

# Equivalence of the Energy Gaps $\Delta I(1,2)$ and $\Delta E(1,2)$ between Corresponding Bands in the Photoelectron ( $I$ ) and Electronic Absorption ( $E$ ) Spectra of Spiro[4.4]nonatetraene. An Amusing Consequence of Spiroconjugation

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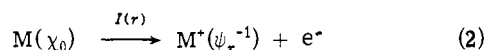
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**Abstract:** Correlation of the photoelectron (PE) spectra of spiro[4.4]nonatetraene (**1**), spiro[4.4]nona-1,3,7-triene (**2**), spiro[4.4]nona-1,3,6-triene (**3**), and spiro[4.4]nona-1,3-diene (**4**) yields the assignment of the first three bands at 7.99, 9.22, and 10.55 eV in the PE spectrum of **1** (symmetry  $D_{2d}$ ) to ionization processes in which the photoelectron vacates the molecular orbitals  $1a_2(\pi)$ ,  $1b_1(\pi)$ , and  $7e(\pi)$ , respectively. The difference  $\Delta I(1,2) = 1.23$  eV between the positions of the first two PE bands of **1** is equal, within the limits of error, to the difference  $\Delta E(1,2) \approx 1.2$  to 1.3 eV between the first two bands  $8e(\pi^*) \leftarrow 1a_2(\pi)$  and  $8e(\pi^*) \leftarrow 1b_1(\pi)$  in the electronic absorption spectrum of **1**. It is shown that this correspondence is the consequence of spiroconjugation between two identical alternant subsystems in a molecule of  $D_{2d}$  symmetry, e.g., in **1**.

Orbital diagrams such as the one shown in Figure 1 (see column a) seem to suggest that the difference  $\Delta I(1,2) = I(2) - I(1)$  between the second and first ionization potentials of a closed shell molecule M should match exactly the difference  $\Delta E(1,2) = E(2,-1) - E(1,-1)$  between the excitation energies corresponding to the second and first bands in the electronic spectrum of M. More generally (see column b of Figure 1), the difference

$$\Delta I(i, j) = I(j) - I(i) \quad (1)$$

between the (vertical) ionization potentials  $I(r)$ , which according to



correspond to the ejection of an electron from one or the other of two nondegenerate orbitals  $\psi_r$  ( $r = i$  or  $j$ ), might naively be expected to equal

$$\Delta E(i, j) = E(j, k) - E(i, k) \quad (3)$$

where  $E(r, k)$  ( $r = i$  or  $j$ ) stands for the electronic excitation energy

$$E(r, k) = E(\chi_r^k) - E(\chi_0) \quad (4)$$

of the neutral, closed shell molecule M. (In (2) and (4),  $\chi_0 \approx (\psi_1)^2 \dots (\psi_r)^2 \dots (\psi_n)^2$  is the ground state configuration of M and  $\chi_r^k \approx (\psi_1)^2 \dots (\psi_r)^1 \dots (\psi_n)^2 (\psi_k)^1$  a singly excited configuration obtained by promoting an electron from  $\psi_r$  to  $\psi_k$ .) However, from the well-known matrix elements of the Hamiltonian for the ground and singly excited states of a closed shell molecule M,<sup>1</sup> it is immediately obvious that the expected equality

$$\Delta E(i, j) = \Delta I(i, j) \quad (5)$$

will generally *not* be true. If

$$\chi_0 = |\psi_1 \bar{\psi}_1 \dots \psi_r \bar{\psi}_r \dots \psi_n \bar{\psi}_n| \quad (6)$$

is the SCF single Slater-determinant wave function of the ground state and

$${}^1\chi_r^k = \frac{1}{\sqrt{2}} \{ |\psi_1 \bar{\psi}_1 \dots \psi_r \bar{\psi}_k \dots \psi_n \bar{\psi}_n| + |\psi_1 \bar{\psi}_1 \dots \psi_k \bar{\psi}_r \dots \psi_n \bar{\psi}_n| \} \quad (7)$$

$${}^3\chi_r^k = \frac{1}{\sqrt{2}} \{ |\psi_1 \bar{\psi}_1 \dots \psi_r \bar{\psi}_k \dots \psi_n \bar{\psi}_n| - |\psi_1 \bar{\psi}_1 \dots \psi_k \bar{\psi}_r \dots \psi_n \bar{\psi}_n| \}$$

singly excited singlet and triplet configurations of M, we have

$${}^1E(r, k) = E({}^1\chi_r^k) - E(\chi_0) = \epsilon(\psi_k) - \epsilon(\psi_r) - J_{rk} + 2K_{rk} \quad (8)$$

$${}^3E(r, k) = E({}^3\chi_r^k) - E(\chi_0) = \epsilon(\psi_k) - \epsilon(\psi_r) - J_{rk}$$

where  $\epsilon(\psi_r)$  stands for the orbital energy of  $\psi_r$  and where  $J_{rk}$  (the Coulomb integral) and  $K_{rk}$  (the exchange integral) have their usual meaning, *i.e.*

$$J_{rk} = \left\langle \psi_r(1)\psi_k(2) \left| \frac{e^2}{r_{12}} \right| \psi_r(1)\psi_k(2) \right\rangle \equiv [rr|kk] \quad (9)$$

$$K_{rk} = \left\langle \psi_r(1)\psi_k(2) \left| \frac{e^2}{r_{12}} \right| \psi_k(1)\psi_r(2) \right\rangle \equiv [rk|kr]$$

Assuming the validity of Koopmans' theorem, *i.e.*<sup>2</sup>

$$I(r) = -\epsilon(\psi_r) \quad (10)$$

it follows from (3), (4), and (8) that

$$\Delta^1 E(i, j) = \Delta I(i, j) + (J_{ik} - J_{jk}) + 2(K_{jk} - K_{ik}) \quad (11)$$

$$\Delta^3 E(i, j) = \Delta I(i, j) + (J_{ik} - J_{jk}) \quad (12)$$

As can be seen from (11) the relationship 5 applied to singlet-singlet transitions will be true only if  $(J_{ik} - J_{jk}) + 2(K_{jk} - K_{ik}) = 0$ , which is generally not the case.<sup>3</sup> Indeed, the sign and the size of  $\Delta^1 E(i, j) - \Delta I(i, j)$  depends critically on the shape of the orbitals  $\psi_i$ ,  $\psi_j$ , and  $\psi_k$ . Haselbach and his coworkers<sup>3,4</sup> have given rules for the qualitative prediction of this difference, rules which can be applied, e.g., for the assessment of "through-space" and "through-bond" interactions<sup>5</sup> between localized (or semilocalized) orbitals.

