

Reduktion des dideuterierten Tetralons mit  $\text{LiAlH}_4$  unter üblichen Bedingungen ergab in ca. 90% Ausbeute **3a**. - IR.: 3630, 3610 (freie OH), ca. 3400 (sehr breit, geb. OH), 2250-2100 ( $\nu$  CD), 1495 (Aromat), 1391 und 1371 ( $\text{C}(\text{CH}_3)_2$ ). - MS.: 178 ( $M^+$ , 58), 177 (33), 176 (5), 161 (9), 160 (46), 159 (12), 146 (8), 145 (54), 144 (19), 143 (12), 142 (7), 131 (8), 130 (17), 129 (15), 128 (8), 123 (8), 122 (63), 121 (18), 120 (100), 119 (81), 118 (15), 117 (14), 116 (13), 115 (9), 105 (15), 104 (6), 93 (8), 92 (20), 91 (48), 90 (10), 89 (8), 79 (6), 78 (11), 77 (13), 65 (15).

5, 2, 2, 5, 7-Tetramethyl-1-tetralol (**4**). **4** wurde wie üblich aus dem entsprechenden Keton [12] bereitet. Smp. (Pentan/Äther): 93-94°. - MS.: 204 ( $M^+$ , 32), 189 (5), 186 (21), 171 (14), 149 (12), 148 (100), 147 (30), 119 (16), 115 (6), 105 (8), 91 (9), 77 (5).

## LITERATURVERZEICHNIS

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## 168. The Conjugative Interaction between $\pi$ -Orbitals and Cyclobutane-Orbitals in Spiro[3.4]octa-5,7-diene and Spiro[3.4]octene-5

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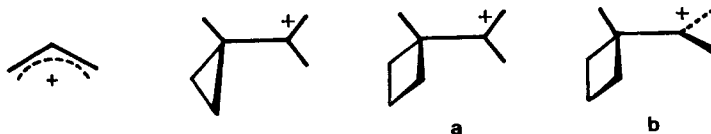
**Summary.** The photoelectron spectra of spiro[3.4]octane (**1**), spiro[3.4]octene-5 (**2**), spiro[3.4]octa-5,7-diene (**3**), spiro[4.4]nonene-2 (**4**) and spiro[4.4]nona-2,4-diene (**5**) have been recorded. The first bands of these spectra are correlated with orbitals which are  $\pi$ -orbitals, Walsh orbitals resp. linear combinations of both. Our assignment is based on a qualitative ZDO-model, it is in

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satisfactory agreement with the results of extended *Hückel* calculations. The interaction found in **2** and **3** is of similar magnitude as the one in **4** and **5** and considerably less than that in homo-fulvene and fulvene.

Experimental evidence strongly suggests an analogy between a carbon-carbon double bond and a cyclopropane ring. This similarity is well documented for the case where a positively charged  $sp^2$  hybridized carbon atom is attached to a vinyl or a cyclopropyl group giving rise to the allyl cation and cyclopropylcarbinyl cation [1] respectively.

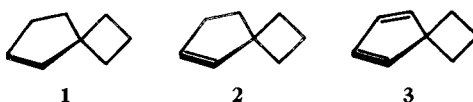


Based on the theoretical calculations [2] [3] it has been predicted that in the cyclobutylcarbinyl cation there should also be a considerable interaction between the positive center and the C-C- $\sigma$ -bonds of the four membered ring in the bisected conformation **a** as well as in the perpendicular conformation **b**. So far experimental evidence for this prediction is sparse [5].

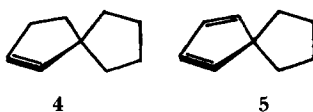
To contribute to this discussion we have measured the photoelectron (PE) spectra of compounds containing vinylcyclobutane units fixed in a conformation corresponding to **a**. The interaction between the  $\pi$ -orbitals of the double bonds and *Walsh*-orbitals of the cyclobutane ring should be a maximum in this conformation [2] [4]. In our study of tricyclo[3.3.0.0<sup>2,6</sup>]octene [6] we described the conjugative interaction between the bonding  $\pi$ -orbital of a double bond and the antisymmetric *Walsh*-orbital of a cyclobutane ring in terms of the atomic resonance integral

$$\beta_{p_a p_r} = \langle p_a | H | p_r \rangle = -1.9 \text{ eV}^3 \quad (1)$$

To test this result we investigated the PE-spectra of the following hydrocarbons: spiro[3.4]octane (**1**)<sup>1)</sup>, spiro[3.4]octene-5 (**2**)<sup>2)</sup>



and spiro[3.4]octa-5,7-diene (**3**) [7]. For a comparison the PE-spectra of spiro[4.4]nonene-2 (**4**) [8], spiro[4.4]nona-2,4-diene (**5**) [9] and methylcyclobutane (**6**) were obtained.



<sup>1)</sup> **1** was obtained from spiro[3.4]octan-5-one by a *Wolff-Kishner* reduction. *A. de Meijere* and *L.-U. Meyer*, unpublished results.

<sup>2)</sup> **2** was prepared by reacting the tosylhydrazone of spiro[3.4]octan-5-one with methyllithium. Cf. 1c. Footnote <sup>1)</sup>. See also: *C. F. Wilcox jr.* and *G. C. Whitney*, *J. Org. Chemistry* **32**, 2933 (1967).

<sup>3)</sup> For the definition of  $p_a$  and  $p_r$  see below.

The PE-spectra of **1-5** are shown in Figure 1 and Figure 2, the relevant data collected from these are summarized in Table 1.

Table 1. Ionization potentials of **1-6**. All values in eV.

