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### 108. A Photoelectron-spectroscopic investigation of the Homoconjugative Interaction between $\pi$ - and *Walsh*-Orbitals in *endo*- and *exo*-Cyclopropano-norbornene<sup>1), 2)</sup>

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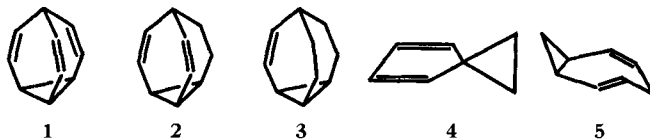
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*Summary.* Photoelectron spectra of *endo*- and *exo*-cyclopropano-norbornene (= *endo*- and *exo*-tricyclo[3.2.1.0<sup>2,4</sup>]octa-6-ene) show that a significant homoconjugation exists between the  $\pi$ -orbital of the double bond and the symmetric *Walsh*-e<sub>S</sub>-orbital of the cyclopropane ring in the *exo*-isomer, whereas the interaction is negligible in the *endo*-derivative.

In many cases the characteristics of the photoelectron (PE) spectrum of a molecule largely depend on its configuration and/or conformation.

A typical example is provided by conjugated dienes for which the overlap controlled interaction between the two  $\pi$ -orbitals,  $\pi_1$  and  $\pi_2$ , leads to an orbital energy split  $\varepsilon ((\pi_1 - \pi_2)/\sqrt{2}) - \varepsilon ((\pi_1 + \pi_2)/\sqrt{2})$  which is a function of the angle of twist  $\varphi$  between the neighbouring double bonds. As a consequence, the difference  $\Delta I_\pi = I_\pi(2) - I_\pi(1)$  between the positions  $I_\pi(1)$  and  $I_\pi(2)$  (in eV) of the two  $\pi$ -bands in the PE. spectrum of a diene depends also on  $\varphi$ : e.g. for 1,3-cyclohexadiene,  $\Delta I_\pi = 2.5$  eV; for 1,3-cyclooctadiene,  $\Delta I_\pi = 1.3$  eV [2]. Making use of this relationship between  $\Delta I_\pi$  and  $\varphi$  *Brundle & Robin* [3] have shown that for hexafluorobutadiene the angle of twist is  $\varphi = 50^\circ$ .

Similar observations apply to the conjugation of cyclopropyl groups with double bonds; in this case the conjugative interaction of the *Walsh*-orbitals e<sub>S</sub>, e<sub>A</sub> of the cyclopropyl moiety with the  $\pi$ -orbital of the double bond is at a maximum in compounds for which the relative orientation of the two subsystems corresponds to the so-called bisected conformation: e.g. in bullvalene (**1**), in dihydro- and tetrahydro-bullvalene (**2**, **3**) [4], in homofulvene (**4**) [1]. On the other hand, the interaction between the two moieties becomes quite small in molecules in which their orientation corresponds to the perpendicular conformation: e.g. homotropyldiene (**5**) [4]. As a final example



<sup>1)</sup> Part 23 of 'Applications of Photoelectron Spectroscopy'. Part 22: [1].

<sup>2)</sup> We use the less cumbersome designation *exo*- or *endo*-cyclopropano-norbornene instead of *exo*- or *endo*-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene.

we mention the large difference in the splits  $\Delta I_\pi$  observed for *cis,cis*-1,6-cyclodecadiene (**6**) ( $\Delta I_\pi = 0.50$  eV) and *trans,trans*-1,6-cyclodecadiene (**7**) ( $\Delta I_\pi = 1.70$  eV) [2].



It has become obvious however that the successful detection of configurational and/or conformational effects by PE. spectroscopy depends on the following conditions:

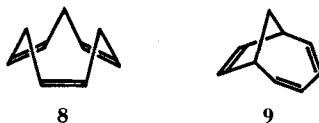
a) The semilocalised basic orbitals  $\varphi_a, \varphi_b, \dots$  of the interacting moieties should be degenerate ( $\varepsilon(\varphi_a) = \varepsilon(\varphi_b) = \dots$ ) (*i.e.* related by symmetry), or nearly (accidentally) degenerate ( $\varepsilon(\varphi_a) \approx \varepsilon(\varphi_b) \approx \dots$ ).

b) If  $\varepsilon(\varphi_a) \neq \varepsilon(\varphi_b)$ , then the interaction matrix element  $\langle \varphi_a | \mathcal{H} | \varphi_b \rangle$  must be large compared to  $|\varepsilon(\varphi_a) - \varepsilon(\varphi_b)|$ .

c) The PE. bands corresponding to the ejection of an electron from the resulting mixed orbitals  $\psi_J = C_{Ja}\varphi_a + C_{Jb}\varphi_b + \dots$  must be well detached from the usually strongly overlapping  $\sigma$ -bandsystem, at higher ionisation potentials.

