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155. The Interaction of *Walsh*-Orbitals in Diademane and Related Hydrocarbons

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(16. IV. 73)

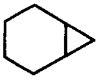
Summary. To obtain further information concerning the interaction between *Walsh*-orbitals of 'conjugated' cyclopropane rings, the photoelectron spectra of the following compounds have been recorded: bicyclo[4.1.0]heptane **1**, *cis*- and *trans*-tricyclo[5.1.0^{3,5}]octane **2**, **3**, diademane **4**, *trans*-pentacyclo[3.3.2.0^{2,9}.0^{4,10}.0^{6,8}]decane **5** and bicyclo[4.1.0]heptene-2 **6**. The first bands in the PE.-spectra of these compounds have been assigned on the basis of a ZDO HMO-approximation. For **2** and **4** the value for resonance integral between linked 2p atomic orbitals of two adjacent eclipsed cyclopropane rings is found to be −1.73 eV.

In previous communications [1] [2] we reported photoelectron spectroscopic evidence concerning the direct conjugation of the *Walsh*-orbitals in a cyclopropane unit with the π-orbitals of adjacent double bonds. It was shown

a) that this interaction is strongly conformation dependent, being maximal (minimal) for the bisected (perpendicular) conformation of the cyclopropylethylene unit, and

b) that the experimentally observed band positions in the photoelectron spectra demand a resonance integral $\beta = \langle \phi_\mu | \mathcal{H} | \phi_\nu \rangle \approx -1.9$ eV, where ϕ_μ, ϕ_ν are the 2p-atomic orbitals of the connected centres μ, ν of the cyclopropane ring and the double bond respectively.

In this paper we wish to discuss the conjugative interaction between *Walsh*-orbitals in diademane [3] **4** (= hexacyclo[4.4.0.0^{2,4}.0^{3,9}.0^{5,7}.0^{8,10}]decane) and, for comparison, in bicyclo[4.1.0]heptane **1**, *cis*- and *trans*-tricyclo[5.1.0.0^{3,5}]octane **2**, **3** and in *trans*-pentacyclo[3.3.2.0^{2,9}.0^{4,10}.0^{6,8}]decane **5**. For reasons to be discussed below we have also included bicyclo[4.1.0]heptene-2 **6**. (The experimental data are shown in Fig. 1 and Tab. 1).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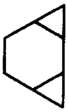
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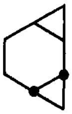
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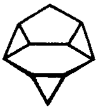
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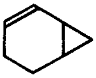
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The first band in the photoelectron spectrum of cyclopropane **7** (D_{3h}) [4] corresponds to the ejection of an electron from one of the degenerate pair of *Walsh*-orbitals [5]

$$e_A = \frac{1}{\sqrt{6}} (2\phi_a - \phi_b - \phi_c)$$
$$e_S = \frac{1}{\sqrt{2}} (\phi_b - \phi_c) \qquad (1)$$

where ϕ_μ stands for the 'tangential' 2p orbitals of the carbon atoms. Consequently the doublet state of the cyclopropane radical cation undergoes a *Jahn-Teller* distortion, which leads to a split of 0.8 eV in the photoelectron band: $I_V = 11.3$ and 10.5 eV; $\overline{I_V} = 10.9$ eV [4]. Alkyl-substitution, which preserves the threefold axis (*e.g.* nortricyclene **8** or hexahydrobullvalene **9** [1]) shifts $\overline{I_V}$ to lower values: 9.7 eV in **8**, 9.3_5 in **9**. Parallel to this shift the *Jahn-Teller* split decreases (0.8 eV in **7**, 0.7 eV in **8**, 0.5_5 eV in **9**) presumably due to increased delocalization of the *Walsh*-orbitals into the alkyl moiety.