Compound	<b>1</b>		<b>2</b>		<b>3</b>		<b>4</b>		<b>5</b>		<b>6</b>	
Band J	$I_{vJ}$	$I_{aJ}$	$I_{vJ}$	$I_{aJ}$	$I_{vJ}$	$I_{aJ}$	$I_{vJ}$	$I_{aJ}$	$I_{vJ}$	$I_{aJ}$	$I_{vJ}$	$I_{aJ}$
①	10.05	9.45	8.97	8.65	8.38 <sup>a)</sup>	8.20 <sup>a)</sup>	8.86	8.73	8.14 <sup>a)</sup>	8.30 <sup>a)</sup>	10.37	9.60
②	10.62 <sup>b)</sup>	-	10.38	9.84	10.12	9.50	10.65	10.05	10.18	9.78	10.94	-
③	11.03 <sup>b)</sup>	-	10.83	-	10.80	-	11.08	-	10.98	-	11.43	-
④	11.60 <sup>b)</sup>	-	11.75	-	11.22	-	11.67	-	11.58	-	11.90	-
⑤	12.35 <sup>b)</sup>	-	12.60	-	12.58	-	12.73	-	12.37	-	12.65	-

a) The two transitions have about the same intensity.

b) The bands are very strongly overlapping.

$I_{vJ}$  refers to vertical ionisation potentials,  $I_{aJ}$  to adiabatic ionisation potentials of the corresponding bands.

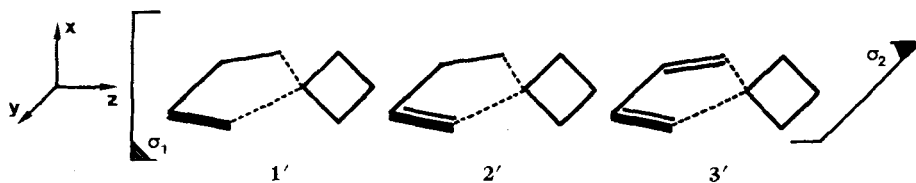
For our interpretations we will make use of *Koopmans* theorem [10]

$$\epsilon_J = -I_{v,J} \quad (2)$$

which allows to correlate the bands of the spectra with molecular orbital energies calculated by semiempirical methods or estimated on the basis of simple perturbation arguments [11].

We will focus our attention mainly on the systems involving the cyclobutane ring, *i.e.* compounds **1**, **2** and **3** and use the other data for comparison.

Compounds **1-3** can be regarded as systems containing formally a cyclobutyl fragment and a *s-cis*-butane-(**1'**), *s-cis*-1-butene-(**2'**) or *s-cis*-butadiene fragment (**3'**) respectively, interacting along the dotted lines in the manner shown below.



In a model treatment, the nature of these interactions can be

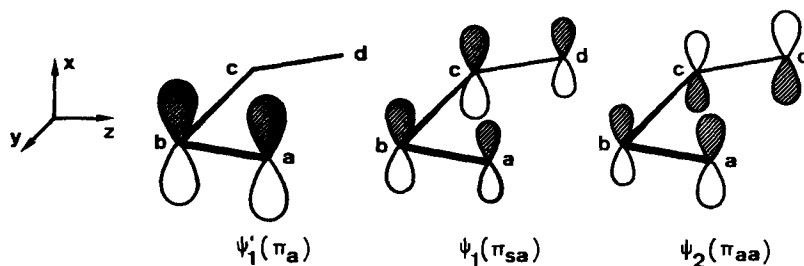
- conjugative
- inductive

or any superposition of the two types of interaction. To simplify our discussion we shall assume that in all three cases the two fragments are planar and lying in perpendicular planes  $\sigma_1(xz)$  and  $\sigma_2(yz)$  as shown in the above drawing. Under this assumption, **1** and **3** are of  $C_{2v}$ -symmetry while **2** is of  $C_s$ -symmetry with  $\sigma_2$  being the corresponding plane of symmetry.

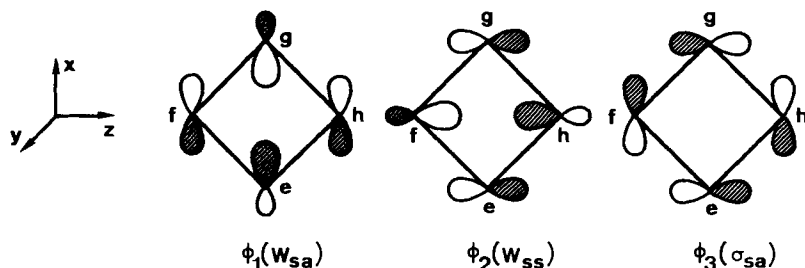
Semiempirical calculations show that any reasonable deviation from this assumption will not alter the qualitative results of our discussion.

To proceed with our analysis, we need to choose an appropriate set of wave functions for the relevant orbitals  $\pi$ ,  $w_{as}$ ,  $w_{ss}$  and  $\sigma_{as}$  of the formal fragments. These orbitals are illustrated below.

a)  $\pi$ -orbitals



b) Cyclobutane C-C- $\sigma$ -orbitals



In contrast to the case of tricyclo[3.3.0.0<sup>2,6</sup>]octene [6], the high lying  $\sigma_{sa}$ -orbital (corresponding to the  $b_{1g}$ -orbital in the parent compound [12]) must be included in the basis set of the relevant orbitals, since it has a comparable energy and the right symmetry to interact with the  $\pi$ -orbitals of the formal olefin fragment.

The corresponding ZDO-wave functions are:

$$\psi'_1 = \frac{1}{\sqrt{2}} (p_{xa} + p_{xb}) \quad [11] \quad (3)$$

$$\psi_1 = 0.372 (p_{xa} + p_{xd}) + 0.602 (p_{xb} + p_{xc}) \quad [11] \quad (4)$$

$$\psi_2 = 0.602 (p_{xa} - p_{xd}) + 0.372 (p_{xb} + p_{xc}) \quad [11] \quad (5)$$

$$\Phi_1 = 0.5 (\varphi_{xe} - p_{xf} + \varphi_{xg} - p_{xh}) \quad [6] \quad (6)$$

$$\Phi_2 = 0.5 (p_{ze} - \varphi_{zf} + p_{zg} - \varphi_{zh}) \quad [6] \quad (7)$$

$$\Phi_3 = 0.5 (p_{ze} + p_{xf} - p_{zg} - p_{xh}) \quad (8)$$

It is important to note that the 'orbital densities' of the C-C- $\sigma$ -orbitals of the formal cyclobutane fragment have the same magnitude on all four carbon atoms in the above notation. In  $\Phi_3$  this is necessarily so due to symmetry. In  $\Phi_1$  and  $\Phi_2$ , however, the choice of a unique wave function is difficult. Semiempirical calculations suggest [2] [4] that both *Walsh*-orbitals are quite equally distributed over all four centers (see also [6]). For sake of simplicity we have therefore selected the ZDO

wave functions described above. In these equations the  $p_{\xi 1}$ 's are pure  $p_{\xi}$  atomic orbitals, while the  $\varphi_{\xi 1}$ 's are  $sp_{\xi}^n$  hybrid atomic orbitals parallel to the  $\xi$ -axis.

