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# INTERACTION OF NONCONJUGATED DOUBLE BONDS IN 1,4,5,8-TETRAHYDRONAPHTHALENE (1)

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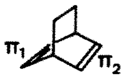
In a previous note (2) of this series (1) we have shown that the interaction of the two non-conjugated $\pi$-bonds, $\pi_1$ and $\pi_2$, in norbornadiene (I) and bicyclooctadiene (II), gives rise to a split $\Delta = \varepsilon(\pi_-)-\varepsilon(\pi_+)$ between the linear combinations $\pi_- = (\pi_1-\pi_2)/\sqrt{2}$ and $\pi_+ = (\pi_1+\pi_2)/\sqrt{2}$. This splitting amounts to 0.85 eV in I and 0.6 eV in II. In such systems through-space interaction (homoconjugation) dominates (3) and $\Delta$ should thus be roughly proportional to the overlap integral $S = \langle\pi_1|\pi_2\rangle$

I



II

III

Therefore it may seem surprising that the split $\Delta$ between the two $\pi$-ionization bands observed in the photoelectron-spectrum (PE-spectrum) of 1,4-cyclohexadiene (III) is larger than for I or II even though S is smaller: I, $S = 0.11$, $\Delta = 0,8_5$ eV; II, $S = 0.10$ $\Delta = 0.6$ eV; III, $S = 0.06$, $\Delta = 1.0$ eV. (These S-values are based on Slater-orbitals). As shown (3), this result can be rationalized by taking hyperconjugation into account.

In a formal way the interaction between $\pi_1$ and $\pi_2$ in III can be described by two parameters (c.f. figure 1):

A) a stabilization $\delta A$ of the individual $\pi$-orbitalenergies $A' = A_a + \delta A = \langle\pi_1|H|\pi_1\rangle = \langle\pi_2|H|\pi_2\rangle = -I_a$, relative to the energy $A_a = \langle\pi_a|H|\pi_a\rangle$ of a $\pi$-orbital in the parent compound cyclohexene (IV) $\delta A = A'-A_a = \dfrac{\varepsilon_1 + \varepsilon_2}{2} - A_a = I_a - \dfrac{I_1 + I_2}{2}$

This stabilization is due to the increased 2s-character of the $\sigma$-frame in III.

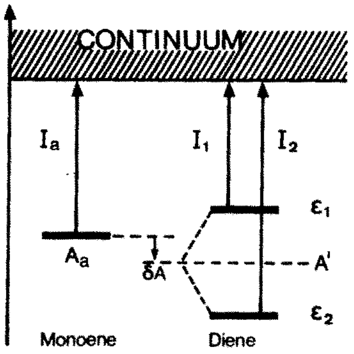


Figure 1: Orbital diagram.

B) an interaction term $B = \langle \pi_1 | H | \pi_2 \rangle$ which yields a split $\Delta = 2B$ between the orbitals $\pi_+$ and $\pi_-$. If B stands for an hyperconjugative interaction, which demands that $\pi_+$ lies above $\pi_-$(3), then B must be defined as a positive quantity:

$$B = \frac{\Delta}{2} = \frac{\varepsilon_1 - \varepsilon_2}{2} = \frac{I_2 - I_1}{2}$$

Depending on whether one uses the adiabatic or the vertical ionization potentials, one obtains:

Adiabatic: $\delta A = 8.9 - \frac{8.8 + 9.7}{2} = -0.35$ eV

$B = \frac{9.7 - 8.8}{2} = 0.45$ eV

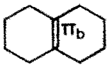
Vertical: $\delta A = 9{,}12 - \frac{8.80 + 9.80}{2} = -0.18$ eV

$B = \frac{9.80 - 8.80}{2} = 0.50$ eV

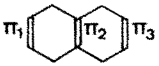
(Note that the precision with which the adiabatic ionization-potentials can be read off the spectra is less than for the vertical ones).

We wish to show that the analysis of the PE-spectrum of 1,4,5,8-tetrahydronaphthalene (VI) yields parameters which are in excellent agreement with those obtained from the PE-spectrum of III.