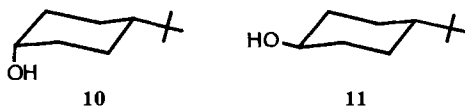
d) Finally, it is essential that reference spectra of a series of compounds having the same or at least a similar topography and each containing only one of the basic orbitals  $\varphi_a, \varphi_b, \varphi_n$  should be available for obtaining correlation diagrams.

For example: i) *cis,cis,cis*-1,4,7-cyclononatriene (**8**) the three basic  $\pi$ -orbitals are symmetry equivalent. In consequence, their homoconjugative interaction can be easily detected by PE. spectroscopy [5].



In contrast, for bicyclo[1.2.4]nonatriene (**9**), where the  $\pi$ -orbitals of the diene moiety and the single double bond are far from being degenerate, homoconjugation leads to band positions which do not differ significantly from those observed in the reference compounds 1,3-cycloheptadiene and norbornene [5].

ii) The ionisation potential corresponding to the ejection of an electron from the oxygen lone pair orbital of the hydroxyl group in substituted cyclohexanes is expected to be different for the axial and equatorial positions respectively. Preliminary results for *cis*- and *trans*-4-*t*-butylcyclohexanol (**10** and **11**) indicate however that this difference cannot be determined with complete

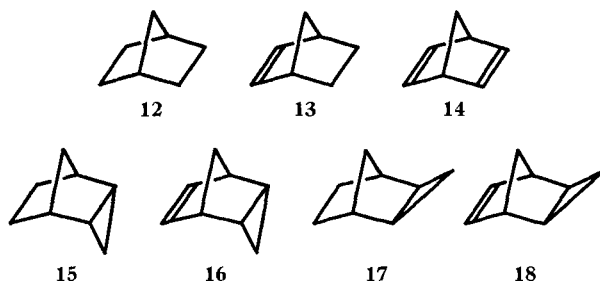


certainty<sup>3)</sup>, as the corresponding PE. bands are strongly overlapped by the remaining  $\sigma$ -bands of the alkyl moiety [6].

<sup>3)</sup> This preliminary investigation, carried out jointly with Prof. *J. Reisse* (Université Libre de Bruxelles), indicates that the vertical ionisation potentials  $I_v(n)$  for lone pair ionisation are:  $I_v(n, \text{axial}) = 9.9$  eV for **10** and  $I_v(n, \text{equatorial}) = 9.75$  eV for **11**; the onset of the bands occurs at 9.6 eV for **10** and 9.4 for **11**.

At the present stage of the art of PE. spectroscopy it is obviously relevant to assess the range of those conformational and configurational problems to which this technique can make significant contributions.

In view of our current interest in the behaviour of *Walsh*-orbitals and in the problem of homoconjugation, the set of compounds **12** to **18** seemed ideal to answer the following: (a) To what extent do *Walsh*-orbitals enter into homoconjugation with  $\pi$ -orbitals? (b) Does such an interaction depend on configurational changes of the *exo-endo*-type? (c) Is PE. spectroscopy at all suited to yield reliable answers in such situation?



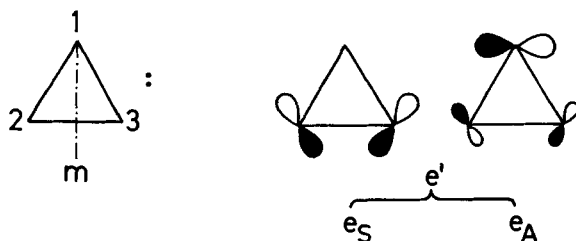
The PE. spectra of **12** (norbornane), **13** (norbornene) and **14** (norbornadiene) have already been described [7]. Their characteristics are given in the Table, together with the, newly determined, ionisation potentials of **15** (*endo*-cyclopropano-norbornane), **16** (*endo*-cyclopropano-norbornene), **17** (*exo*-cyclopropano-norbornane) and **18** (*exo*-cyclopropano-norbornene). The PE. spectra of **16** and **18** are shown in Fig. 1.