**PE-Spectrum of 3.** – Due to the higher symmetry of **3** compared with **2**, the analysis of the interaction between  $\pi$ -orbitals of the double bonds and the *Walsh* orbitals of the four-membered ring is easier to perform. Therefore we will start our discussion with the interaction diagram corresponding to **3**.

The relevant orbitals are characterized in eq. (4) to (8). They transform according to the following irreducible representations

$$\begin{aligned} \psi_1 (\pi_{sa}) &: B_1; & \psi_2 (\pi_{aa}) &: A_2 \\ \Phi_1 (w_{sa}) &: B_1; & \Phi_2 (w_{ss}) &: A_1 \\ \Phi_3 (\sigma_{sa}) &: B_1. \end{aligned}$$

In our basis set there are three orbitals of  $B_1$  symmetry which can interact while  $\psi_2$  and  $\Phi_2$  don't have a counterpart. All the other molecular orbitals belonging to the  $A_1$  and  $A_2$  symmetry class are expected to have much lower ( $\sigma$ ) or much higher energies ( $\sigma^*$ ) than our basis orbitals. According to second order perturbation theory [11], the shift resulting from the interaction is inversely proportional to the energy difference of the orbitals in question. The influence of such orbitals is therefore expected to be small and we will neglect them in our qualitative treatment.

The next step is to estimate the energies of the basis orbitals.

The  $\pi$ -orbital  $\psi_2$  is known to be the HOMO in butadiene. Due to symmetry, it cannot interact with any orbital of the cyclobutane ring which is similar in energy. Its energy is found to be

$$\varepsilon (\psi_2) = -8.40 \text{ eV} \quad (9)$$

from the spectra shown in Figure 1.

Compared with the assumed energy of the corresponding orbital in *s-cis*-butadiene ( $-9.10 \text{ eV}$  [13]) we therefore come to the conclusion, that it is shifted inductively by

$$\delta\varepsilon (\psi_2) = \Delta_1 = -8.40 + 9.10 = +0.70 \text{ eV} \quad (10)$$

towards higher energies.

Assuming that the inductive shift is the same for both  $\pi$ -orbitals and considering the orbital energy of  $-11.6$  [14] for the corresponding  $\pi$ -orbital in butadiene, we obtain an estimated basis orbital energy of

$$\varepsilon (\psi_1) = -11.6 + 0.7 = -10.9 \text{ eV} \quad (11)$$

for the lower lying  $\pi$ -orbital  $\psi_1$ .

The basis orbital energies  $\varepsilon(\Phi_1)$  can be derived as follows. The inductive shift of a vinyl substituent is thought to be small [15]. If we assume this shift in cyclobutane [12] to be  $0.1 \text{ eV}$  per vinyl group, we obtain a basis orbital energy of