It will be shown that in certain spiro-conjugated systems,<sup>6</sup> e.g., in spiro[4.4]nonatetraene (**1**),  $J_{ik} - J_{jk}$  and  $K_{jk} - K_{ik}$  should be zero in a first approximation, due to the prevailing symmetry and (almost) pairing properties of selected bonding ( $\psi_i$ ,  $\psi_j$ ) and virtual ( $\psi_k$ ) orbitals. Thus this class of compounds will yield examples where the naive ex-

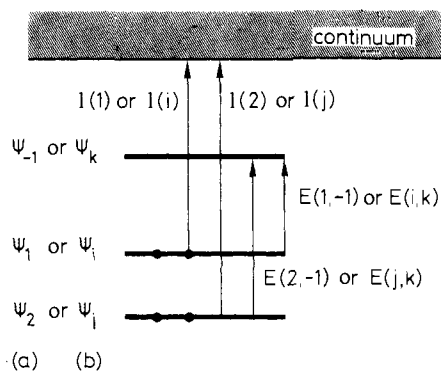
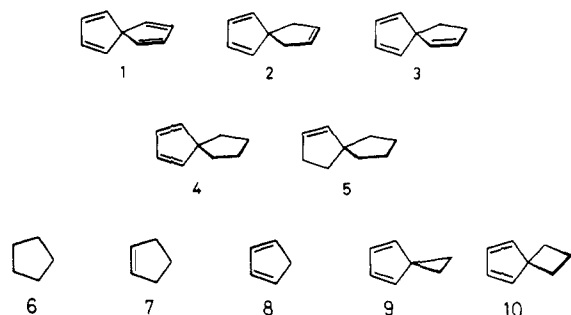


Figure 1. Level scheme for ionization and electronic transitions in the framework of an independent electron treatment.

pectation expressed by (5) is exceptionally fulfilled.

### I. The Photoelectron Spectrum of Spiro[4.4]nonatetraene (1)<sup>7</sup>

Figure 2 shows the photoelectron spectra of **1** and its di- and tetrahydro derivatives **2**, **3**, and **4**. The corresponding



ionization potentials of **1**, and those of the reference compounds **2** (spiro[4.4]nona-1,3,7-triene),<sup>7,8</sup> **3** (spiro[4.4]nona-1,3,6-triene), **4** (spiro[4.4]nona-1,3-diene),<sup>7,9</sup> **5** (spiro[4.4]non-1-ene),<sup>10</sup> **6** (cyclopentane), **7** (cyclopentene),<sup>11</sup> **8** (cyclopentadiene),<sup>11b,12</sup> **9** (spiro[4.3]hepta-1,3-diene = "homofulvene"),<sup>9,13</sup> and **10** (spiro[4.3]octa-1,3-diene)<sup>10</sup> are given in Table I. These potentials refer to the

Table I. Photoelectron Spectra<sup>a</sup>

Compd	π band			σ onset
	1st	2nd	3rd	
<b>1</b>	7.99; 8.17; 8.32	9.22	10.55	11.7 <sup>b</sup>
<b>2</b>	8.25; 8.42 <sup>c</sup>	9.03; 9.20; 9.37	10.36	11.4
<b>3</b>	8.27; 8.44	9.25; 9.45	10.50	11.5
<b>4</b>	8.10; 8.38	10.30		11.0
<b>5</b>	8.86 <sup>d</sup>			10.65 <sup>d</sup>
<b>6</b>				10.5
<b>7</b>	9.20			10.9
<b>8</b>	8.60	10.75		11.2
<b>9</b>	8.15	9.45	12.7 <sup>f</sup>	<sup>e</sup>
<b>10</b>	8.38 <sup>d</sup>	10.12 <sup>d</sup>		10.8 <sup>d</sup>

<sup>a</sup> All ionization potentials are given in eV. Italic values are the most intense component(s) of the band. <sup>b</sup> Band correlated with orbital 6e(σ); see text. <sup>c</sup> Both components of same intensity. <sup>d</sup> Values taken from ref. 10. <sup>e</sup> Band at 10.90 eV correlated with Walsh-orbital 12a; (σ); band at 11.90 eV correlated with orbital 7b(σ). <sup>f</sup> Corresponding orbital mainly of Walsh-type, centered on cyclopropane moiety.

position of the corresponding band maximum or to the highest intensity fine-structure component and are thus close to the vertical ionization potential  $I_{v,j}$ . All spectra have been recorded on a modified PS-15 spectrometer (Perkin-Elmer Ltd., Beaconsfield, England).

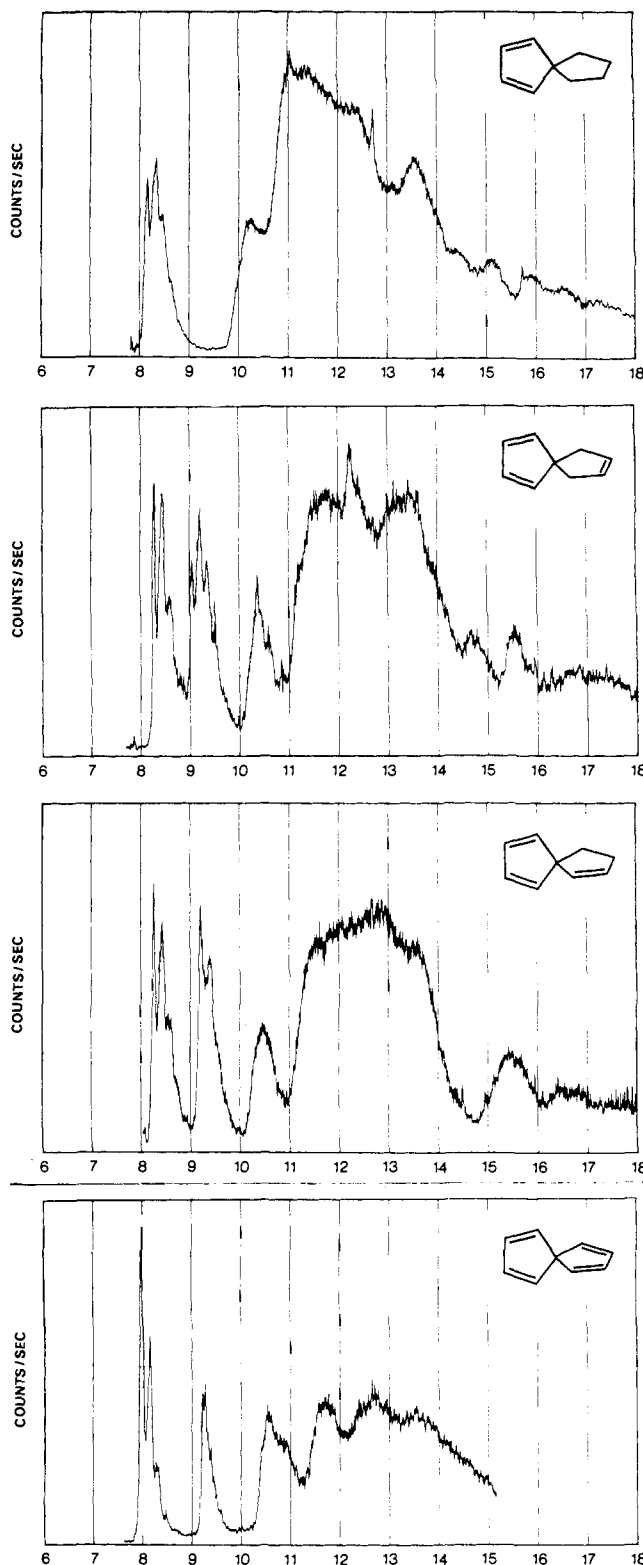


Figure 2. Photoelectron spectra.

