value is smaller than $B_{ac}' = -0.37$ to -0.45 eV derived above.

This decrease in B_{ac}', if significant, could be rationalized in terms of one, or of a combination of the following effects. Models suggest that the exocyclic double bond in **5** is presumably bent away from the endocyclic one (as indicated schematically in **9**), which entails a decrease in overlap between π_a and π_c and thus a reduction in B_{ac}'. Furthermore the change in

9   10   11
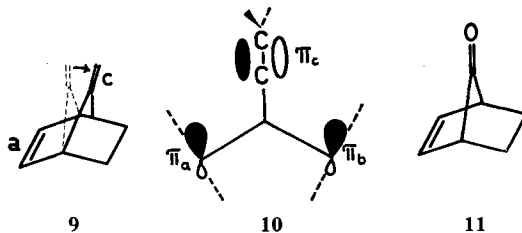
conformation depicted in **9** will lead to an increase in through bond interaction among π_a and π_c. The resulting reduction in orbital split is formally absorbed in the now smaller parameter B'_{ac}. Finally there is the possibility that the orbitals π_a and π_b in **6** and **8** distort as indicated in **10** so as to minimize electron-electron repulsion on the endo-side of the six-membered ring. Such an effect has been suggested as an explanation for the direction of the dipole moments of 1,6-bridged [10]-annulenes [11]. Again this would lead to an increase in B'_{ac} in **6** and **8** relative to **5**. However, all these possibilities need further examination.

3) A situation similar to that in **5** occurs in norbornene-7-one **11** [12]. The energy of the highest occupied π-orbital (essentially π_a) is -9.6 eV, i.e. lower by 0.6 eV than in **2**. This shift towards lower energies has been attributed to through-space interaction between π_a and the *antibonding* π_c^* orbital of the carbonyl group. Such an interaction would indeed be favoured by the large size of the 2p atomic orbital coefficient of π_c^* at the carbon atom of the carbonyl group. However, a major part of the shift is due to the presence of the electronegative oxygen centre, as shown by the PE.-spectra obtained for other unsaturated ketones [13].

Orbital interaction in 7-isopropylidene-substituted *endo*-cyclopropanonorbornane and *endo*-cyclopropanonorbornene.

There is ample experimental evidence that an *endo*-cyclopropane ring in position 2, 3 of a norbornane system stabilizes a positive charge in position 7 to a larger extent than a double bond in the same position [14]. The PE.-spectra of 8-isopropylidene-tricyclo[3.2.1.0^{2,4}]-octane (**13**) and of 8-isopropylidene tricyclo[3.2.1.0.^{2,4}]oct-6-ene (**15**), shown in Fig. 5 (cf. Tab. 2), support this observation. The PE.-spectra of **12** and **14** have been discussed previously [15].
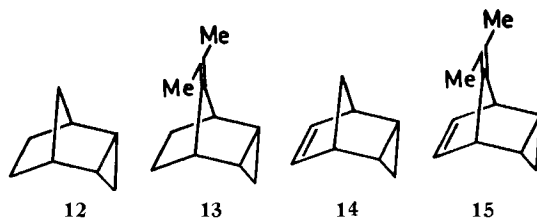

Table 2. *Vertical* $(I_{v,j})$ *and adiabatic* $(I_{a,j})$ *ionization potentials of the hydrocarbons* **13** *and* **15**. All values in eV. The symbols π or Δ indicate that the corresponding orbital is essentially a π- or a *Walsh*-e-orbital. The numbering ⓙ of the bands refers to Fig. 5.

	①			②			③			④			⑤		
Cpd.	$I_{a,1}$	$I_{v,1}$	ψ_1	$I_{a,2}$	$I_{v,2}$	ψ_2	$I_{a,3}$	$I_{v,3}$	ψ_3	$I_{a,4}$	$I_{v,4}$	ψ_4	$I_{a,5}$	$I_{v,5}$	ψ_5
13	8.18	8.28	a'(π)	8.9	9.31	a'(Δ)	9.7	9.97	a''(Δ)	–	10.38	σ			
15	7.9	8.14	a'(π)	8.8	9.11	a'(π)	–	9.46	a'(Δ)	–	10.06	a''(Δ)	10.7	10.98	σ