$$\varepsilon(\Phi_1) = -10.8 \text{ eV} \quad (13)$$

and

$$\varepsilon(\Phi_3) = -12.3 \text{ eV}. \quad (14)$$

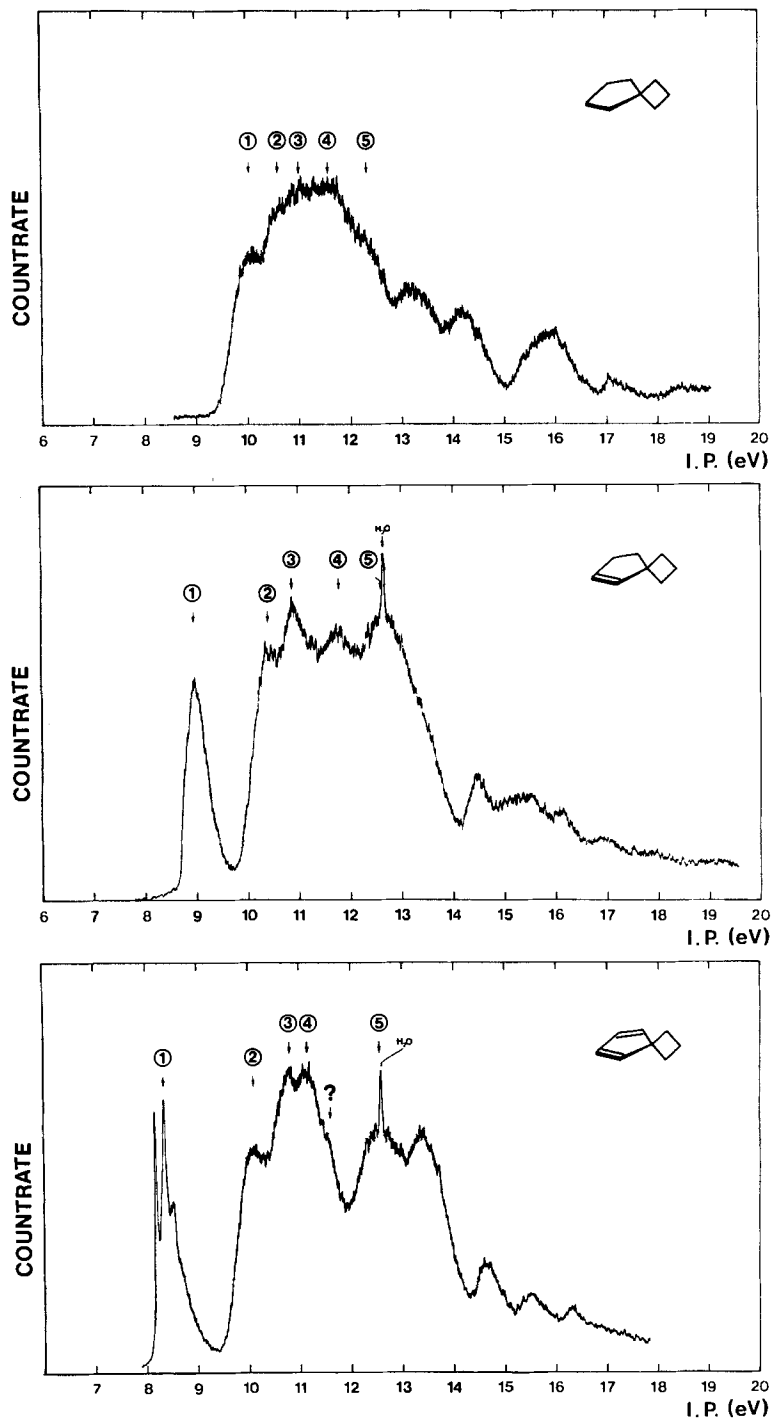


Fig. 1. PE-spectra of *spiro[3.4]octane* (1), *spiro[3.4]octene-5* (2), *spiro[4.4]octa-5,7-diene* (3). The numbering of the bands refers to that given in the table

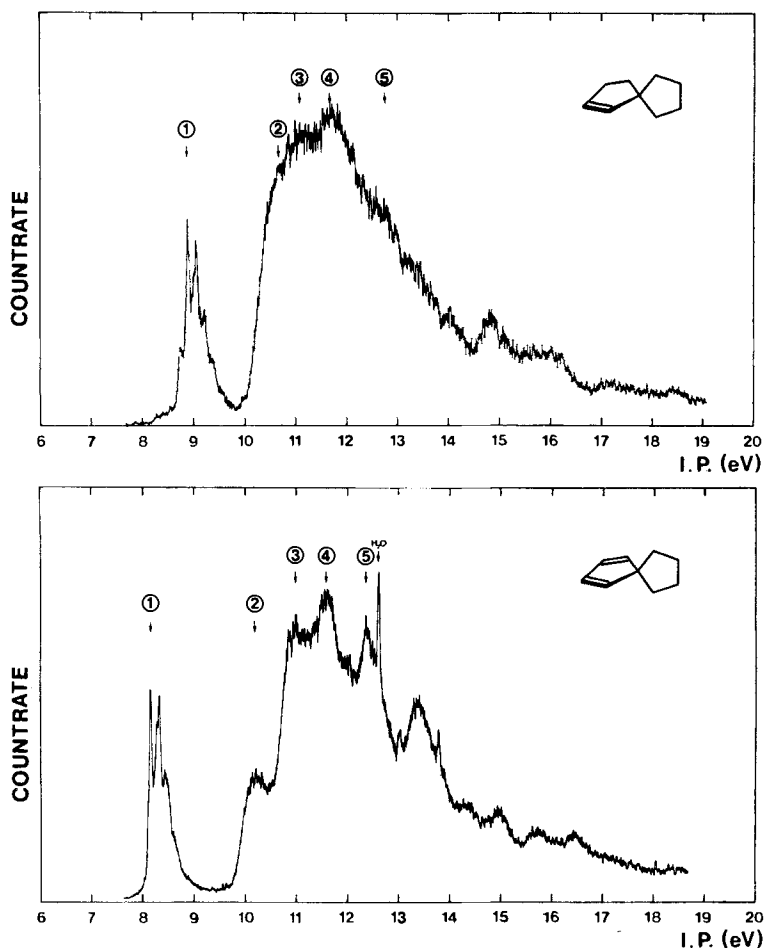


Fig. 2. PE-spectra of *spiro[4.4]nonene-2* (4) and *spiro[4.4]nona-2,4-diene* (5) (see legend to Fig. 1)

The same basis orbital energies are found by applying the rules proposed by *Heilbronner* [16] to the correlation of the systems **1** and **3**. Specifically the introduction of a double bond in place of a single bond shifts the adjacent C–C- $\sigma$ -orbitals by 0.3 eV towards lower energies. Assuming a symmetric pseudo-*Jahn-Teller*-split in **1** this yields

$$\varepsilon(\Phi_1) = \varepsilon(\Phi_2) = \frac{1}{2} (-10.0 - 10.6) - 2 \cdot 0.3 = -10.9 \text{ eV.} \quad (15)$$

This is another confirmation of the value estimated above.

In order to derive the interaction matrix, we now have to estimate values for the resonance integrals  $H_{ij}$ . We obtain from equations (4)–(8):

$$H_{\pi w} = \langle \psi_1 | H' | \Phi_1 \rangle = 2 \cdot 0.372 \cdot 0.5 \cdot \langle p_{xp} | H' | p_{xa} \rangle. \quad (16)$$

Equation (16) is derived under the assumption, that all resonance integrals between atomic orbitals can be neglected, if their corresponding centers are separated by more than one carbon-carbon bond. In (16)  $H'$  is the perturbation operator while  $\psi_1$  and  $\Phi_1$  are the basis orbital wave functions.