Disubstitution such as is present in **1**, in *endo*- (**10**) or *exo*-cyclopropanonorbornane (**11**) [6], in cyclopropano-bicyclo[2.2.2]octane (**12**) [7] and in *trans*-bicyclo[6.1.0]non-

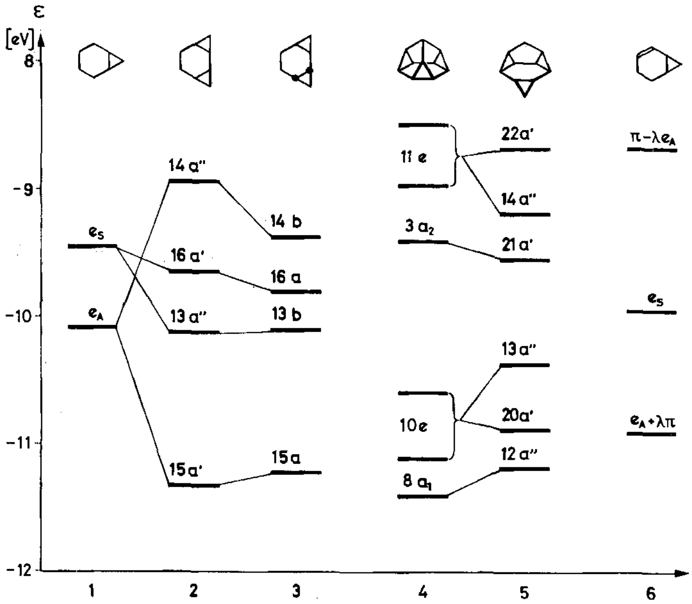


Fig. 1. *Proposed correlation diagram for the 'observed' orbital energies of the hydrocarbons* **1** *to* **6**

Table 1. *Vertical ionization potentials of* **1**–**5**. All values in eV.

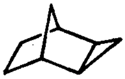
Compound	Band	Orbital	$I_{v,J}$
1	①	e_S	9.46
C_s	②	e_A	10.01
	①	14a''	8.95
2	②	16a'	9.66
C_s	③	13a''	10.14
	④	15a'	11.34
	①	14b	9.39
3	②	16a	9.82
C_2	③	13b	10.14
	④	15a	11.24
	①	11e	8.50
	②		8.97
4	③	$3a_2$	9.42
C_{3v}	④	10e	10.61
	⑤		11.13
	⑥	$8a_1$	11.42
	①	22a'	8.78
	②	14a''	9.20
5	③	21a'	9.56
C_s	④	13a''	10.38
	⑤	20a'	10.90
	⑥	12a''	11.20
	①	π-λe_A	8.69
6	②	e_S	9.96
	③	$e_A + \lambda\pi$	10.92


7


8


9


10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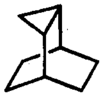
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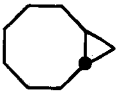
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ane (**13**) [8] lifts the degeneracy of e_S and e_A, whereby e_S suffers a larger destabilization than e_A. This results again in a split $\Delta I_{1,2} = I_{v,2} - I_{v,1}$ between the first two bands in the photoelectron spectrum. $\Delta I_{1,2}$ is due to two effects, namely

a) a pseudo *Jahn-Teller* distortion, which decreases with increasing difference $\varepsilon(e_S) - \varepsilon(e_A)$ and

b) the differing inductive destabilization of e_S and e_A caused by the alkyl moieties.

As the contribution a) becomes smaller with increasing b), the observed split $\Delta I_{1,2}$ stays roughly constant for the series of hydrocarbons **1** and **10** to **13**:

1	$\overline{I_v} = 9.73$ eV	$\Delta I_v = 0.54$ eV
10	9.80 eV	0.80 eV
11	9.70 eV	0.60 eV
12	9.75 eV	0.50 eV
13	9.63 eV	0.55 eV

(2)

For simplicity we shall absorb both effects formally in an inductive perturbation $\delta\alpha$ of the *Coulomb* integral $\alpha_\mu = \langle\phi_\mu|\mathcal{H}|\phi_\mu\rangle$ of the substituted centre μ, and of $m \cdot \delta\alpha$ of the centres ortho to μ.