The homoconjugative interaction between the *Walsh* orbital e_S [16] (see formula (1) of [15]) and π_a in **14** has been shown [15] to be very small, so that we can safely neglect it in a first approximation. Consequently, the energies of the orbitals to be
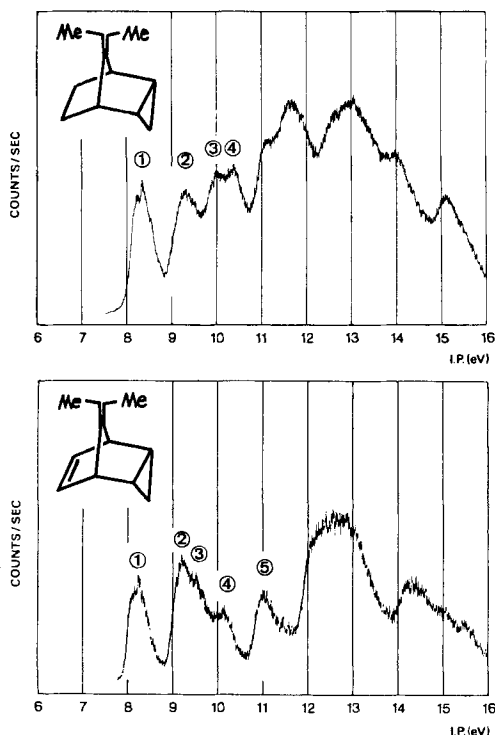
Fig. 5. *Photoelectron spectra of 7-isopropylidene substituted endocyclopropanonorbornane* (**13**) *and endo-cyclopropanonorbornene* (**15**)

correlated with the first three PE.-bands in the spectrum of **15** should depend only on predominantly through-space interaction of π_c with e_S and π_a (C_s symmetry is assumed for the molecules **12** to **15**).

To assign orbital energies to the basis orbitals in **13** and **15** we follow the rules set down above and those derived in [15]. In particular, the shifts induced by one moiety in the basis orbital energies of another can be summarized as follows:

$$\text{Double bond a} \qquad\qquad : \delta A_c = -0.1 \text{ eV}; \; \delta\varepsilon(e_{S,A}) = -0.1 \text{ eV}$$
$$\text{8-Isopropylidene group} : \delta A_a = +0.1 \text{ eV}; \; \delta\varepsilon(e_{S,A}) = +0.3 \text{ eV} \qquad (15)$$
$$\text{endo-Cyclopropane ring}: \delta A_a = -0.1 \text{ eV}; \; \delta A_c \quad = -0.1 \text{ eV}$$

a) PE.-spectrum of **13**

From the first ionization potential of **4** ($I_{v,1} = 8.49$ eV) and the corrections (15) we deduce $A_c = -8.6$ eV. As shown in [15] the *Walsh*-orbitals of **12** are found at $\varepsilon°(e_S) = -9.4$ eV and $\varepsilon°(e_A) = -10.2$ eV, which yields according to (15) $\varepsilon(e_S) = \varepsilon°(e_S) + \delta\varepsilon(e_S) = -9.1$ eV and $\varepsilon(e_A) = \varepsilon°(e_A) + \delta\varepsilon(e_A) = -9.9$ eV. For symmetry reasons only e_S can interact with π_c, which leads to the orbital diagram shown in Fig. 6 and thus to the following band assignment: band ①: $a'(\pi_c - \lambda e_S)$, band ②:
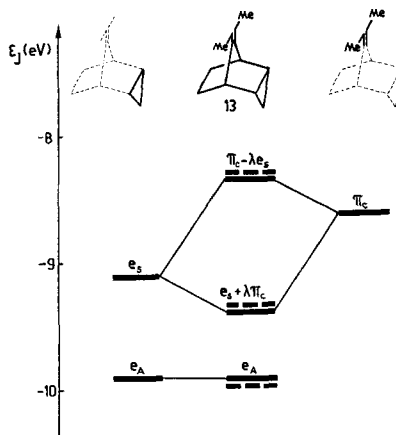
Fig. 6. *Correlation diagram for the orbital sequence in the hydrocarbon* **13**

The solid lines are the values derived according to the scheme described in the text. The broken lines are the orbital energies derived from the PE.-spectrum (see Fig. 5 and Tab. 2)

$a'(e_S + \lambda \pi_c)$ (with $\lambda < 1$); band ③: $a''(e_A)$. The observed split $\varepsilon(a'(\pi_c - \lambda e_S)) - \varepsilon(a'(e_S + \lambda \pi_c)) = 1.03$ eV demands $B_{ce_S} = -0.44$ eV. This is almost twice the value $B_{ac} = -0.24$ eV found for **5** and also larger than the interaction parameter $B_{ae_S} = -0.30$ eV observed in the case of exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene, the exo-isomer of **14** [15]. We conclude that the stereoelectronic conditions in **13** are conducive to strong homoconjugative interaction of the cyclopropane e_S *Walsh*-orbital with the π_c orbital of the exocyclic double bond, in agreement with the results derived from solvolysis experiments [14].