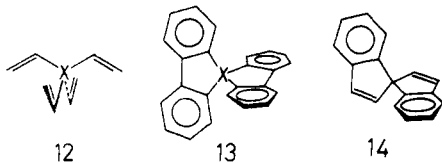
It is known<sup>14</sup> that **1** rearranges to indene **11** by a unimolecular process at 65° with  $t_{1/2} = 65$  min, and also on irradiation, direct (Pyrex filter) or sensitized (thioxanthone). Therefore one might have expected that the reaction



occurs also under the conditions prevailing in the inlet system and/or the target chamber of the photoelectron spec-

trometer. The photoelectron spectrum of **11** has been described by Eland and Danby.<sup>15</sup> Our own spectrum of **11** confirms their data within +0.02 eV, *i.e.*, 8.12, 8.95, and 10.30 eV for the first three  $\pi$  bands. These fine-structured bands are intense and sharp, the 0  $\leftarrow$  0 vibrational component being the most prominent. As can be seen from Figure 2 there is no indication of these bands in the photoelectron spectrum of **1**. Recordings taken at different times and from two independently prepared samples of **1** yield exactly the same spectrum, *i.e.*, the one shown in Figure 2.

The photoelectron spectroscopic evidence for spiroconjugation has been first described by Schweig and his coworkers. In a series of papers they investigated the photoelectron



spectra of tetravinylmethane (**12**, X  $\equiv$  C),<sup>16</sup> tetravinylsilane (**12**, X  $\equiv$  Si),<sup>17</sup> 9,9'-spirobifluorene (**13**, X  $\equiv$  C), 9,9'-spirobi(9-silafluorene) (**13**, X  $\equiv$  Si),<sup>18</sup> and 1,1'-spirobiindene (**14**).<sup>19</sup>

## II. Simple Molecular Orbital Model for Spiro[4.4]nonatetraene (1)

As a basis for the discussion of the photoelectron and electronic spectra of **1** we construct a simple MO model for **1** following the rules given by Simmons and Fukunaga<sup>6a</sup> and by Hoffmann, Imamura, and Zeiss.<sup>6b</sup>

The 62 electrons of **1** (symmetry  $D_{2d}$ ) occupy the following set of bonding molecular orbitals

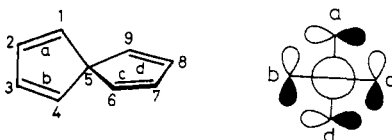
$$8 \times a_1 + 1 \times a_2 + 1 \times b_1 + 7 \times b_2 + 7 \times e \quad (13)$$

The three highest occupied orbitals  $1a_2(\pi)$ ,  $1b_1(\pi)$ , and  $7e(\pi)$  of local  $\pi$  symmetry are best visualized as linear combinations of either the  $1a_2(\pi)$  or the  $2b_1(\pi)$  orbitals of the two spiro-connected cyclopentadiene moieties of individual  $C_2$  symmetry. To avoid confusion of the orbital labels we have marked the orbitals of **8** ( $C_2$ ) with a dot, *e.g.*,  $a_2$  belongs to the irreducible representation  $A_2$  of  $C_{2v}$  and  $a_2$  to the representation  $A_2$  of  $D_{2d}$ . Note that  $2b_1(\pi)$  is a "true"  $\pi$  orbital of **8** while  $1b_1(\pi)$  is best described as a pseudo- $\pi$  orbital of the bridging methylene group.

Because of the high symmetry of **1** a ZDO linear combination of bond orbitals will be sufficient for our purposes. The numbering and the relative phases of the basis  $\pi$  orbitals

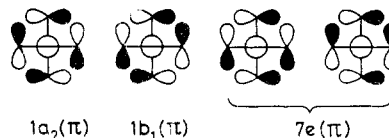
$$\pi_n = \frac{1}{\sqrt{2}}(\phi_\mu + \phi_\nu) \quad (14)$$

(*e.g.*,  $n = a$ ,  $\mu = 1$ ,  $\nu = 2$ ) and thus of the atomic 2p orbitals  $\phi_\mu$  are shown in the following diagram and Newman projection:



The four highest occupied LCBO molecular orbitals (in descending order) are

$$\begin{aligned} 1a_2(\pi) &= \frac{1}{2}(\pi_a - \pi_b - \pi_c + \pi_d) \\ 1b_1(\pi) &= \frac{1}{2}(\pi_a - \pi_b + \pi_c - \pi_d) \\ 7e(\pi) &\begin{cases} = \frac{1}{2}(\pi_a + \pi_b + \pi_c + \pi_d) \\ = \frac{1}{2}(\pi_a + \pi_b - \pi_c - \pi_d) \end{cases} \end{aligned} \quad (15)$$



If the basis orbitals  $\pi_n$  are assigned an orbital energy  $\langle \pi_n | \mathcal{H} | \pi_n \rangle = A_\pi$  and if the interaction matrix elements (resonance integrals) are  $\langle \pi_a | \mathcal{H} | \pi_b \rangle = \langle \pi_c | \mathcal{H} | \pi_d \rangle = B$ ,  $\langle \pi_a | \mathcal{H} | \pi_c \rangle = -\langle \pi_a | \mathcal{H} | \pi_d \rangle = -\langle \pi_b | \mathcal{H} | \pi_c \rangle = \langle \pi_b | \mathcal{H} | \pi_d \rangle = b$ , then the energies of the LCBO orbitals in eq 15 are

$$\begin{aligned} \epsilon(1a_2(\pi)) &= A_\pi - B - 2b \\ \epsilon(1b_1(\pi)) &= A_\pi - B + 2b \\ \epsilon(7e(\pi)) &= A_\pi + B \end{aligned} \quad (16)$$

The lowest unoccupied (antibonding) molecular orbitals have to be written in terms of the antibonding basis orbitals  $\pi_n^*$  of energy  $A_{\pi^*}$ . They form the degenerate set

$$8e(\pi^*) \begin{cases} = \frac{1}{2}(\pi_a^* + \pi_b^* + \pi_c^* + \pi_d^*) \\ = \frac{1}{2}(\pi_a^* + \pi_b^* - \pi_c^* - \pi_d^*) \end{cases} \quad (17)$$

Had we used the traditional conventions of HMO theory [*i.e.*, all Coulomb integrals equal  $\alpha$ ; resonance integrals equal  $\beta$  if  $\mu, \nu = 1, 2; 3, 4; 6, 7; 8, 9$ ; if  $\mu, \nu = 2, 3; 7, 8$  use  $n\beta$  and for the homoconjugative interactions,  $m\beta$  if  $\mu, \nu = 1, 6; 4, 9$ ; and  $-m\beta$  if  $\mu, \nu = 1, 9; 4, 6$ ; note that  $m < n < 1$ ] then the orbital energies associated with the highest occupied bonding orbitals would be

$$\begin{aligned} \epsilon(1a_2(\pi)) &= \alpha - (2m + n - ((2m - n)^2 + 4)^{1/2})\beta/2 \\ \epsilon(1b_1(\pi)) &= \alpha + (2m - n + ((2m + n)^2 + 4)^{1/2})\beta/2 \\ \epsilon(7e(\pi)) &= \alpha + (n + (n^2 + 4)^{1/2})\beta/2 \end{aligned} \quad (18)$$

## III. Interpretation of the Photoelectron Spectra of 1, 2, 3, and 4

The following discussion makes use of Koopmans' theorem (eq 10) with  $I(r)$ , the (almost) vertical ionization potentials, taken from Table I.