Using *Koopmans* approximation, *i.e.* $I_{v,J} = -\varepsilon_J$ (where ε_J is the orbital energy of the molecular orbital ψ_J vacated in the ionization process giving rise to the band at position $I_{v,J}$) and the linear combinations (1) we obtain by a first-order perturbation treatment for the displacements $\delta\varepsilon(e_S)$ and $\delta\varepsilon(e_A)$ of the *Walsh*-orbitals under dialkylsubstitution:

$$\begin{aligned} \delta\varepsilon(e_S) &= (1+m)\,\delta\alpha \\ \delta\varepsilon(e_A) &= \frac{1}{3}(1+5\,m)\,\delta\alpha \end{aligned} \tag{3}$$

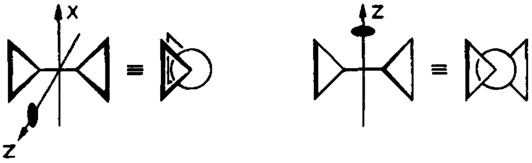
Comparing $-\overline{I_v} = \varepsilon(e) = -10.9$ eV of **7** with $-I_{v,1} = \varepsilon(e_S) = -9.46$ eV and $-I_{v,2} = \varepsilon(e_A) = -10.01$ eV of **1** yields $\delta\varepsilon(e_S) = 1.44$ eV and $\delta\varepsilon(e_A) = 0.89$ eV. Insertion into (3) leads to

$$\delta\alpha = 1.13 \text{ eV}; \qquad m = 0.31\,. \tag{4}$$

These values are consistent with the observed band positions for the reference compounds **8** to **12**, if the different sizes of the alkyl moieties attached to the cyclopropane ring are taken into consideration.

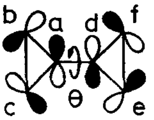
Independent of the particular parametrization (4), it follows from (3) that $\delta\varepsilon(\mathbf{e}_S) > \delta\varepsilon(\mathbf{e}_A)$ because of $m < 1$. Consequently the highest occupied orbital in **1**, **10**, **11** and **12** corresponds to $\mathbf{e}_S$ of **7**, followed by that corresponding to $\mathbf{e}_A$: $I_{v,1} = -\varepsilon(\mathbf{e}_S)$; $I_{v,2} = -\varepsilon(\mathbf{e}_A)$.

We shall now discuss the photoelectron spectrum of **2**. *Dreiding* models suggest that the cyclohexane ring assumes a twist conformation. The methylene groups are staggered and the two cyclopropane rings are twisted relative to each other by $\theta \approx 20°$, if their 'syn planar' conformation is characterized by $\theta = 0°$. To a first approximation we may assume that the dicyclopropyl moiety of **2** has local C_{2v} symmetry.



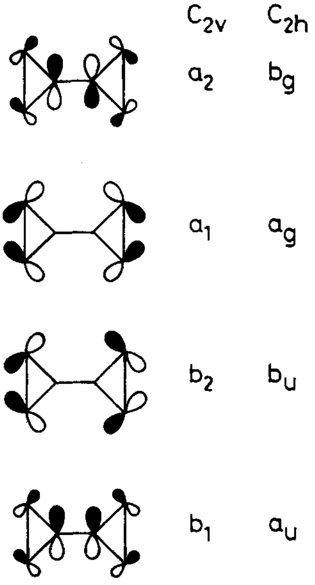
$\theta = 0°$; C_{2v} $\theta = 180°$; C_{2h} (5)

For a discussion of the dicyclopropyl system we define the relative phases of the basis atomic orbitals ϕ_μ as follows:



(6)

Note that all interaction terms $\langle\phi_\mu|\mathcal{H}|\phi_\nu\rangle$ between bonded atomic 2p-orbitals a to f are positive $(-\beta)$. Depending on the twist angle θ between the two rings (*i.e.* between ϕ_a and ϕ_d), the above system exhibits C_{2v} ($\theta = 0$; 'syn planar'), C_2 ($0 < \theta < 180°$) or C_{2h} ($\theta = 180°$; 'anti-planar') symmetry.