The spectra have been recorded on a PS-16 Photoelectron spectrometer of *Perkin-Elmer Ltd.* (Beaconsfield, England) [8]; for experimental details the reader is referred to previous publications in this series, *e.g.* [4].

This discussion is based on semi-localised orbitals, *i.e.* the  $\pi$ -orbital of the double

$$\begin{aligned} \mathbf{e}_S &= (1/\sqrt{2}) (2\mathbf{p}_2 - 2\mathbf{p}_3) \\ \mathbf{e}_A &= (1/\sqrt{6}) (2 \cdot 2\mathbf{p}_1 - 2\mathbf{p}_2 - 2\mathbf{p}_3) \end{aligned} \quad (1)$$

bond and the *Walsh*-orbitals [9] of the cyclopropyl moiety. The labels and sign convention are defined as follows:



In cyclopropane ( $C_3H_6$ ; symmetry  $D_{3h}$ )  $\mathbf{e}_S$  and  $\mathbf{e}_A$  are degenerate ( $\mathbf{e}'$ ), belonging to the irreducible representation  $E'$  of the group  $D_{3h}$ . An orbital energy value ( $\epsilon(\mathbf{e}_A) = \epsilon(\mathbf{e}_S) = -10.9$  eV) is derived from the mean ionisation potential ( $I_V(^2E') = 10.9$  eV), which corresponds to the centre of the *Jahn-Teller*-split PE-band ① of cyclopropane;

( $I_v = 10.5$  eV and  $11.3$  eV [10]). By taking  $\varepsilon(\mathbf{e}_A) = \varepsilon(\mathbf{e}_S) = -I_v(^2E')$  we have implicitly assumed that *Koopmans'* theorem [11] is valid.

We shall now investigate the influence of alkyl substituents on the orbital energies  $\varepsilon(\mathbf{e}_A)$  and  $\varepsilon(\mathbf{e}_S)$  of the cyclopropane ring, in order to obtain the orbital energies of the basic functions  $\mathbf{e}_S$  and  $\mathbf{e}_A$  to be used in the discussion of the PE. spectra of **15**, **16**, **17** and **18**.