$\sigma$  Bands. As can be deduced from the photoelectron spectra of **6**, **7**, and **8**, the onset of the  $\sigma$  bands moves to higher ionization potentials with increasing unsaturation (**6**, 10.5 eV; **7**, 10.9 eV; **8**, 11.2 eV). This is a quite general phenomenon which has already been observed previously for a large variety of hydrocarbons.<sup>20</sup> In a similar fashion we observed  $I(\sigma \text{ onset})$  11.0 eV for **4**, 11.5 eV for **3**, 11.4 eV for **2**, and 11.7 eV for **1**. The latter band is probably due to the ejection of an electron from orbital  $6e(\sigma)$  as can be shown by the following argument. In the photoelectron spectra of fulvene<sup>21</sup> and of homofulvene **9**<sup>13b</sup> one observes bands at 12.1 and 11.9 eV, respectively, which are due to the ejection of the photoelectron from the orbital  $7b_2(\sigma)$ , localized in the CC- $\sigma$  bonds 1,2 and 3,4. As two such orbitals contained in the two cyclopentadiene moieties of **1** will have zero interaction for symmetry reasons (*cf.* the following diagram)



their linear combination yields the degenerate pair  $6e(\sigma)$ , the orbital energy of which should be roughly the same as that observed in fulvene and **9**, *i.e.*, approximately -12 eV. The observed value is -11.7 eV.

**$\pi$  Bands.** Once the onset of the  $\sigma$ -band system has been established, all bands at lower ionization potentials must necessarily be bands due to the ejection of an electron from orbitals which are dominantly  $\pi$  in character.

**Spiro[4.4]nona-1,3-diene (4).** The PE spectrum of this compound has been discussed previously by Gleiter and his coworkers.<sup>10</sup> The two components at 8.10 and 8.38 eV of the first band have roughly the same intensity. This yields  $\epsilon(3a_2(\pi)) \approx -8.10$  to  $-8.38$  eV. The second band defines  $\epsilon(7b_1(\pi)) = -10.30$  eV. Compared to the orbital energies  $\epsilon(1a_2(\pi)) = -8.60$  eV and  $\epsilon(2b_1(\pi)) = -10.75$  eV of **8**, both orbitals of **4** are shifted by approximately 0.5 eV, due to the destabilizing influence of the alkyl moiety. The orbital split  $\epsilon(3a_2(\pi)) - \epsilon(7b_1(\pi)) = 2.10$  to  $1.92$  eV is in complete agreement with that observed for **8**, *i.e.*, 2.15 eV.<sup>11a,12</sup>

**Spiro[4.4]nona-1,3,7-triene (2).** As shown in the correlation diagram of Figure 3 the photoelectron spectrum of **2** is almost self-explanatory. We observe three  $\pi$  bands of which the first and third correspond to an ionization process, in which the electron vacates  $2a_2(\pi)$  or  $7b_1(\pi)$ , respectively. Both these orbitals are displaced in energy by 0.20 to 0.35 eV (first band) or 0.40 (third band) relative to the orbitals  $1a_2(\pi)$  and  $2b_1(\pi)$  of **8**, as expected in view of the substituting cyclopentene moiety present in **2**. For the split we observe  $\epsilon(2a_2(\pi)) - \epsilon(7b_1(\pi)) = 2.11$  to  $1.95$  eV, *i.e.*, the same value as in **4**.

The second band in the spectrum of **2** corresponds to ejection from orbital  $8b_2(\pi)$  which is centered almost exclusively on the  $\pi$  orbital in position 7,8. That  $\epsilon(8b_2(\pi))$  happens to be exactly equal to  $\epsilon(3b_1(\pi))$ , *i.e.*, the  $\pi$ -orbital energy of **7**, is presumably accidental; the small effects due to the cyclopentadiene ring, *i.e.*, destabilization caused by enlarging the  $\sigma$  frame and stabilization as a result of its unsaturation, cancel each other.

**Spiro[4.4]nona-1,3,6-triene (3).** From the data collected in Table I or viewed in Figure 2, it can be seen that there is little difference between the PE spectra of **2** and **3**. Hence the discussion and assignment given for **2** should apply to **3** with only slight modifications. This might seem surprising at first, because of the presence of spiroconjugation between  $\pi_c$  and the linear combination  $(\pi_a - \pi_b)/\sqrt{2}$  (both belonging to  $A''$  in  $C_s$ ) in **3** and its absence in **2**. However, as was shown previously in a similar case<sup>22</sup> this result can easily be explained by a second-order perturbation argument.

From the correlation diagram of Figure 3 and the arguments given in the previous paragraph we have to conclude that the semilocalized orbitals  $\pi_c$  and  $(\pi_a - \pi_b)/\sqrt{2}$  of **3** differ in energy by about 0.9 eV. In terms of the parameters used in (16) the interaction term between these two orbitals is  $\langle \pi_c | \mathcal{H} | (\pi_a - \pi_b)/\sqrt{2} \rangle = b\sqrt{2}$ . As we shall see, the analysis of the PE spectrum of **1** yields  $b = -0.3$  eV (see also ref 19). Accordingly,  $\epsilon(\pi_c)$  and  $\epsilon((\pi_a - \pi_b)/\sqrt{2})$  would suffer at best perturbations of the order of  $(-0.3\sqrt{2})^2/0.9 = 0.2$  eV. This is presumably an upper limit. The lack of fine structure of the second PE band in the spectrum of **3** (as compared to the corresponding band of **2**) indicates a certain lack of rigidity in the molecule. Relief of conformational strain between the two eclipsing methylene groups would lead to a decrease in size of  $b$  and thus of the perturbation derived above. In view of all the other effects neglected in our argument, such a small shift in orbital energy and thus in the observed band position would pass unnoticed.

**Spiro[4.4]nonatetraene (1).** As has been discussed in the previous section, only the semilocalized  $1a_2(\pi)$  orbitals of each ring can interact, yielding the orbitals  $1a_2(\pi)$  and  $1b_1(\pi)$ . It is obvious from the correlation diagram of Figure 3 that these have to be correlated with the first two bands at 7.99 and 9.22 eV. The two highest occupied orbitals lie

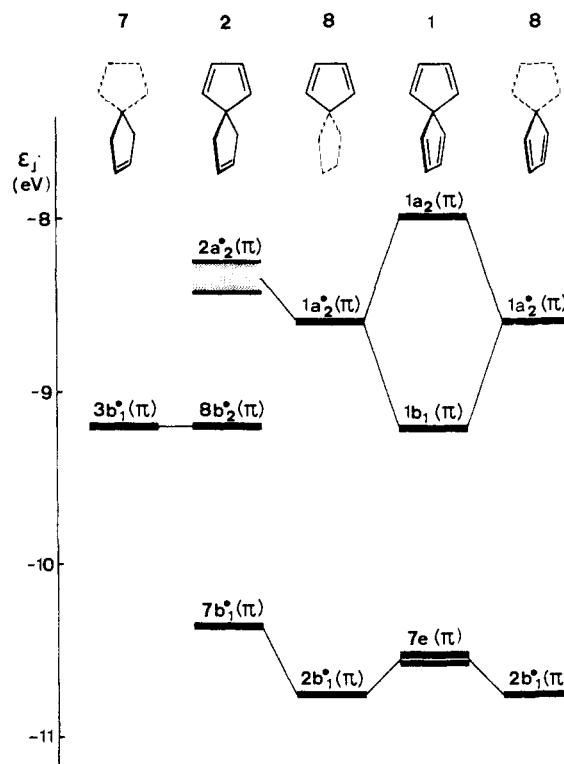


Figure 3. Orbital diagram.