(7)

$\theta = 0$; $\theta = 180°$

C_{2v};	C_{2h}	ε	linear combination
$\mathbf{a}_2$	$\mathbf{b}_g$	$\alpha + (\sqrt{2} - 1)\beta$	$0.500\,(\phi_a + \phi_d) - 0.354\,(\phi_b + \phi_c + \phi_e + \phi_f)$
$\mathbf{a}_1$	$\mathbf{a}_g$	$\alpha + \beta$	$0.500\,(\phi_b - \phi_c + \phi_e - \phi_f)$
$\mathbf{b}_2$	$\mathbf{b}_u$		$0.500\,(\phi_b - \phi_c - \phi_e + \phi_f)$
$\mathbf{b}_1$	$\mathbf{a}_u$	$\alpha + \sqrt{3}\beta$	$0.628\,(\phi_a - \phi_d) - 0.230\,(\phi_b + \phi_c - \phi_e - \phi_f)$

(8)

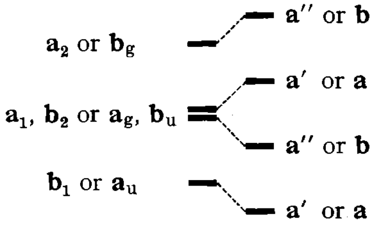
Assuming all bond lengths in (3) to be R(CC) = 1.52 Å the overlap integral between two tangential 2p-orbitals is $\langle \phi_a | \phi_b \rangle = -0.23$ as compared to $\langle \phi_a | \phi_d \rangle = -0.20$ if $\theta = 0°$. In a first approximation we can therefore solve the variational problem defined by (6) under the usual assumptions of standard *Hückel* theory (*i.e.* all α_μ and $\beta_{\mu\nu}$ equal). We obtain for the highest four bonding orbitals of (6).

The 'central' orbitals $\mathbf{a}_1$, $\mathbf{b}_2$ (or $\mathbf{a}_g$, $\mathbf{b}_u$) are accidentally degenerate and will not mix under C_{2v} or C_{2h} symmetry with any of the other *Walsh*-orbitals, even if long range interactions are introduced into model (2) (the antibonding *Walsh*-orbitals are $\mathbf{a}_2^*$, $\mathbf{b}_1^*$ or $\mathbf{b}_g^*$, $\mathbf{a}_u^*$ respectively). However, for intermediate values of θ (C_2 symmetry) or under a reduction to C_s symmetry, such interactions will split the degeneracy because of the following changes in the irreducible representations:

C_s ←	C_{2v}	C_{2h}	→ C_2
A″	A_2	B_g	B
A′	A_1	A_g	A
A″	B_2	B_u	B
A′	B_1	A_u	A

(9)

Assuming that other interactions, *i. e.* with non-*Walsh*-orbitals are of lesser importance we may expect that this will result in the following orbital sequence:



(10)

However, in the following discussion we shall not make use of the order suggested in (10) for the two central orbitals, but rather pool the data for the bands ② and ③.

In **2** the centres b and f of (3) are substituted and, as shown in (4), their *Coulomb* integrals experience therefore a destabilization $\delta\alpha_b = \delta\alpha_f = \delta\alpha = 1.13$ eV. According to (4) the transmission of the inductive effect to the unsubstituted centres a, c, d and e will be $m\delta\alpha$ with m = 0.31. From the observed ionization potentials $I_{v,1} =$

8.95 eV and $I_{v,4} = 11.34$ eV of **2** and the corresponding orbital energies and linear combinations (7) (8) we obtain, using a first order perturbation treatment:

$$\begin{aligned} -8.95 - 2\,(0.354^2\,(1 + m) + 0.5^2\,m)\,\delta\alpha &= \alpha + (\sqrt{2} - 1)\,\beta \\ -11.34 - 2\,(0.230)\,(1 + m) + 0.628^2\,m)\,\delta\alpha &= \alpha + \sqrt{3}\,\beta \end{aligned} \qquad (11)$$

Solving (11) for α and β (with $\delta\alpha = 1.13$ eV and $m = 0.31$) yields:

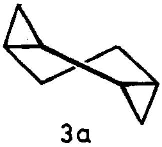
$$\alpha = -\,8.78\ \text{eV};\quad \beta = -\,1.73\ \text{eV} \qquad (12)$$

From this we can derive a value for the orbital energies of the two accidentally degenerate orbitals $\mathbf{a}_1$, $\mathbf{b}_2$ (under C_{2v}) or $\mathbf{a}_g$, $\mathbf{b}_u$ (under C_{2h}) and thus for the mean ionization potential $\overline{I_{2,3}} = (I_{v,2} + I_{v,3})/2 = 9.90$ eV:

$$\overline{I_{2,3}} = -\,\alpha - \beta - 2\,(0.5^2\,(1 + m))\,\delta\alpha = 9.77\ \text{eV} \qquad (13)$$

As can be seen the observed and predicted values agree as well as can reasonably be expected.