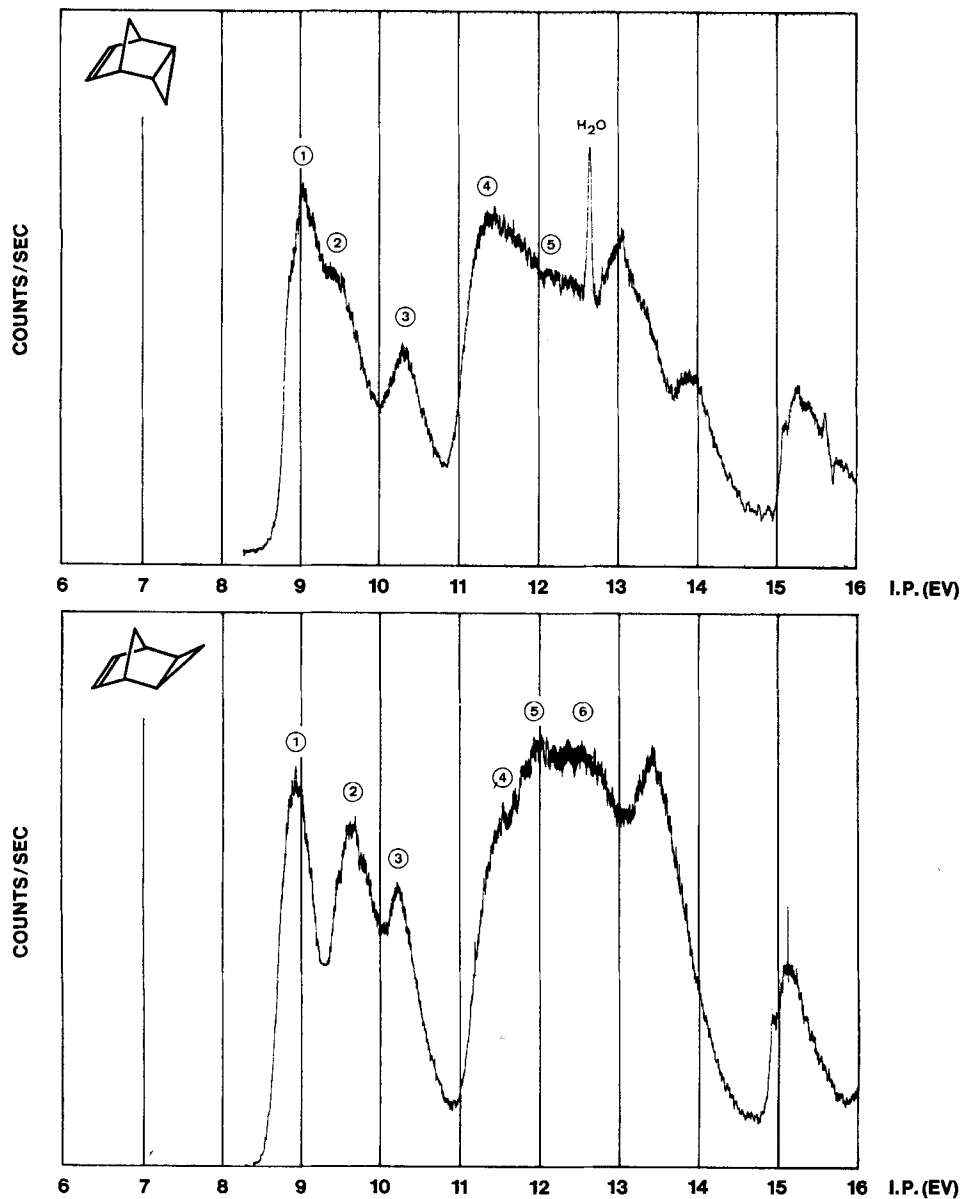
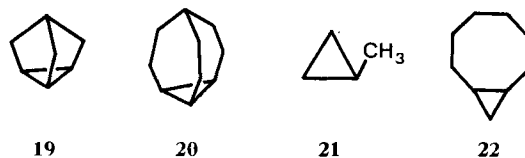


Fig. 1. PE. spectra of endo- and exo-cyclopropanonorborene



In nortricyclene (**19**) and hexahydrobullvalene (**20**) the threefold axis is conserved (symmetry  $C_{3v}$ ) and the *Walsh*-orbitals  $e_A$ ,  $e_S$  are therefore still degenerate. From the PE. spectra we obtain: for **19**,  $\epsilon(e_A) = \epsilon(e_S) = -9.7$  eV [12], and for **20**,  $\epsilon(e_A) = \epsilon(e_S) = -9.3$  eV [4]. Assuming that the shift in  $\epsilon(e_A)$  and  $\epsilon(e_S)$  (induced by an alkyl substituent in position  $\mu$  of the cyclopropane ring) is proportional to the squared coefficient of the atomic orbital  $2p_\mu$  in the linear combination  $e_S$  or  $e_A$  (see 1), we find that the perturbation parameter  $\langle 2p_\mu | \hat{h} | 2p_\mu \rangle$  per substituent amounts to  $+1.2$  eV in **19** and  $+1.6$  eV in **20**.