symmetrically with respect to  $\epsilon(1a_2(\pi))$  of **8**, rather than to  $3a_2(\pi)$  of **4** or  $2a_2(\pi)$  of **2**. The reason is that in the latter two compounds these orbitals are destabilized by the alkyl moieties whereas in **1** the relative inductive influence of the two cyclopentadiene units on each other is about zero. This is not unexpected. When  $\pi$  systems are joined together to form larger ones (*e.g.*, two or three ethylene units to yield butadiene, hexatriene,<sup>12</sup> fulvene, or bismethylenecyclobutene<sup>21</sup> or two benzene rings to yield biphenyl,<sup>15,23</sup> the mean of the orbital energies of the resulting  $\pi$  orbitals is equal to the orbital energy of the parent orbitals within small limits of error. On the other hand, alkyl substitution will always lead to large destabilizations.<sup>12,24</sup>

The linear combinations of the semilocalized orbitals  $2b_1(\pi)$  of the two rings yield the degenerate pair  $7e(\pi)$ . Ejecting an electron from  $7e(\pi)$  should therefore induce a Jahn-Teller distortion of the radical cation **1**<sup>+</sup> in the  ${}^2E(\pi)$  state. Indeed the third band in the photoelectron spectrum shows the characteristic shape usually observed when an electron is ejected from a degenerate orbital of an unsaturated hydrocarbon, *e.g.*, 1,3,7-cyclononatriene,<sup>22</sup> barrelene,<sup>20c</sup> bullvalene,<sup>20b</sup> triquinacene,<sup>25</sup> or allene.<sup>26</sup>

Two orbital energy (ionization potential) differences will be of importance in the ensuing discussion: (a) the orbital energy split  $\Delta I(1,2) = \epsilon(1a_2(\pi)) - \epsilon(1b_1(\pi)) = 1.23$  eV, which measures the homoconjugative spirointeraction between the two semilocalized orbitals  $1a_2(\pi)$ , and (b) the orbital energy split  $\Delta I_D$  between the mean of  $\epsilon(1a_2(\pi))$  and  $\epsilon(1b_1(\pi))$  and the energy of the degenerate pair  $\epsilon(7e(\pi))$ , *i.e.*,  $\Delta I_D = \frac{1}{2}[\epsilon(1a_2(\pi)) + \epsilon(1b_1(\pi))] - \epsilon(7e(\pi)) = 1.95$  eV. It is a measure of the interaction responsible for the split in energy between the semilocalized basis orbitals  $1a_2(\pi)$  and  $2b_1(\pi)$  of each subsystem, neglecting spiroconjugation.

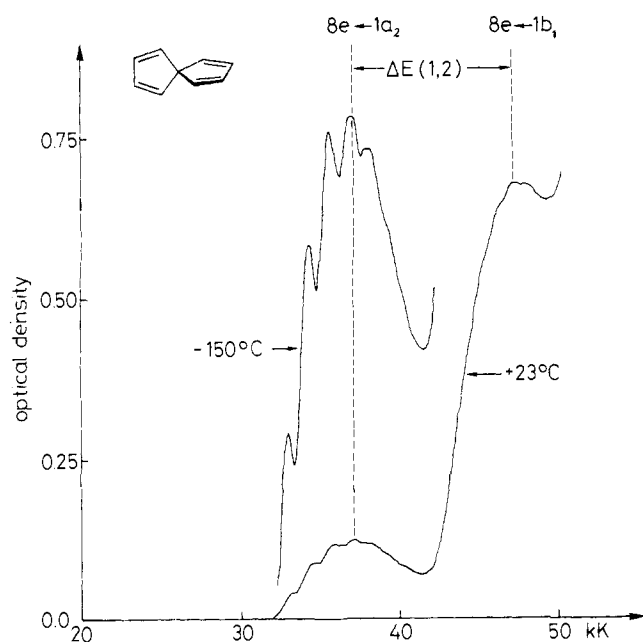
#### IV. Electronic Spectra of **1**, **2**, and **4**

The electronic spectrum of **1**<sup>7</sup> (see Table II and Figure 4) in the region  $\lambda > 1500$  Å consists of four bands at 60,000,

**Table II.** Electronic Spectrum of Spiro[4.4]nonatetraene (1)<sup>a</sup>

	1st band	2nd band	3rd band
Gas Phase			
$\bar{\nu}_{\max}$ , cm <sup>-1</sup>	36,500 <sup>b</sup>	48,780	54,600
$\bar{\nu}_{\text{onset}}$ , cm <sup>-1</sup>	34,000	43,500	53,000 <sup>c</sup>
$\Delta E_{\max}$ , eV	4.53	6.05	6.78
$\Delta E_{\text{onset}}$ , eV	4.20	5.39	6.6 <sup>c</sup>
$\tilde{\omega}$ , cm <sup>-1</sup>	1150		400
<i>n</i> -Hexane			
$\bar{\nu}_{\max}$ , cm <sup>-1</sup>	37,200 <sup>d</sup>	47,200	
$\bar{\nu}_{\text{onset}}$ , cm <sup>-1</sup>	33,100	43,100	
$\Delta E_{\max}$ , eV	4.61	5.85	
$\Delta E_{\text{onset}}$ , eV	4.11	5.34	
$\tilde{\omega}$ , cm <sup>-1</sup>	1350	800	
Rigisolve (23°)			
$\bar{\nu}_{\max}$ , cm <sup>-1</sup>	37,200 <sup>d</sup>	47,300	
$\bar{\nu}_{\text{onset}}$ , cm <sup>-1</sup>	33,100	43,500	
$\Delta E_{\max}$ , eV	4.61	5.86	
$\Delta E_{\text{onset}}$ , eV	4.11	5.39	
$\tilde{\omega}$ , cm <sup>-1</sup>	1350	800	
Rigisolve (-150°)			
$\bar{\nu}_{\max}$ , cm <sup>-1</sup>	37,200		
$\bar{\nu}_{\text{onset}}$ , cm <sup>-1</sup>	33,100		
$\Delta E_{\max}$ , eV	4.61		
$\Delta E_{\text{onset}}$ , eV	4.09		
$\tilde{\omega}$ , cm <sup>-1</sup>	1300		

<sup>a</sup> Band positions  $\bar{\nu}$  have been rounded to the nearest 100 cm<sup>-1</sup>, transition energies  $\Delta E$  to the nearest 0.01 eV, and vibrational fine-structure spacings  $\tilde{\omega}$  to the nearest 50 cm<sup>-1</sup>. Numbers in italics refer to the 0 ← 0 transition. <sup>b</sup> Third vibrational fine-structure maximum in the band (2 ← 0, ?). <sup>c</sup> Uncertain by ~500 cm<sup>-1</sup> or ~0.1 eV. <sup>d</sup> Fourth vibrational fine-structure maximum in the band (3 ← 0, ?).