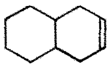
IV



V



VI



VII

The three lowest **ionization-potentials** of VI, which are ascribed to $\pi$-**ionization**, are (c.f. figure 2):

|  | $I_1$ | $I_2$ | $I_3$ |
|---|---|---|---|
| Adiabatic: | 8.2 | 9.0 | 9.5 |
| Vertical: | 8.29 | 9.05 | 9.59 |

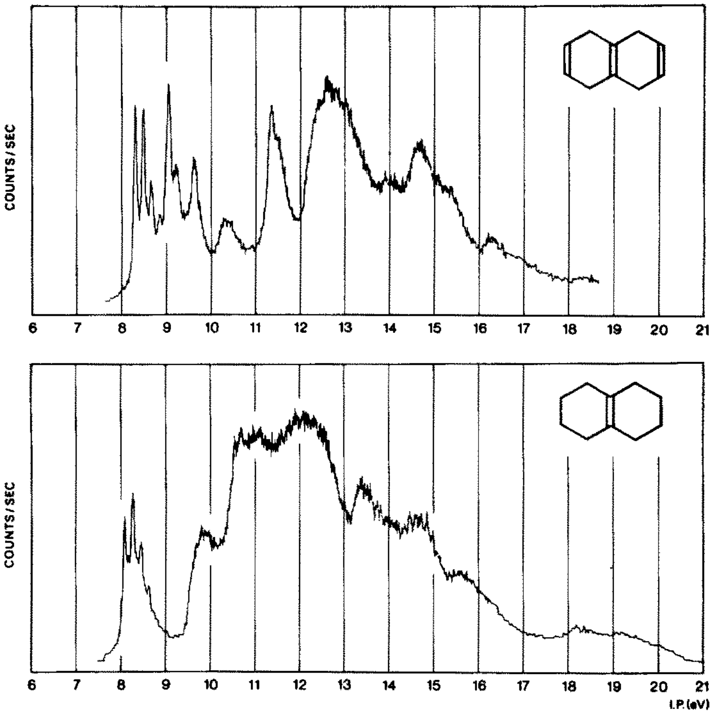


Figure 2: Photoelectron spectra of tetrahydronaphthalene (VI) and of octahydronaphthalene (V). (The spectra were recorded on a modified Perkin-Elmer photoelectron spectrometer of the type described by Turner (4): $\pi/\sqrt{2}$ - electrostatic energy analyser; excitation by photons from the 584 Å He resonance line (21.21 eV).

We assume a model for which we postulate that the individual $\pi$-orbital energies are $A'_a = \langle\pi_1|H|\pi_1\rangle = \langle\pi_3|H|\pi_3\rangle$, $A'_b = \langle\pi_2|H|\pi_2\rangle$ and that there shall be an interaction $B = \langle\pi_1|H|\pi_2\rangle = \langle\pi_2|H|\pi_3\rangle$ only between $\pi$-bonds in the same ring i.e. $\langle\pi_1|H|\pi_3\rangle = 0$. Thus the orbital energies $\varepsilon_1 = -I_1$, $\varepsilon_2 = -I_2$, $\varepsilon_3 = -I_3$ are obtained by solving the secular determinant.

$$\begin{Vmatrix} A'_a - \varepsilon & B & \\ B & A'_b - \varepsilon & B \\ & B & A'_a - \varepsilon \end{Vmatrix} = 0$$

A little algebra will show that

$A'_a = -I_2$; $A'_b = I_2 - I_1 - I_3$; $B = \sqrt{(I_1-I_2)(I_2-I_3)/2}$

This yields:

| | $A'_a$ | $A'_b$ | B |
|---|---|---|---|
| Adiabatic: | -9.0 | -8.7 | 0.45 |
| Vertical: | -9,05 | -8.83 | 0.453 |

As $A'_b = A_b + 2\delta A$, where $A_b$ is the π-orbital energy observed for the monoene V (c.f. figure 2) and where the perturbation $2\delta A$ is that due to the two π-bonds $\pi_{a1}$ and $\pi_{a2}$ in VI, we find that $\delta A = (8.1-8.7)/2 = -0.3$ eV (adiabatic) or $\delta A = (8.27-8.83)/2 = -0.28$ eV(vertical). Hence, both B and δA are identical (inside the limits of error of the experiment) with the values obtained from the PE-spectra of III. If a correction of $\delta A = -0.3$ eV (adiabatic) or $\delta A = -0.28$ eV vertical is applied to $A'_a$, a value of I = 8.7 (adiabatic) or I = 8.77 (vertical) is predicted for the π-ionization of the monoene VII. These values are slightly smaller than those observed for III, as one would expect, because of the increased inductive effect of the larger σ-frame of VII on the π-bond.

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