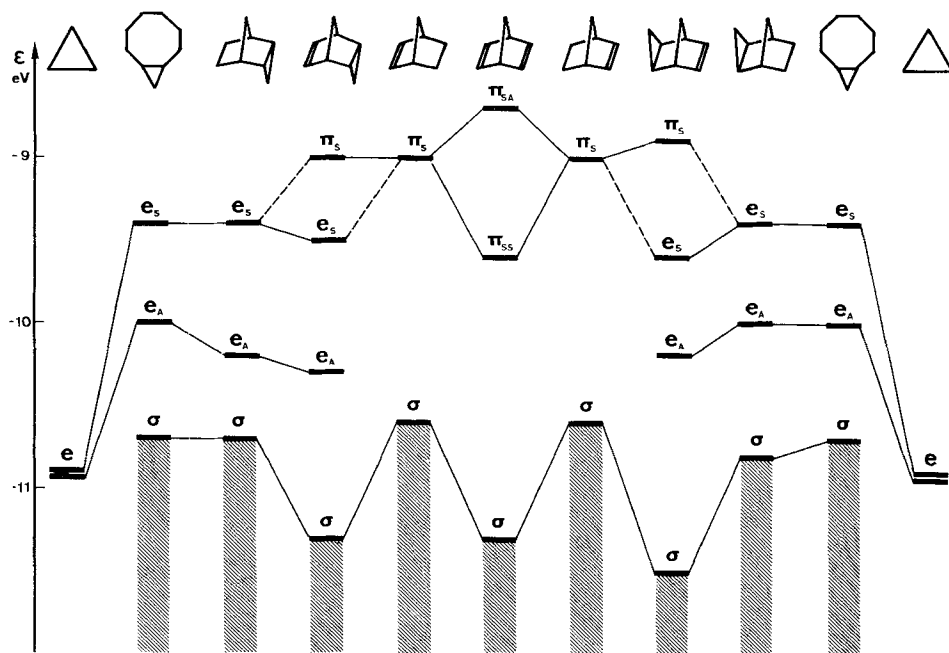


Fig. 2. Correlation diagram for the orbital energies of the top occupied orbitals in cyclopropane, bicyclo[0.1.6]octane and hydrocarbons **13-18**

The orbital energies  $\epsilon$  are those obtained on the assumption  $\epsilon = -I_V$  (*Koopmans'* theorem). The shading under the first  $\sigma$ -level indicates that this is followed by a series of lower lying levels which give rise to the system of strongly overlapping PE. bands at higher ionisation potentials

Using the parameter obtained from **19** we can predict that in methylcyclopropane (**21**), the orbital energy  $\epsilon(e_S)$  remains unperturbed ( $-10.9$  eV) whereas  $\epsilon(e_A)$  is shifted by  $(2/\sqrt{6})^2 \cdot 1.2 = 0.8$  eV to a value of  $\epsilon(e_A) = -10.1$  eV. This prediction is in com-

plete agreement with observation [13] and confirms the numerical value of our parameter.

For bicyclo[0.1.6]nonane (**22**) the perturbation parameter  $\langle 2\mathbf{p}_\mu | \mathfrak{h} | 2\mathbf{p}_\mu \rangle = 1.6$  eV derived from the PE. spectrum of **20** is that to be used, in view of the size of the substituting alkyl moiety. In this case, both  $\mathbf{e}_A$  and  $\mathbf{e}_S$  are shifted,  $\mathbf{e}_A$  by  $((1/\sqrt{6})^2 + (1/\sqrt{6})^2) \cdot 1.6 = 0.5$  eV and  $\mathbf{e}_S$  by  $((1/\sqrt{2})^2 + (1/\sqrt{2})^2) \cdot 1.6 = 1.6$  eV. This leads to the prediction  $\varepsilon(\mathbf{e}_A) = -10.4$  eV and  $\varepsilon(\mathbf{e}_S) = -9.3$  eV, which can be compared with the experimental values for the first two PE.-bands ① and ② in the PE. spectrum of **22**:  $I_V(1) = -\varepsilon(\mathbf{e}_S) = 9.4$  eV,  $I_V(2) = -\varepsilon(\mathbf{e}_A) = -10.0$  eV. It should be borne in mind that we are completely neglecting the changes in  $\varepsilon(\mathbf{e}_A)$  and  $\varepsilon(\mathbf{e}_S)$  due to conjugation with lower lying or antibonding  $\sigma$ -orbitals of the remaining  $\sigma$ -frame; it is obvious that these effects, which are known to be significant [14] [15], must be of different size in **20** and in **22**.

Comparing the positions of the bands ① and ② of *endo*- and of *exo*-cyclopropano-norbornane (**15** and **17**) with those of **22**, there is no doubt that the two highest bonding orbitals in **15** and **17** must be localised almost entirely in the cyclopropyl moiety, *i.e.* they are to be identified with  $\mathbf{e}_S$  and  $\mathbf{e}_A$  respectively.