**Figure 4.** Electronic absorption spectrum of spiro[4.4]nonatetraene: solvent, rigisolve.

55,000, 48,000, and 37,000 cm<sup>-1</sup> (*i.e.*,  $E(r,k) = 7.4, 6.6, 5.3,$  and  $4.1$  eV) with an intensity ratio of approximately 25:50:5:1. We assign the three bands at longest wavelength to the following transitions (in orbital language).

1st band	8e( $\pi^*$ ) ← 1a <sub>2</sub> ( $\pi$ ); state symm: <sup>1</sup> E, <i>xy</i>
2nd band	8e( $\pi^*$ ) ← 1b <sub>1</sub> ( $\pi$ ); state symm: <sup>1</sup> E, <i>xy</i>
3rd band	8e( $\pi^*$ ) ← 7e( $\pi$ ); state symm: <sup>1</sup> B <sub>2</sub> , <i>z</i>

(19)

As expected for a rigid molecule, all three bands show vibrational fine structure which is especially prominent in the gas-phase spectrum of **1** (McPherson double-beam spectrometer, Model 225) and in the spectrum recorded at -150° in rigisolve (*i.e.*, 2,2-dimethylbutane-*n*-pentane, ratio 8:3, Cary Model 14 spectrometer). The fine structure of the second and third bands is more diffuse and does not sharpen up at low temperature.

Relative to the gas phase there is a slight change in the Franck-Condon factors when the spectrum is recorded in solution. In the gas phase the 2 ← 0 component of the progression is the most intense whereas the 3 ← 0 is the most prominent in the solution spectrum. Also a solvent shift of ~5 nm is observed.

The most notable feature is that the difference  $\Delta E(1,2)$  between the band positions for the first and second band (1.19 eV in the gas phase, 1.23 to 1.28 eV in solution) is the same, within the limits of error, as the split  $\Delta I(1,2) = 1.23$  eV observed in the photoelectron spectrum of **1**.

The spectra of **2** and **4** (Figure 5) show a single band at 39,500 cm<sup>-1</sup> (4.90 eV) in the region  $\lambda > 2000$  Å which is devoid of vibrational fine structure, presumably because of the greater flexibility of the molecular framework. The position of this band is thus intermediate of the positions of the first two bands in the electronic spectrum of **1**, lying 0.3 eV below their mean (5.2 eV, from the positions of the maxima).

## V. Discussion

We discuss first the split  $\Delta I_D = \frac{1}{2}[\epsilon(1a_2(\pi)) + \epsilon(1b_1(\pi))] - \epsilon(7e(\pi))$  of **1** (*i.e.*, mean of first and second band position *vs.* third band position). It corresponds to the difference between the orbital energies of the two  $\pi$  orbitals of the *s-cis*-butadiene moieties of **2** (2.1 to 1.9<sub>5</sub> eV), **3** (2.2 eV), **4** (2.2 to 2.0<sub>5</sub> eV), and **8** (2.15 eV). In **9** (1.30 eV) and **10** (1.74 eV) the gap is reduced, as a consequence of the interaction of the b<sub>1</sub>( $\pi$ ) orbital with the Walsh orbitals of the cyclopropane or cyclobutane ring, this interaction being larger in the former case. The observed value  $\Delta I_D = 1.95$  eV for **1** is in good agreement with the above results for other systems, especially if one considers that an LCAO model (see (18)) predicts a small decrease relative to the split characteristic for each of the individual spiro-connected moieties. From (16) we deduce that  $\Delta I_D = -2B$ , which yields  $B = -1.0$  eV and in a first approximation according to (14)  $n\beta = -\Delta I_D = -1.95$  eV. However, from (18) we deduce that  $\Delta I_D \approx -(n - m^2/(n^2 + 4))^{1/2}\beta$  which implies that the above calibration of the LCAO model is true only if  $m \ll n$ .

$\Delta I(1,2) = \epsilon(1a_2(\pi)) - \epsilon(1b_1(\pi)) = 1.23$  eV measures the spiro interaction of the a<sub>2</sub>( $\pi$ ) orbital in **1**. According to the LCBO model (eq 16) we have  $\Delta I(1,2) = -4b$  or  $b = -0.31$  eV. With reference to (16) this yields  $m\beta = -0.62$  eV. Again the LCAO model underlying the formula in (18) leads to a slightly more complex relationship, namely  $\Delta I(1,2) \approx -2m(1 + n/(n^2 + 4))^{1/2}\beta$ .

If one wants to adjust the orbital energies (eq 18) to the observed band positions of the  $\pi$  bands of **1**, the following set of parameters is obtained:  $\alpha = -6.42$  eV,  $\beta = -2.93$  eV,  $n\beta = -2.05$  eV ( $n = 0.70$ , assumed),  $m\beta = -0.46$  eV ( $m = 0.16$ ). With these we calculate from (18):  $\epsilon(1a_2(\pi)) = -7.91$  eV,  $\epsilon(1b_1(\pi)) = -9.15$  eV, and  $\epsilon(7e(\pi)) = -10.55$  eV in agreement with the observed band positions. Note that  $m\beta$  is only  $\frac{3}{4}$  of the value found by assuming nonpolarizable, fixed  $\pi$ -basis orbitals  $\pi_x$  (see (16)).

A comparison of the electronic and photoelectron spectra of **1** is of particular interest. As shown above we find that the difference between the positions of the first and second

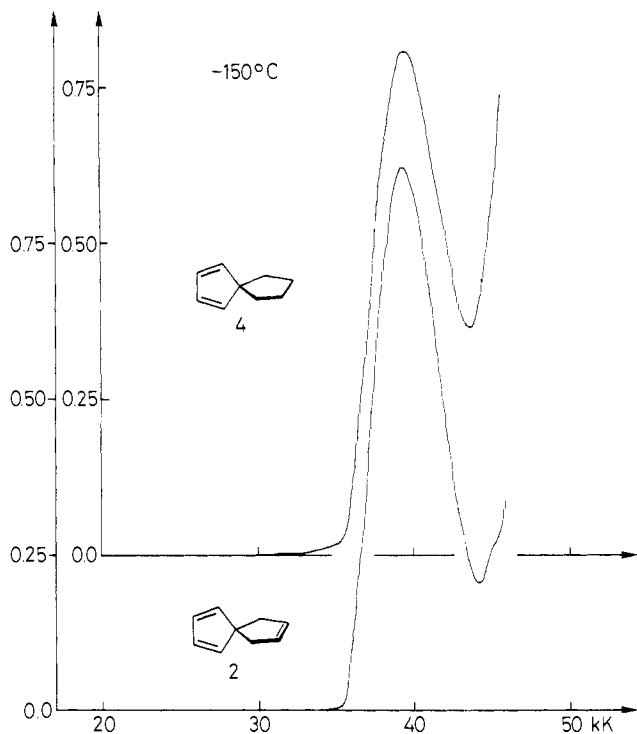
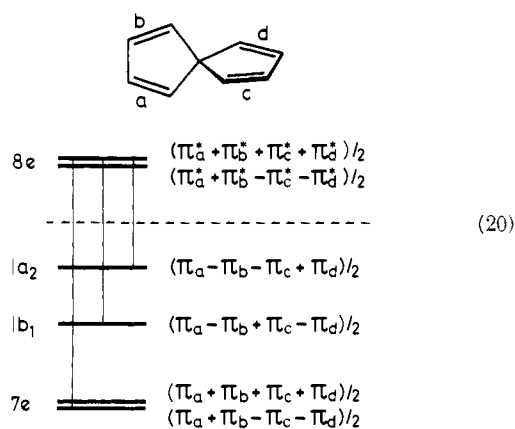