In an analogous way we find

$$H_{\pi\sigma} = \langle \psi_1 | H' | \Phi_3 \rangle = 2 \cdot 0.372 \cdot 0.5 \langle p_{xt} | H' | p_{xa} \rangle. \quad (17)$$

From (1) we obtain

$$H_{\pi w} = H_{\pi\sigma} = -0.707 \text{ eV}. \quad (18)$$

This leads to the following secular determinant for the three interacting basis orbitals:

$$D = \begin{vmatrix} \varepsilon_\sigma - \varepsilon & H_{\pi\sigma} & 0 \\ H_{\pi\sigma} & \varepsilon_\pi - \varepsilon & H_{\pi w} \\ 0 & H_{\pi w} & \varepsilon_w - \varepsilon \end{vmatrix} = \begin{vmatrix} -12.3 - \varepsilon & -0.707 & 0 \\ -0.707 & -10.9 - \varepsilon & -0.707 \\ 0 & -0.707 & -10.8 - \varepsilon \end{vmatrix} = 0$$

Solving this secular determinant yields the following eigenvalues

$$\varepsilon_1(b_1) = -10.03 \text{ eV}$$

$$\varepsilon_2(b_1) = -11.33 \text{ eV}$$

$$\varepsilon_3(b_1) = -12.64 \text{ eV}.$$

The predictions derived with this model are shown in Figure 3. The agreement with the experimental data is quite close.

The estimate of the basis orbital energies of the C-C- $\sigma$ -orbitals appears to be reasonable since the energy of the noninteracting *Walsh*-orbital  $\Phi_2$  is 'found' in the spectrum where it was estimated to be.

However, the estimate of the  $\pi$ -orbital energy  $\varepsilon(\psi_1)$  in the outlined analysis may be questioned. If one assumes, that the inductive shift is due to charge drifts in the sigma frame (thus lowering the effective core charge of the carbon atoms of the  $\pi$ -part), one can write in terms of first order perturbation theory:

$$\delta\varepsilon_\pi = \Delta_1 = \Sigma c_1^2 \delta\alpha_1. \quad (19)$$

It is accepted that inductive shifts of substituents in organic molecules have about half their magnitude at the second center compared to the one directly at the substituted carbon center [17].

Hence, it follows from equations (5) and (19) and the 'observed' orbital energy of the HOMO

$$\begin{aligned} \delta\varepsilon_\pi &= 2 \cdot 0.602^2 \cdot \delta\alpha_1 + 2 \cdot 0.372^2 \cdot \delta\alpha_2 \\ &= 2 \cdot 0.602^2 \delta\alpha_1 + 2 \cdot 0.372^2 \cdot \frac{1}{2} \delta\alpha_1 \\ &= 0.863 \delta\alpha_1 = 0.7 \text{ eV}; \quad \text{or} \quad \delta\alpha_1 = 0.81 \text{ eV}. \end{aligned}$$

From this we derive by applying the same formula an estimated orbital energy of  $-11.08 \text{ eV}$  for the symmetric  $\pi$ -orbital. This leads to the slightly different eigenvalues



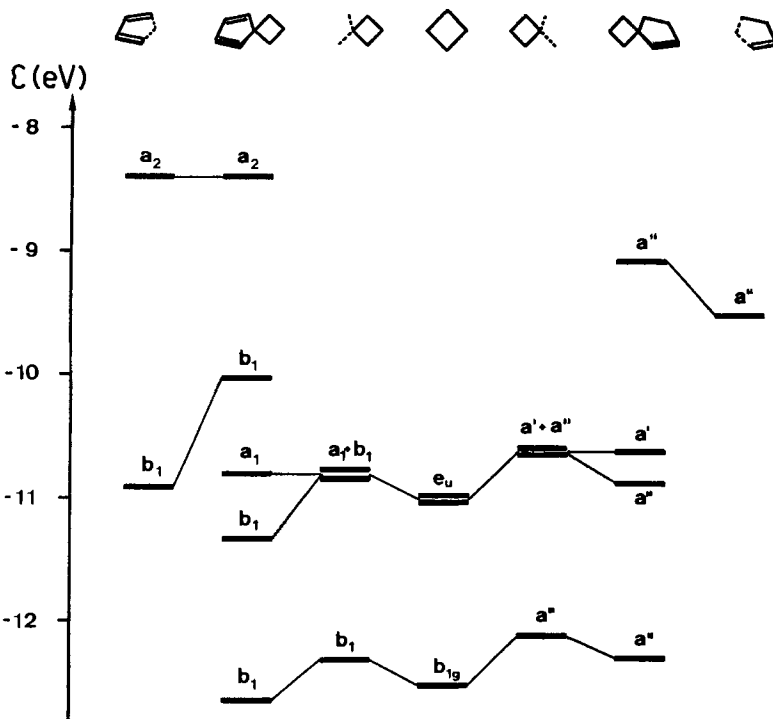


Fig. 3. Orbital correlation diagram for *spiro[3.4]octene-5* (**2**) and *spiro[3.4]octa-5,7-diene* (**3**) based on perturbation arguments

of  $-10.12$  eV,  $-11.38$  eV and  $-12.67$  eV for  $\varepsilon_1$ ,  $\varepsilon_2$  and  $\varepsilon_3$  respectively. These energies again are in close agreement with the 'observed' ones.

Experimental evidence for  $-9.1$  eV as the orbital energy for *cis*-butadiene is not sound. Assuming values in between  $-8.8$  [15] and  $-9.1$  eV [13] and using the same arguments as above leads to values for  $\langle p_{x1} | H' | p_{x2} \rangle$  from  $-1.9$  to  $-2.4$  eV. Although values in this range give reasonable orbital energies for **3**, compared with experiment, we tend to favour the former value. The reason for this is that this value allows us to interpret the PE-spectra of tricyclo[3.3.0<sup>2,6</sup>]octene [6], *cis*- and *trans*-divinylcyclobutane [18], *cis*- and *trans*-diethynylcyclobutane and norpinenederivatives [19] while larger values give serious discrepancies.

**PE-Spectrum of 2.** – The interpretation of the PE-spectrum of **2** is hampered by the fact that there are several strongly overlapping bands between 10 and 13 eV. We use the interaction parameter derived from **3** to try to interpret the first bands of this spectrum.

The four basis orbitals in this case are  $\psi_1'$ ,  $\Phi_1$ ,  $\Phi_2$  and  $\Phi_3$  shown in eq. (3), (6), (7) and (8). From these four basis orbitals  $\psi_1'$ ,  $\Phi_1$  and  $\Phi_3$  are antisymmetric and  $\Phi_2$  is symmetric with respect to the plane of symmetry  $\sigma_2$ .