This assignment is justified as follows: The first band in the PE. spectrum of norbornane (**12**) is found at  $I_V(1) = 10.2$  eV [7] which corresponds to the ejection of an electron from the highest occupied orbital of the norbornane  $\sigma$ -system ( $\varepsilon(\sigma) = -10.2$  eV). Successive introduction of double bonds shifts  $\varepsilon(\sigma)$  to  $-10.6$  eV in **13** and to  $-11.3$  eV in **14** [7]. Assuming that the replacement of the double bond by a cyclopropano group will cause the same shifts, then the highest  $\sigma$ -orbital *not* of a *Walsh*-type in **15** and **17** is expected to be well below  $-10.2$  eV, presumably around  $-10.6$  eV. In consequence we have to assign band ③ in the PE. spectra of **15** ( $I_V(3) = -10.8$  eV) and **17** ( $I_V(3) = -10.7$  eV) to an ionisation process in which the photoelectron leaves this particular  $\sigma$ -orbital. It follows that bands ① and ② in the PE. spectra of **15** and **17** have to be correlated with  $\mathbf{e}_S$  and  $\mathbf{e}_A$ , as previously shown.

Referring to the correlation diagram of Fig. 2, the levels shown correspond to orbital energies taken from the corresponding PE. spectra with the implicit assumption that  $\varepsilon(J) = -I_V(J)$ , the latter being the vertical ionisation potential or, more precisely, the position of the maximum of the PE. band ④. The  $\sigma$ -orbital energies of the saturated hydrocarbons cyclopropane, **15**, **17** and **22** have been discussed above.

The centre of the correlation diagram summarises our previous results concerning the interaction of the two  $\pi$ -orbitals in norbornadiene (**14**) [7]. It had been assumed originally that the observed split  $\varepsilon(\pi_{SA}) - \varepsilon(\pi_{SS}) = 0.8_5$  eV is due solely to through space interaction [16], but recent results show that through bond interactions are by no means negligible [14]. Nevertheless, we shall discuss orbital interactions between  $\pi$ - and *Walsh*-orbitals as if the through bond contribution could be neglected (c. f. [15]). We shall use a value of  $\varepsilon(\pi) = -9.1$  eV for the orbital energy of a basic  $\pi$ -orbital in **16** and **18**.

Conversely, we assume that the presence of a double bond in **16** and **18** lowers the orbital energies  $\varepsilon(\mathbf{e}_S)$  and  $\varepsilon(\mathbf{e}_A)$  of the *Walsh*-orbitals by the same amount, *i.e.*  $\approx -0.1$  eV. This will place them (relative to their values in **15** and **17**) at the following energies: **16**,  $\varepsilon(\mathbf{e}_S) = -9.5$  eV,  $\varepsilon(\mathbf{e}_A) = -10.3$  eV; **18**,  $\varepsilon(\mathbf{e}_S) = -9.5$  eV,  $\varepsilon(\mathbf{e}_A) = -10.1$  eV. To summarise, the orbital energies of the basic orbitals (in eV) are:

Orbital	<b>16</b>	<b>18</b>
$\pi$	– 9.1	– 9.1
$e_S$	– 9.5	– 9.5
$e^A$	–10.3	–10.1

(3)

It should be noted that this assignment of orbital energies to the basic orbitals  $\pi$ ,  $e_S$  and  $e^A$  is consistent with the observed mean values  $\bar{\epsilon} = (\epsilon(\pi) + \epsilon(e_S))/2$  for the two highest occupied orbitals in the compounds **16** and **18**, viz.:

$$\begin{aligned}
 \mathbf{16} \quad \bar{\epsilon} &= -(9.03 + 9.5)/2 = -9.27 \text{ eV} \\
 \mathbf{18} \quad \bar{\epsilon} &= -(8.90 + 9.61)/2 = -9.26 \text{ eV} \\
 (\text{Basis: } \bar{\epsilon} &= -(9.1 + 9.5)/2 = -9.30 \text{ eV})
 \end{aligned}$$
(4)

From these agreeing values we conclude that we can justifiably calculate an interaction term  $\kappa = \langle \pi_S | \mathcal{H} | e_S \rangle$  according to the simple pythagorean rule [17]

$$\left( \frac{\epsilon(\pi) - \epsilon(e_S)}{2} \right)^2 + \kappa^2 = \left( \frac{\epsilon(1) - \epsilon(2)}{2} \right)^2$$
(5)

where  $\epsilon(1)$  and  $\epsilon(2)$  are the orbital energies of the two highest occupied molecular orbitals from which electrons are ejected in the ionisation processes leading to the bands ① and ② in the PE. spectra of **16** and **18**).