Molecular models indicate that **3** could exist in two conformations, **3a** and **3b**, both of C_2 symmetry, in which the cyclohexane ring is again present in the twist form:



3a
0≈40°

3b
0≈90°

The twist angle between the two cyclopropane moieties is $\theta \approx 40°$ in **3a** and $\theta \approx 90°$ in **3b** so that conjugation would be practically zero in the latter case. Thus if **3** existed in conformation **3a**, we would expect rather small differences between the orbital energies of the four highest occupied orbitals. This, however, is not the case. In fact the 'observed' orbital energies $\varepsilon(\mathbf{b}_g) = -\,9.39$ eV, $\varepsilon(\mathbf{a}_{(g)}) \approx \varepsilon(\mathbf{b}_{(u)}) \approx 10.0$ eV, $\varepsilon(\mathbf{a}_{(u)}) = 11.24$ eV (where the lower indices in brackets refer to the limiting situation $\theta = 180°$ of local C_{2h} symmetry) agree rather nicely with what would be expected on the basis of conformation **3b**. Relative to **2**, the difference $\Delta I_{1,4} = I_{v,4} - I_{v,1} = 2.39$ eV in **2** has decreased to $\Delta I_{1,4} = 1.85$ eV in **3** *i.e.* by $\delta\Delta I_{1,4} = -\,0.54$ eV. If we assume that $\beta_{ad} = \beta \cdot \cos\theta$, we derive from (8) by first order perturbation theory that the gap $\Delta I_{1,4} = \varepsilon(\mathbf{b}_{(g)}) - \varepsilon(\mathbf{a}_{(u)})$ should decrease by

$$\delta\Delta I_{1,4} = (1 - \cos 40°)\,2\,(0.628^2 + 0.500^2) \cdot \beta = 0.52\ \text{eV} \qquad (14)$$

in excellent agreement with observation. However, it should be mentioned that relative to **2**, the system of bands ① to ④ has been shifted as as whole by 0.13 eV towards higher ionization potentials.

We are now in a position to advance a plausible rationalization of the photoelectron spectrum of diademane **4** (Fig. 2). In this molecule we have by symmetry $\theta = 0°$ for all pairs of cyclopropane units, *i.e.* maximum conjugation. The following

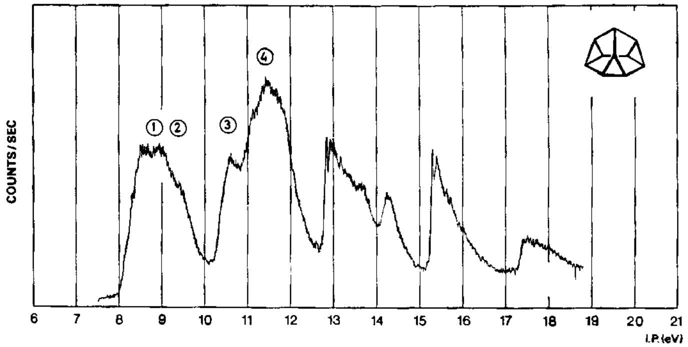
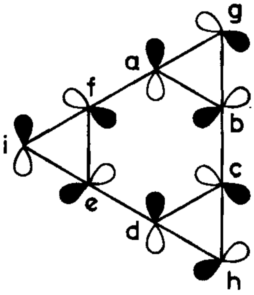


Fig. 2. *Photoelectron spectrum of diademane* (**4**).

choice of relative phases of the basis 2p atomic orbitals ϕ_μ makes again all interaction terms positive $(-\beta)$:



(15)

Solving the corresponding variational problem yields the following bonding orbitals $\psi_J = \sum_\mu c_{J\mu} \phi_\mu$ of orbital energies $\varepsilon_J = \alpha + x_J\beta$:

	11e		$3a_2$	10e		$10a_1$
ψ_J	ψ_6	ψ_5	ψ_4	ψ_3	ψ_2	ψ_1
x_J	0.347		0.732	1.532		2.000
$\mu =$ a	0.082	0.464	0.188	0.303	0.361	0.408
b	0.082	−0.464	0.188	−0.303	0.361	0.408
c	0.361	−0.303	0.188	0.161	−0.443	0.408
d	−0.443	0.161	0.188	0.464	0.082	0.408
e	−0.443	−0.161	0.188	−0.464	0.082	0.408
f	0.361	0.303	0.188	−0.161	−0.443	0.408
g	−0.471	0.000	−0.513	0.000	−0.471	0.000
h	0.236	0.408	−0.513	−0.408	0.236	0.000
i	0.236	−0.408	−0.513	0.408	0.236	0.000

(16)

With the parameters (12) one derives from (16) the following orbital energies, which are compared to the 'observed' ones (assuming *Koopmans* approximation):

Orbital	Calculated	Observed	Diff. (Obs.-Calc.)
$\mathbf{11e}$	– 9.38 eV	– 8.74 eV	0.64 eV
$\mathbf{3a_2}$	– 10.04	– 9.42	0.62
$\mathbf{10e}$	– 11.43	– 10.87	0.56
$\mathbf{10a_1}$	– 12.23	– 11.42	0.81
			Mean 0.66 eV

(17)

We see that the calculated values are below the observed ones (mean displacement 0.66 eV). The reason for the observed destabilization is obvious: it is due to the inductive effect of the central sp^3 carbon atom, which ties the cyclopropane rings together. Applying the same type of perturbation treatment as in the case of **2** and **3**, using the parameters (4), we find that on the basis of the orbital coefficients c_{J_μ} given in (16), a mean displacement of $0.64\ \delta\alpha = 0.72$ eV is to be expected, *i.e.* of the size observed (*cf.* (1)).

Thus the orbital sequence in **4** is (counting from the highest occupied orbital downwards):

$$\begin{array}{ccccc} \mathbf{11e} & \mathbf{3a_2} & \mathbf{10e} & \mathbf{8a_1} & \ldots \\ \text{(HOMO)} & \multicolumn{4}{c}{\xrightarrow{\hspace{6cm}}} \end{array} \qquad (18)$$

Apart from the excellent agreement between the orbital energies derived from our model and the observed ionization potentials, the sequence is strongly supported by the observation that bands ① and ③ in the spectrum of **4** clearly show the typical shape of induced by a *Jahn-Teller* distortion, which indicates that the vacated orbital belongs to a degenerate set.

We have also carried out a semiempirical calculation of the EHT type [9] for **4**, using the parameters described in [9], except that for the *Slater* exponent on hydrogen, a value of 1.3 was chosen. For **4** a C_{3v} geometry was assumed with all C–C and C–H bond distances equal to 1.52 Å and 1.10 Å, respectively. It is our experience that this treatment yields in most cases the same relative ordering of the upper occupied orbitals as does a SCF calculation, even though the absolute orbital energies may be seriously in error. The EHT orbital energies of **4** are: $\varepsilon(\mathbf{11e}) = -11.76$ eV, $\varepsilon(\mathbf{3a_2}) = -11.92$ eV, $\varepsilon(\mathbf{10e}) = 13.09$ eV, $\varepsilon(\mathbf{10a_1}) = 13.87$ eV. The EHT results agree with our semi-qualitative considerations with respect to the ordering of the *Walsh*-orbitals, which is identical to that given in (18). The computed orbital gaps are $\varepsilon(\mathbf{11e}) - \varepsilon(\mathbf{3a_2}) = 0.16$ eV, $\varepsilon(\mathbf{3a_2}) - \varepsilon(\mathbf{10e}) = 1.17$ eV, $\varepsilon(\mathbf{10e}) - \varepsilon(\mathbf{10a_1}) = 0.78$ eV, as compared to the observed values $\Delta I_{1,2} = 0.68$ eV, $\Delta I_{2,3} = 1.45$ eV and $\Delta I_{3,4} = 0.55$ eV.

To conclude we discuss briefly the photoelectron spectra of **5** and **6**.