It is a matter of the point of view, whether one regards **2** as consisting of a formal cyclobutane fragment interacting with a formal 1-butene fragment or a methyl substituted cyclobutane fragment interacting with a formal 1-propene-fragment.

Both models should lead to the same conclusion although the latter is easier to handle for a variety of reasons. Using the same arguments as in the above analysis we estimate the basis orbital energies to be

$$\varepsilon(\Phi_1) = \varepsilon(\Phi_2) = \varepsilon(\Phi_1^0) + \delta\varepsilon_A + \delta\varepsilon_V$$

where  $\delta\varepsilon_A$  is the inductive shift due to the alkylsubstitution and  $\delta\varepsilon_V$  the one for vinylsubstitution ( $\simeq 0.1$  eV) and  $\varepsilon(\Phi_1^0)$  is the energy of the corresponding orbital in the parent compound.

By examining the spectrum of methylcyclobutane we derive

$$\delta\varepsilon_A = -11.0 - \frac{1}{2}(-10.37 - 10.94) = 0.3 \text{ eV}$$

or

$$\varepsilon(\Phi_1) = \varepsilon(\Phi_2) = -11.0 + 0.3 + 0.1 = -10.6 \text{ eV}$$

and

$$\varepsilon(\Phi_3) = -12.5 + 0.4 = -12.1 \text{ eV}.$$

Considering a basis orbital energy for the  $\pi$ -orbital of  $-9.5$  eV and a resonance integral of

$$\begin{aligned} H_{\pi w} = H_{\pi\sigma} &= 0.5 \cdot 0.707 \cdot \langle p_{x\pi} | H | p_{x\sigma} \rangle \\ &= 0.5 \cdot 0.707 \cdot -1.9 \text{ eV} = -0.67 \text{ eV} \end{aligned}$$

we find the following secular determinant:

$$D = \begin{vmatrix} -10.6 - \varepsilon & -0.67 & 0 \\ -0.67 & -9.5 - \varepsilon & -0.67 \\ 0 & -0.67 & -12.1 - \varepsilon \end{vmatrix} = 0$$

yielding the following eigenvalues:

$$\varepsilon_1 = -9.06 \text{ eV}$$

$$\varepsilon_2 = -10.86 \text{ eV}$$

$$\varepsilon_3 = -12.28 \text{ eV}.$$

Again, there is a very good agreement with the experimental data. These values clearly demonstrate that in contrast to the case of **3** the interaction between  $\Phi_3$  and the  $\pi$ -orbital is small. This seems reasonable due to the large energy difference separating both basis orbitals.

The resulting interaction diagram is shown in Figure 3.

**Semiempirical calculations.** – To test the analysis given above we have compared the results with those of extended *Hückel* (EH) [20] calculations assuming standard bond lengths and angles with the parameters used by *Hoffmann* [20]. According to our experience this treatment in many cases yields the same ordering of the upper occupied orbitals as does a semiempirical SCF calculation.

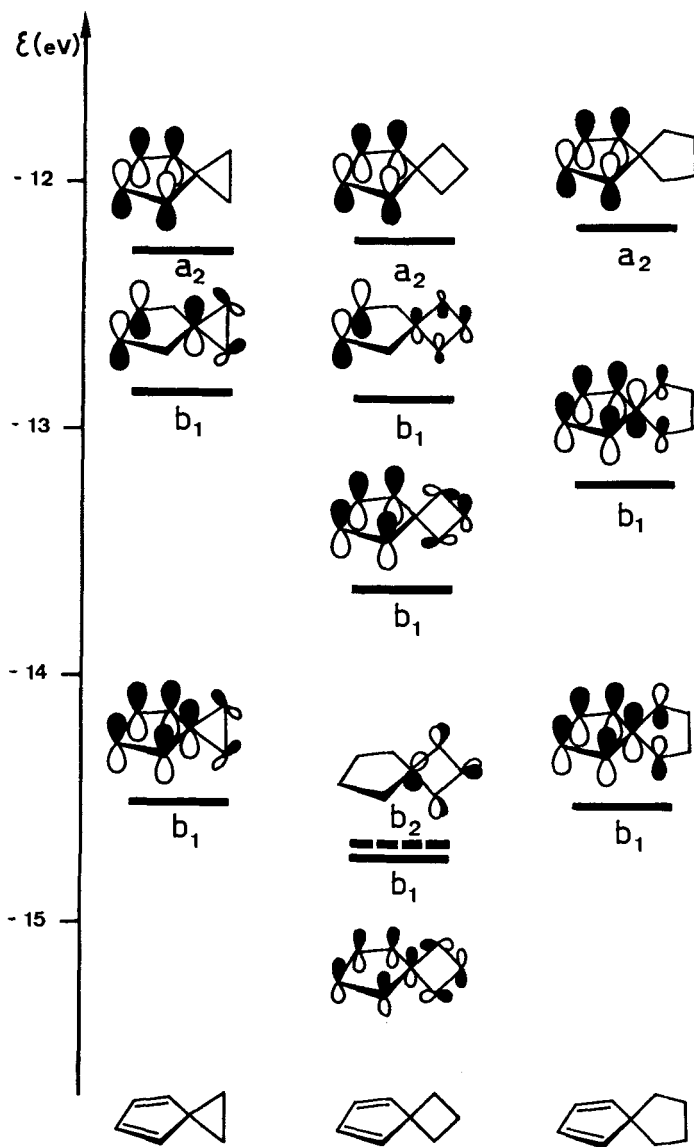


Fig. 4. Comparison of the  $\pi$ -orbital energies of homofulvene, spiro[3.4]octa-5,7-diene (**3**) and spiro[4.4]nona-2,4-diene (**5**) calculated by EHT [20]

Figure 4 shows the orbitals of  $\pi$ -type of homofulvene [15], **3** and **5** as obtained by an EH calculation.