b) PE.-spectrum of **15**

This hydrocarbon allows a direct comparison of the competitive interaction of π_a and e_S with π_c. Using the corrections (15) we obtain the energies for the basis orbitals of **15** directly from the values given previously for **5** and **13**: $A'_a = -8.8 - 0.1 = -8.9$ eV, $A'_c = -8.6 - 0.1 = -8.7$ eV and $\varepsilon(e_S) = -9.1 - 0.1 = -9.2$ eV. It is known that the antisymmetric *Walsh*-orbital e_A lies 0.8 eV below e_S, leading to $\varepsilon(e_A) = -10.0$ eV.

The orbital energies $\varepsilon_J (J = 1, 2, 3)$ of the three highest occupied orbitals of **15** belonging to the irreducible representation A' are obtained by solving the following secular determinant:

$$0 = \begin{Vmatrix} -8.7 - \varepsilon & B_{ac} & B_{ce_S} \\ B_{ac} & -8.9 - \varepsilon & 0 \\ B_{ce_S} & 0 & -9.2 - \varepsilon \end{Vmatrix} \qquad (16)$$

With $B_{ac} = -0.45$ eV and $B_{ce_S} = -0.44$ eV, as derived from the analysis of the PE.-spectra of **6** and **13**, we obtain the orbital energies ε_1, ε_2, ε_3 which, together with $\varepsilon_4 = \varepsilon(e_A)$ are in perfect agreement with those derived from the PE.-spectrum (see Fig. 7):

ε_1: calc. -8.21 eV; obs. $-\ 8.14$ eV

ε_2: $\quad\quad -9.04$ eV; $\quad\quad -\ 9.11$ eV

ε_3: $\quad\quad -9.56$ eV; $\quad\quad -\ 9.46$ eV

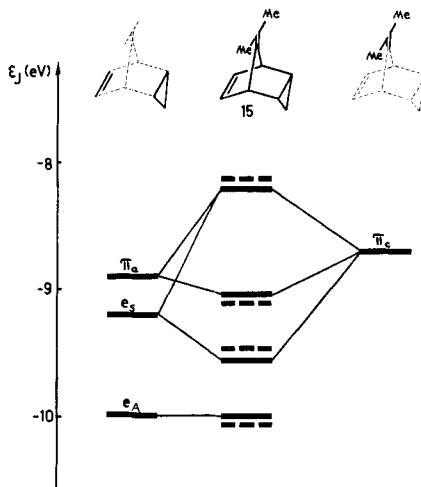ε_4: $\quad\quad -10.0$ eV; $\quad\quad -10.06$ eV

Fig. 7. *Correlation diagram for the orbital sequence in the hydrocarbon* **15**

The solid lines are the values derived according to the scheme described in the text. The broken lines are the orbital energies derived from the PE.-spectrum (see Fig. 5 and Tab. 2).

Comments

It is of interest to compare the differences between the observed orbital energies of the *Walsh*-orbitals, i.e. $\varepsilon(\mathbf{a}'(\mathbf{e_S})) - \varepsilon(\mathbf{a}''(\mathbf{e_A}))$ in the molecules **12** to **15**:

	12	**13**	**14**	**15**
$\varepsilon(\mathbf{a}'(\mathbf{e_S})) - \varepsilon(\mathbf{a}''(\mathbf{e_A}))$	0.80	0.66	0.80	0.60 eV (17)

The trend is obvious. Insertion of a double bond into **12** (yielding **14**) influences both $\varepsilon(\mathbf{e_S})$ and $\varepsilon(\mathbf{e_A})$ to the same extent, leaving the gap $\varepsilon(\mathbf{a}'(\mathbf{e_S})) - \varepsilon(\mathbf{a}''(\mathbf{e_A}))$ invariant at 0.80 eV; the strong interaction of $\mathbf{e_S}$ with $\pi_{\mathbf{c}}$ shifts $\varepsilon(\mathbf{a}'(\mathbf{e_S}))$ towards lower energies, thus reducing the gap to 0.60 to 0.66 eV. In addition, the differences (17) confirm the previous observation [15] that interaction of $\pi_{\mathbf{a}}$ and $\mathbf{e_S}$ can be neglected in *endo*-cyclopropanonorbornene derivatives.