Inserting in (5) of the values for  $\epsilon(\pi)$  and  $\epsilon(e_S)$  (given in (3)) and those for  $\epsilon(1) = -I_V(1)$  and  $\epsilon(2) = -I_V(2)$ , given in the Table, it is obvious that in the case of the *endo*-derivative (**16**) the interaction parameter  $\kappa$  becomes zero within the limits of error. On the other hand we find that  $\kappa = -0.3$  eV for the *exo*-derivative (**18**), indicating that in this isomer we have substantial interaction between the  $\pi$ -orbital and the *Walsh*-orbital.

*Ionisation potentials  $I_V$  (J) in eV, for the hydrocarbons **12** to **18***

All values refer to the position of the band maxima and have been rounded to the nearest 0.05 eV. The numbers in circles refer to those in fig. 1. Values for **12**, **13** and **14** from [7].

Compd.	PE. band					
	①	②	③	④	⑤	⑥
<b>12</b>	10.1 <sub>5</sub>	10.7 <sub>0</sub>	–	–	–	–
<b>13</b>	8.9 <sub>5</sub>	10.5 <sub>5</sub>	11.8 <sub>5</sub>	–	–	–
<b>14</b>	8.7 <sub>0</sub>	9.5 <sub>5</sub>	11.2 <sub>5</sub>	12.5 <sub>0</sub>	–	–
<b>15</b>	9.4 <sub>0</sub>	10.2 <sub>0</sub>	10.7 <sub>0</sub>	11.4 <sub>0</sub>	12.0 <sub>0</sub>	–
<b>16</b>	9.0 <sub>5</sub>	9.5 <sub>0</sub>	10.3 <sub>0</sub>	11.3 <sub>0</sub>	12.2 <sub>0</sub>	–
<b>17</b>	9.4 <sub>0</sub>	10.0 <sub>0</sub>	10.8 <sub>0</sub>	11.5 <sub>0</sub>	11.8 <sub>0</sub>	–
<b>18</b>	8.9 <sub>0</sub>	9.6 <sub>0</sub>	10.2 <sub>0</sub>	11.5 <sub>5</sub>	11.9 <sub>0</sub>	12.5 <sub>5</sub>

The reason for this characteristic dependence of the interaction term  $\kappa$  on the configuration of the cyclopropane ring in **16** and **18** is immediately evident on consideration of the molecular models. In the *endo*-derivative (**16**) the two atomic orbitals  $2p_2$  and  $2p_3$  of  $e_S$  are directed away from the *endo*-oriented lobe of the  $\pi$ -orbital  $\pi$  of the double bond. On the other hand,  $2p_2$  and  $2p_3$  of  $e_S$  are directed towards this lobe in the *exo*-derivative (**18**). A calculation yields the following values for the overlap:  $S = \langle \pi | e_S \rangle$ :  $S(\textit{endo}) = 0.02$  in **16**;  $S(\textit{exo}) = 0.12$  in **18**. The above result, *i.e.*  $\kappa(\textit{endo}) \approx 0$  eV and  $\kappa(\textit{exo}) \approx -0.3$  eV is thus in complete agreement with that expected on theoretical grounds.

Furthermore, the PE. spectroscopic behaviour of **16** and of **18** is also in agreement with chemical observations. The configurational change *endo*  $\rightarrow$  *exo* of the cyclopropano group in cyclopropano-norbornene is accompanied by an extraordinary change in the course of their photo-induced and metal-catalysed valence isomerisation reactions [18]. Thus, both the chemical evidence concerning the tricyclic systems **16** and **18** and their PE. spectra, point to the dominating influence of stereoelectronic factors, *i.e.* the homoconjugative interaction between the  $\pi$ -orbital of the double bond and the *Walsh*-orbital  $\mathbf{e}_S$  of the cyclopropane ring.