We are using in this Figure only the orbitals of  $\pi$ -type since according to our experience [15] [21] [22] for systems containing small rings, semiempirical calculations yield several  $\sigma$ -orbitals in between the  $\pi$ -orbitals and place those  $\sigma$ -orbitals which do not interact with the  $\pi$ -system too high in their orbital energy.

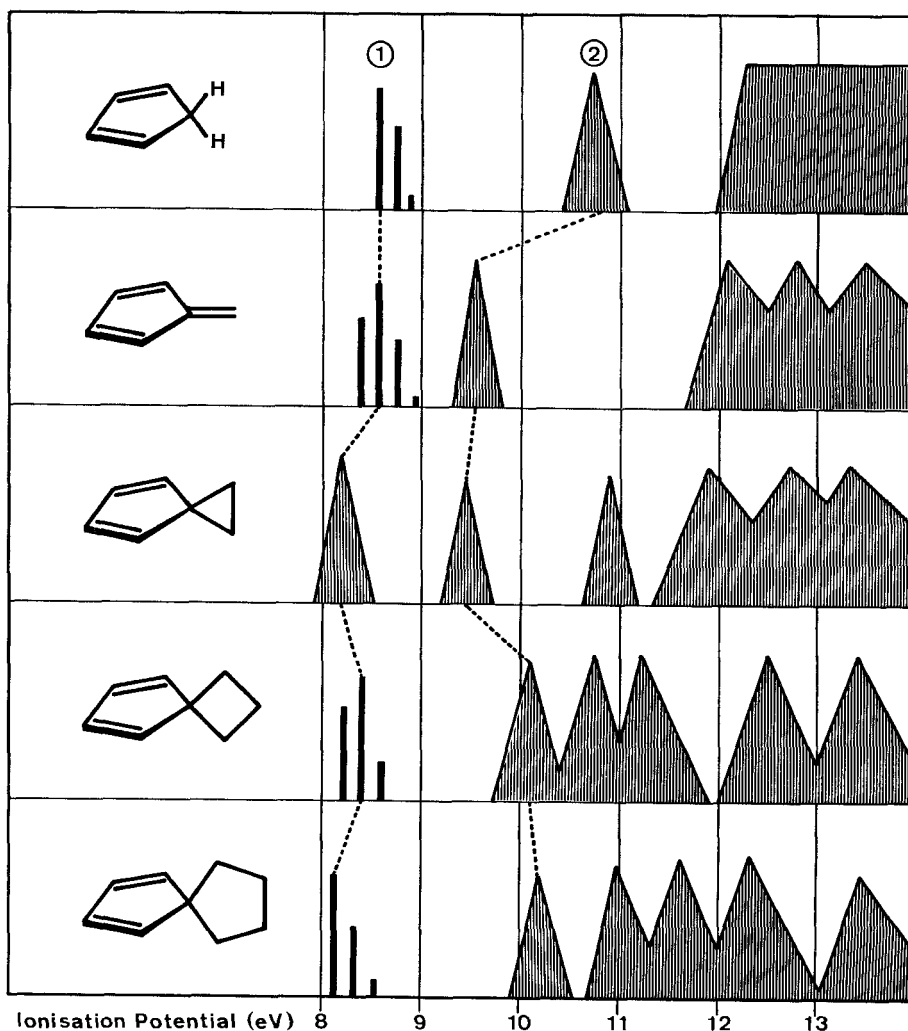


Fig. 5a) Schematic diagram of the PE-spectra of cyclopentadiene, fulvene, homofulvene, spiro[3.4]octa-5,7-diene (3) and spiro[4.4]nona-2,4-diene (5)

This fact makes it rather difficult to assign other orbitals than the ones shown in Figures 3 and 4.

The pattern derived by these calculations (Fig. 4) compares well on a qualitative basis with the one shown in the lower part of Figure 5a. The calculated energy differences between the orbitals of  $b_1$  symmetry are 0.77 and 1.06. The ratio  $0.77 : 1.06 = 0.72$  compares reasonably well with the experimental value of  $1.10 : 1.36 = 0.81$ .

The agreement, however, between prediction and experiment concerning the energy gap between the HOMO ( $a_g$ ) and the highest occupied orbital of  $b_1$  symmetry is rather poor (0.65 eV versus 1.74 eV). This result confirms our experience that semiempirical methods place the  $\sigma$ -orbitals especially in four membered rings too