Figure 5. Electronic absorption spectra of spiro[4.4]nona-1,3,7-triene (2) and of spiro[4.4]nona-1,3-diene (4): solvent, rigisolve.

bands in the electronic spectrum is  $\Delta E(1,2) = 1.19$  eV in the gas phase and 1.23 to 1.28 eV in solution, *i.e.*, the same within experimental error as the gap  $\Delta I(1,2) = 1.2$  eV between the orbital energies  $\epsilon(a_2(\pi))$  and  $\epsilon(b_1(\pi))$  derived from the photoelectron spectrum. We shall now show why the naive expectation in eq 5 is fulfilled in this particular case.<sup>27</sup>

With reference to Figure 1 the relevant orbitals are those given in (15) and (17), *i.e.*,  $\psi_1 \equiv 1a_2(\pi)$ ,  $\psi_2 \equiv 1b_1(\pi)$ , and  $\psi_{-1} \equiv 8e(\pi^*)$ , as shown in the following diagram:



For simplicity we shall now drop the designations  $\pi$  and  $\pi^*$ . The ground configuration (eq 6) of **1** is

$$\chi_0 = | \dots 1b_1 \overline{1b_1} 1a_2 \overline{1a_2} | \quad (21)$$

The two singly excited configurations which correspond to the promotions  $8e \leftarrow 1a_2$  and  $8e \leftarrow 1b_1$  (see (20)) are both degenerate because of  $E \times A_2 = E \times B_1 = E$  under  $D_{2d}$ . From (7) one obtains

$${}^1\chi_{1,-1} = \frac{1}{\sqrt{2}} \{ | \dots 1b_1 \overline{1b_1} 1a_2 \overline{8e} | + | \dots 1b_1 \overline{1b_1} 8e \overline{1a_2} | \} \quad (22)$$

$${}^1\chi_{2,-1} = \frac{1}{\sqrt{2}} \{ | \dots 1b_1 \overline{8e} 1a_2 \overline{1a_2} | + | \dots 8e \overline{1b_1} 1a_2 \overline{1a_2} | \}$$

Relative to (14) the antibonding  $\pi_n^*$  orbitals are defined as

$$\pi_n^* = \frac{1}{\sqrt{2}} (\phi_\mu - \phi_\nu) \quad (23)$$

*i.e.*, in such a way that the spiro-connected 2p AO's  $\phi_\mu$  ( $\mu = 1, 4, 6$ , or  $9$ ) have the same sign in  $\pi_n^*$  as in  $\pi_n$ . The ZDO approximation underlying formulas 15 and 17 implies that for  $n \neq m$  one has  $\pi_n \pi_m = \pi_n \pi_m^* = \pi_n^* \pi_m^* = 0$  and  $\pi_n^2 = \pi_n^{*2}$ . The transition densities  $\pi_n \pi_n^*$  can be characterized in a first approximation by the corresponding local transition moments  $\vec{\mu}_{nn^*}$ , which have their negative ends (positive electron density) directed toward the spiro-connected centers 1, 4, 6 and 9.

To prove that (5) is true (in first order) for **1** we have to evaluate the Coulomb and exchange integrals 9 of expression 11, *i.e.*

$$\begin{aligned} J_{1,-1} &= [1a_2 1a_2 | 8e 8e] \\ J_{2,-1} &= [1b_1 1b_1 | 8e 8e] \\ K_{1,-1} &= [1a_2 8e | 8e 1a_2] \\ K_{2,-1} &= [1b_1 8e | 8e 1b_1] \end{aligned} \quad (24)$$

and to show that (11) covers to (5).

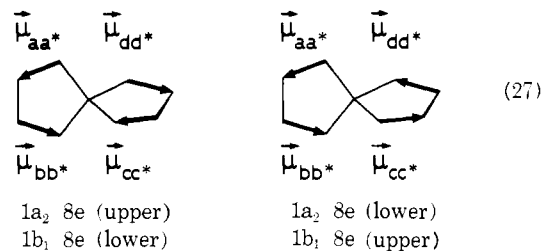
Because of the ZDO approximation introduced above one finds after inserting (15) and (17) into (24) that  $J_{1,-1}$  and  $J_{2,-1}$  yield

$$J_{1,-1} = \frac{1}{16} \sum_m \sum_n [\pi_n \pi_n | \pi_m^* \pi_m^*] = J_{2,-1} \quad (25)$$

leading to  $J_{1,-1} - J_{2,-1} = 0$ . In a similar fashion it is found that  $K_{1,-1}$  and  $K_{2,-1}$  are equal, *i.e.*

$$K_{2,-1} = \left\{ \begin{aligned} &\frac{1}{16} [\pi_a \pi_a^* - \pi_b \pi_b^* - \pi_c \pi_c^* + \\ &\quad \pi_d \pi_d^* | \pi_a \pi_a^* - \pi_b \pi_b^* - \pi_c \pi_c^* + \pi_d \pi_d^*] \\ &\frac{1}{16} [\pi_a \pi_a^* - \pi_b \pi_b^* + \pi_c \pi_c^* - \\ &\quad \pi_d \pi_d^* | \pi_a \pi_a^* - \pi_b \pi_b^* + \pi_c \pi_c^* - \pi_d \pi_d^*] \end{aligned} \right\} = K_{1,-1} \quad (26)$$

Note that the upper and lower exchange integrals, resulting from the corresponding components of  $8e$  shown in (17), have necessarily the same value, because the underlying pair of transition densities span the  $E$  representation of  $D_{2d}$ . This is obvious by inspection of the following diagrams, in which these transition densities are characterized by the ensemble of the local transition moments  $\vec{\mu}_{nn^*}$ :



Again one finds that  $K_{1,-1} - K_{2,-1} = 0$  and consequently that  $\Delta^1 E(1,2) = \Delta I(1,2)$  to first order.

To support this conclusion SCF calculations have been performed for **1** using the CNDO/2,<sup>28</sup> MINDO/2,<sup>29</sup> and

SPINDO<sup>30</sup> procedures and a standard  $D_{2d}$  geometry for **1**. The results agree with those derived above, as shown by the CNDO/2 and MINDO/2 values obtained for the Coulomb (eq 25) and exchange integrals (eq 26) (values in eV):

	$\Delta^1 E(1, 2) -$				
	$J_{1,-1}$	$J_{2,-1}$	$K_{2,-1}$	$K_{1,-1}$	$\Delta I(1, 2)$
CNDO/2	7.43	7.35	0.70	0.80	-0.12 (28)
MINDO/2	6.05	6.01	0.47	0.52	-0.05

Thus the difference  $\Delta^1 E(1,2) - \Delta I(1,2)$  is practically zero, within the limits of error of such semiempirical calculations.