In conclusion, the PE.-spectroscopic behaviour of compounds **5**, **6**, **13** and **15** confirms the hypothesis that in a norbornane system, interaction of an sp²-centre in position 7 with an *endo*-cyclopropano moiety is more important than with a π-bond in position 2, 3.

BIBLIOGRAPHY

[1] *E. Heilbronner*, Israel J. of Chem., in print.
[2] *P. Bischof, J. A. Hashmall, E. Heilbronner & V. Hornung*, Helv. *52*, 1745 (1969).
[3] *R. Hoffmann, E. Heilbronner & R. Gleiter*, J. Amer. chem. Soc. *92*, 706 (1970).
[4] *R. Hoffmann*, Accounts of chem. Research *4*, 1 (1971).
[5] *E. Heilbronner*, XXIIIrd International Congress of Pure and Applied Chemistry, Vol. 7, Butterworth, London 1971, p. 9.
[6] *H. D. Martin & D. Forster*, Angew. Chem. *84*, 65 (1972).
[7] *T. Koopmans*, Physica *1*, 104 (1933).
[8] *P. Bischof, J. A. Hashmall, E. Heilbronner & V. Hornung*, Tetrahedron Letters *1970*, 1033; *P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung & G. Schröder*, Helv. *53*, 1645 (1970); *E. Haselbach, E. Heilbronner & G. Schröder*, Helv. *54*, 153 (1971).
[9] *R. W. Hoffmann, R. Schüttler, W. Schäfer & A. Schweig*, Angew. Chem., *84*, 533 (1972).
[10] *R. W. Kiser*, 'Tables of Ionization Potentials', US Atomic Energy Commission, Washington D.C., 1960; *W. J. Wedenejew, L. W. Gurwitsch, W. H. Kondratjew, W. A. Madwedew & E. L. Frankewitsch*, 'Energien chemischer Bindungen, Ionisationspotentiale und Elektronenaffinitäten', Deutscher Verlag für Grundstoffindustrie, Leipzig 1971.
[11] *W. Bremser, H. T. Grunder, E. Heilbronner & E. Vogel*, Helv. *50*, 84 (1967).
[12] *D. Chadwick, D. C. Frost & L. Weiler*, J. Amer. chem. Soc. *93*, 4962 (1971).
[13] *D. W. Turner, C. Baker, A. D. Baker & C. R. Brundle*, 'Molecular Photoelectron Spectroscopy', Wiley-Interscience, London 1971; *D. Chadwick, D. C. Frost & L. Weiler*, J. Amer. chem. Soc. *93*, 4320 (1971).
[14] *H. Tanida, T. Tsuji & T. Irie*, J. Amer. chem. Soc. *89*, 1953 (1967); *M. A. Battiste, C. L. Deyrup, R. E. Pincock & J. Haywood-Farmer*, ibid. *89*, 1954 (1967); *R. Hoffmann*, Tetrahedron Letters *1965*, 3819.
[15] *P. Bischof, E. Heilbronner, H. Prinzbach & H. D. Martin*, Helv. *54*, 1072 (1971).
[16] *A. D. Walsh*, Nature *159*, 167, 712 (1947); Trans. Farad. Soc. *45*, 179 (1949).

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148. Reactions of Group 3 Metal Alkyls in the Gas Phase. Part 10[1]): The Addition of Olefins to the Monomeric Diisobutylaluminiumhydride

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Summary. The relative rate constants for adding ethylene (k_1), propylene (k_2) and 2-methylbut-1-ene (k_3) to gaseous diisobutylaluminium hydride produced *in situ* from Al^{t}Bu$_3$ have been measured in the temperature range 104–169° in the presence of an excess of equimolar olefin mixtures. The following temperature dependences of the relative rate constants have been obtained:

$$\log(k_1/k_2) = 0.6 - 0.8/4.58 \times 10^{-3}\ T(°K)$$

$$\log(k_1/k_3) = 1.2 - 2.2/4.58 \times 10^{-3}\ T(°K)$$

Two compensating factors determine the rate of addition of olefins to Al–H and Al–C bonds: (a) the steric effect, reflected in the differences in the preexponential factors and (b) the polar effects, reflected in differences in the activation energies.

In the addition of olefins to R$_2$Al–H bonds in contrast to R$_2$Al–C bonds, the steric effect (a) does not always overrule the opposing energy effect. At temperatures below 125° e.g., isobutene

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[1])   Part 9: *K. W. Egger*, J. chem. Soc. Faraday I, *68*, 1017 (1972).