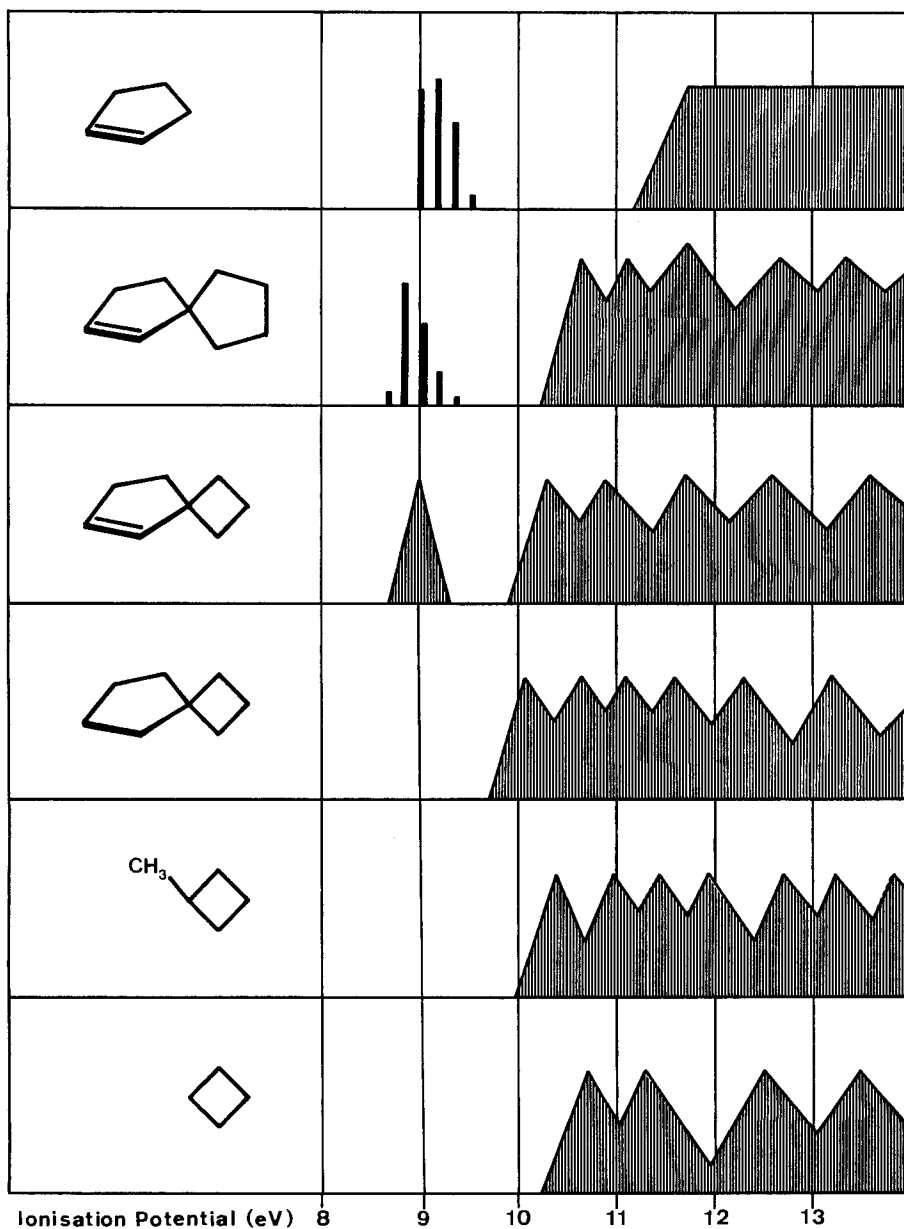


Fig. 5b). Schematic diagram of the PE-spectra of cyclopentene [24], spiro[4.4]nonene-2 (4), spiro[3.4]octene-5 (2), spiro[3.4]octane (1), methylcyclobutane (6) and cyclobutane [12]

high. This is corroborated by comparing the calculated orbital sequence for tricyclo[4.2.0.0<sup>2,5</sup>]octadien [23] with the reported PE-spectra [22].

In Figure 4 we have indicated with a dotted line the energy of the orbital ( $b_2$ ) which corresponds to the  $b_{1u}$  orbital of cyclobutane. It is interesting to note that the

EH-method predicts the corresponding orbital in **2** at the same position (–14.7 eV). From this result one is tempted to assign band ④ of **2** and the shoulder of band ④ in **3** to an ionization process corresponding to an ejection out of this orbital.

**Conclusion.** – A current question in small ring chemistry is the one, whether a cyclobutyl substituent can stabilize a positive charge or not. Since in photoelectron spectroscopy we are ejecting an electron from the neutral molecule we should be able, in the framework of the one electron approach, to contribute a qualitative answer to this question.

In Figure 5a the PE-spectra of fulvene [11], homofulvene [12], **3** and **5** and in Figure 5b those of **2** and **3** are compared. Our assignment shows that the ionization potential of each second band in Figure 5a is due to an ionization out of the orbital

$$\psi = N (\pi - \lambda \omega)$$

where  $\omega$  stands for the exocyclic  $\pi$  bond in fulvene, a *Walsh* or a  $\sigma$ -orbital of appropriate symmetry. A comparison between these ionization potentials clearly shows, that the effect of the cyclobutane ring is comparable to the effect of a five membered ring while the shift caused by a cyclopropane ring is close to the one due to a double bond.

This observation is corroborated by a comparison of the resonance integrals  $H_{\pi w}$  between a double bond and a three- or fourmembered ring respectively in the bisected conformation in which the interaction is at a maximum.

For the vinylcyclopropane case we obtain

$$H_{\pi w} = -1.9 \cdot \frac{2}{\sqrt{6}} \cdot \frac{1}{\sqrt{2}} = -1.1 \text{ eV}$$

and for the vinyl-cyclobutane case

$$H_{\pi w} = -1.9 \cdot 0.5 \cdot \frac{1}{\sqrt{2}} = -0.76 \text{ eV.}$$

The much smaller value for the vinylcyclobutane systems confirms the conclusion drawn by others [1] that there is a considerable difference to be expected between a cyclopropyl and a cyclobutyl group, as far as stabilizing a positively charged center is concerned. The fact that the cyclobutane basisorbitals are lower in energy than the ones in cyclopropane contributes to this trend.

**Experimental.** – The PE spectra were recorded on a PS 18 Photoelectron Spectrometer (Perkin-Elmer Ltd., Beaconsfield England) of the type described by Turner [24]. For further experimental details see [21].

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## 169. Formation and Properties of Losod, a New Sodium Zeolite

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(15. III. 74)

*Summary.* Losod, a new type of crystalline hydrated sodium aluminosilicate,  $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot q \text{H}_2\text{O}$ , has been prepared from reaction mixtures containing bulky quaternary alkylammonium ions, particularly azonia-spiro[4.4]nonane, besides sodium ions. Losod crystallizes from batches with a low sodium content ( $\text{Na}/\text{Al} \leq 1$  and  $\text{Si}/\text{Al} \approx 1$ ). The quaternary ammonium hydroxide primarily serves as a source of hydroxide ions and is not incorporated into the zeolite crystals. These bulky bases provide a useful means for controlling the alkalinity of the system independently of the concentration of the necessary cations built into the zeolite.

The crystals of Losod are hexagonal ( $a = 12.91$  and  $c = 10.54 \text{ \AA}$ ) and the proposed framework structure shows a polytypic relationship to sodalite and cancrinite. Losod has reversible