As expected, a closer examination of the computed orbitals reveals that the three models differ significantly in many respects. This points out once more the danger of relying on a single procedure only, when interpreting photoelectron-spectroscopic data.<sup>31</sup>

Of course all three models agree in making  $1a_2(\pi)$  and  $1b_1(\pi)$  the two highest occupied molecular orbitals of **1**. For symmetry reasons these orbitals are strictly of local  $\pi$  character, *i.e.*, there is no contribution from  $\sigma$  orbitals. However, this is where the agreement ends! In contrast to SPINDO, both CNDO/2 and MINDO/2 yield as an artefact a high-lying  $\sigma$  orbital between the orbitals  $7e(\pi)$  and  $1b_1(\pi)$ , a result hardly compatible with the photoelectron-spectroscopic result (*cf.* Figure 2). In addition according to CNDO/2 and MINDO/2 the orbital  $7e(\pi)$  shows roughly the same degree of  $\sigma/\pi$  mixing as does the much lower lying orbital  $5e$ , so that it becomes almost impossible to assign more  $\pi$  character to one or the other of the two. On the other hand  $7e(\pi)$  appears almost pure  $\pi$  with very little  $\sigma$  contribution according to the SPINDO results. A much more serious discrepancy is that the lowest unoccupied orbital (LUMO) is  $8e(\pi^*)$  in the CNDO/2 and MINDO/2 model, as also assumed in our primitive treatment, but a  $\sigma$  orbital if the SPINDO calculations were to be believed. (This is the reason why this model has been excluded from the comparison given in (28).)

This lack of agreement on important points between such semiempirical calculations, even in a case where one might have expected that the orbital sequence is predetermined by symmetry, should serve as a warning when such models are used as a basis for the interpretation of photoelectron spectra. We believe that the correlation technique, *i.e.*, the empirical comparison of the photoelectron spectra of systematically varied and closely related systems (*e.g.*, **1**, **2**, etc.), yields much more reliable assignments.

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## References and Notes

- (1) C. C. J. Roothaan, *Rev. Mod. Phys.*, **2**, 69 (1951); J. A. Pople, *Proc. Phys. Soc., London, Sect. A*, **68**, 81 (1955); *cf.* J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen and Co. Ltd., London, 1963.
- (2) T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).
- (3) E. Haselbach and A. Schmelzer, *Helv. Chim. Acta*, **54**, 1575 (1971).
- (4) E. Haselbach and A. Schmelzer, *Helv. Chim. Acta*, **55**, 1745 (1972); E. Haselbach, Z. Lanyiova, and M. Rossi, *ibid.*, **56**, 2889 (1973); E. Haselbach, Z. Lanyiova, M. Rossi, and A. Schmelzer, *Chimia*, **28**, 19 (1974); E. Heilbronner, J. P. Maier, and E. Haselbach, "Physical Methods in Heterocyclic Chemistry," A. R. Katritzky, Ed., Academic Press, New York, N.Y., in press.
- (5) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968); R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).
- (6) (a) H. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); (b) R. Hoffmann, A. Imamura, and G. Zeiss, *ibid.*, **89**, 8215 (1967).
- (7) M. F. Semmelhack, J. S. Foos, and S. Katz, *J. Amer. Chem. Soc.*, **94**, 8637 (1972).
- (8) D. Schoenleber, *Chem. Ber.*, **102**, 1789 (1969).
- (9) C. F. Wilcox and R. R. Craig, *J. Amer. Chem. Soc.*, **83**, 3866 (1961).
- (10) P. Bischof, R. Gleiter, A. de Meijere, and L.-U. Myer, private communication.
- (11) (a) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970); (b) F. Brogli, E. Giovannini, E. Heilbronner, and R. Schurter, *Chem. Ber.*, **106**, 961 (1973).
- (12) M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, **56**, 1028 (1973).
- (13) (a) R. Ya. Levina, N. N. Mezentsoba, and O. Lebedev, *Zh. Obsch. Khim.*, **25**, 1097 (1955); B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 646 (1958); (b) R. Gleiter, E. Heilbronner, and A. de Meijere, *Helv. Chim. Acta*, **54**, 1029 (1971).
- (14) M. F. Semmelhack and J. S. Foos, manuscript submitted for publication.
- (15) J. H. D. Eland and C. J. Danby, *Z. Naturforsch. A*, **23**, 355 (1968).
- (16) A. Schweig, U. Weidner, J. G. Berger, and W. Grah, *Tetrahedron Lett.*, 557 (1973).
- (17) U. Weidner and A. Schweig, *Angew. Chem.*, **84**, 551 (1972).
- (18) A. Schweig, U. Weidner, D. Hellwinkel, and W. Krapp, *Angew. Chem.*, **85**, 360 (1973).
- (19) A. Schweig, U. Weidner, R. K. Hill, and D. A. Cullison, *J. Amer. Chem. Soc.*, **95**, 5426 (1973).
- (20) (a) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969); (b) P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung, and G. Schröder, *ibid.*, **53**, 1645 (1970); (c) E. Haselbach, E. Heilbronner, and G. Schröder, *ibid.*, **54**, 153 (1971); (d) C. Batich, P. Bischof, and E. Heilbronner, *J. Electron Spectrosc.*, **1**, 333 (1972/73).
- (21) E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung, and A. de Meijere, *Helv. Chim. Acta*, **54**, 783 (1971); F. Brogli, P. A. Clark, E. Heilbronner, and M. Neuenschwander, *Angew. Chem.*, **85**, 414 (1973).
- (22) P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1425 (1970).
- (23) J. P. Maier and D. W. Turner, *Discuss. Faraday Soc.*, **54**, 149 (1972).
- (24) M. Kiessinger, *Angew. Chem.*, **84**, 544 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 525 (1972); R. Sustmann and R. Schubert, *Tetrahedron Lett.*, 2739 (1972); P. A. Clark, *Theor. Chim. Acta*, **28**, 75 (1972), and references given therein.
- (25) J. C. Bünzli, D. C. Frost, and L. Weiler, *Tetrahedron Lett.*, 1159 (1973).
- (26) C. Baker and D. W. Baker, *Chem. Commun.*, 480 (1969); F. Brogli, J. K. Crandall, E. Heilbronner, E. Kloster-Jensen, and S. A. Sojka, *J. Electron Spectrosc.*, **2**, 455 (1973).
- (27) C. Batich, E. Heilbronner, and M. Semmelhack, *Helv. Chim. Acta*, **56**, 2110 (1973); E. Heilbronner, "The World of Quantum Chemistry," R. Daudel and B. Pullman, Ed., D. Reidel Publishing Co., Dordrecht, 1974.
- (28) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N.Y., 1970; J. N. Murrell and A. J. Harget, "Semi-empirical Self-consistent-field Molecular-orbital Theory of Molecules," Wiley-Interscience, London, 1972.
- (29) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970); M. J. S. Dewar, E. Haselbach, and S. D. Worley, *Proc. Roy. Soc., London, Sect. A*, **315**, 431 (1971).
- (30) C. Fridh, L. Åsbrink, and E. Lindholm, *Chem. Phys. Lett.*, **15**, 282 (1972); L. Åsbrink, C. Fridh, and E. Lindholm, *J. Amer. Chem. Soc.*, **94**, 5501 (1972).
- (31) E. Heilbronner, *J. Pure Appl. Chem.*, in press; E. Heilbronner, R. Pauncz, and A. Schmelzer, in preparation.
- (32) J. P. Maier and J.-F. Müller, *J. Chem. Soc., Faraday Trans. 2*, in press.