Extended *Hückel* calculations (EHT.) [19] for the hydrocarbons **15** to **18** confirm the conclusions derived above. The orbitals which have to be classified as essentially  $\mathbf{e}_S$  and  $\mathbf{e}_A$  in the saturated compounds **15** and **17** are found to have the following orbital energies: for **15**,  $\epsilon(\mathbf{e}_S) = -12.06$  eV,  $\epsilon(\mathbf{e}_A) = -13.10$  eV; for **17**,  $\epsilon(\mathbf{e}_S) = -12.38$  eV,  $\epsilon(\mathbf{e}_A) = -12.57$  eV. (In the case of **15** an additional  $\sigma$ -orbital is found at  $-12.86$  eV; from previous experience with the ETH. model, as applied to PE. spectroscopy, it is highly probable that this is an artefact and therefore the orbital should occur at lower energies.) In **16** and **18** the orbital energies of the linear combinations to be characterised by  $\pi - \lambda\mathbf{e}_S$  and  $\mathbf{e}_S + \lambda\pi$  ( $\lambda \ll 1$  being a positive constant) are: for **16**,  $\epsilon(\pi - \lambda\mathbf{e}_S) = -12.06$  eV,  $\epsilon(\mathbf{e}_S + \lambda\pi) = -12.30$  eV; in **18**,  $\epsilon(\pi - \lambda\mathbf{e}_S) = -12.00$  eV,  $\epsilon(\mathbf{e}_S + \lambda\pi) = -12.61$  eV. Therefore the following splits between the bands ① and ② are predicted: 0.24 eV for **16** and 0.62 eV for **18**; they have to be compared with the experimental results,  $I_V(2) - I_V(1) = 0.45$  eV and 0.70 eV respectively. The fact that the combination  $\pi - \lambda\mathbf{e}_S$  is found to lie above  $\mathbf{e}_S + \lambda\pi$ , is consistent with the assumption that through space interaction dominates, or in other words, that the interaction term  $\kappa$  is a negative quantity.

We are now in a position to answer the questions raised at the beginning of this paper:

a) There is substantial homoconjugation in *exo*-cyclopropano-norbornene **18**, due to the direct overlap between the  $\pi$ -orbital of the double bond and the symmetric *Walsh*-orbital  $\mathbf{e}_S$  of the cyclopropano moiety. The term  $\kappa(\textit{exo}) \approx -0.3$  eV, which describes this interaction in a formal way, is slightly smaller than that observed for the interaction between the two bonding  $\pi$ -orbitals of the double bonds in norbornadiene **14** ( $\kappa \approx -0.4$  eV; see however [14]); the negative sign for  $\kappa$  is in accordance with the results derived from an EHT. model, which puts the linear combination with the node higher than that without node. Our analysis indicates that the through-space interaction between  $\pi$  (of the double bond) and  $\mathbf{e}_S$  (in the cyclopropane ring) dominates the through bond interaction.

b) The homoconjugation in cyclopropano-norbornene is strongly dependent on configuration; there is no detectable interaction in the *endo*-isomer **16**. This behaviour is consistent with that predicted on the assumption that the interaction term  $\kappa$  is proportional to the overlap  $S = \langle \pi | \mathbf{e}_S \rangle$  and with the results obtained by EHT. treatment; it is also that expected on chemical grounds.

c) The PE. spectra of **16** and of **18**, shown in fig. 1, suggest that the greater homoconjugative interaction between the double bond  $\pi$ -orbital and the  $\mathbf{e}_S$  *Walsh*-orbital of the cyclopropano group can be easily detected, as shown by the larger split between the bands ① and ② in the spectrum of **18**. However, the differences in the



corresponding ionisation potentials, *i.e.*  $I_v(2) - I_v(1)$ , are only 0.4<sub>5</sub> eV for **16** as compared with 0.7<sub>0</sub> eV for **18**. This means that no significant conclusions could have been drawn if only these two spectra, let alone that of only one of the isomers, had been available. The deductions concerning homoconjugation in **16** and **18** have only been made possible by investigation of *all* compounds listed in the correlation diagram of Fig. 2.

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