In **5** the angles of twist are $\theta = 0°$ for the two *cis* cyclopropane units and $\theta \approx 50$ to 60° between the pairs of *trans* connected cyclopropane rings. With reference to the basis shown in (15), we use $\beta_{af} = \beta_{bc} = 0.6\,\beta$ and $\beta_{ed} = \beta$ together with the parameters given in (12). The 'inductive' perturbation of the bridging methylene group between the centres i and h is again taken care of by a first order perturbation calculation, *i.e.*

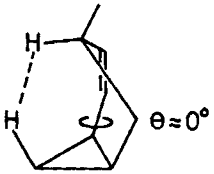
$$\delta\varepsilon_J = 2\,(c_{Jh}^2 + m\,(c_{Jc}^2 + c_{Jd}^2))\,\delta\alpha \tag{19}$$

where m and $\delta\alpha$ are as defined in (4). This yields the following results (calc.), which are in reasonable agreement with the observed ones (obs.):

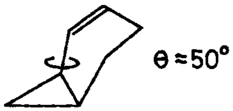
Orbital	I_V(obs.)	I_V(calc.)
22**a**′	8.78	8.99
14**a**″	9.2	9.39
21**a**′	9.56	9.65
13**a**″	10.38	10.72
20**a**′	10.90	10.73
12**a**″	11.20	11.55

(20)

Models of **6** suggest that two conformations should be taken into considerations: conformation **6a** in which the double bond assumes the bisected conformation $\theta \approx 0°$, leading to maximum conjugation of the *Walsh* $\mathbf{e}_A$ orbital of the three membered ring with the π-orbital and **6b**, in which the angle of twist is $\theta \approx 50°$.



6a



6b

(21)

Using again the parameters given in (4) and the basis *Walsh*-orbitals (1), we deduce that $\mathbf{e}_A$ and $\mathbf{e}_S$ should be destabilized by $\delta\varepsilon(\mathbf{e}_A) = 0.48$ eV and $\delta\varepsilon(\mathbf{e}_S) = 0.74$ eV, leading to basis energies of -10.42 ($\mathbf{e}_A$) and -10.16 eV ($\mathbf{e}_S$) relative to $\varepsilon(\mathbf{e}_A) = \varepsilon(\mathbf{e}_S) = -10.9$ eV in **7**. From the π-ionization potential of cyclohexene [10], we deduce $\varepsilon(\boldsymbol{\pi}) = -9.12$ eV. This value may be lowered somewhat due to the presence of the cyclopropano group. However, it is expected that this lowering should not exceed 0.1 to 0.2 eV. From the above values it is obvious that the first three bands in the photoelectron spectrum of **6** should be correlated with orbitals, which are essentially of character $\boldsymbol{\pi} - \lambda\,\mathbf{e}_A$, $\mathbf{e}_S$, $\mathbf{e}_A + \lambda\boldsymbol{\pi}$. From the observed ionization potentials $I_{v,1} = 8.69$ eV, $I_{v,3} = 10.92$ eV and the above basis orbital energies ~ -9.2 eV for the π- and -10.42 eV for the *Walsh* $\mathbf{e}_A$-orbital we deduce according to

$$\left(\frac{10.92 - 8.69}{2}\right)^2 - \left(\frac{10.42 - 9.20}{2}\right)^2 = \left(\beta \cdot \frac{2}{\sqrt{6}} \cdot \frac{1}{\sqrt{2}} \cdot \cos\theta\right)^2 \tag{22}$$

that $\beta \cdot \cos\theta = -1.62$ eV. With $\beta = -1.9$ eV as obtained earlier for the maximum conjugation between $\mathbf{e}_A$ and $\boldsymbol{\pi}$, we find $\theta = 32°$. This value seems to point towards **6b** being the preferred conformation, which is reasonable in view of the smaller steric interference of the hydrogen atoms (*cf.* **6a**).

Experimental part. The compounds **1**, **2**, **3** and **6** have been prepared by cyclopropanation of cyclohexene and cyclohexadiene as described by *Doering & Roth* [11]. The products were separated by gas chromatography.

Compound **5** has been obtained by irradiation of a mixture of both isomers of bis-homobarrelene [12] in pentane with a mercury high pressure lamp [13]. The yield was 10–15%. The preparation of **6** has been reported in the literature [3].

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156. Contribution à l'étude de dérivés O-β-hydroxyéthylés de la quercétine

Identification des dérivés par spectrophotométrie UV.

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(15 V 73)

Résumé. Par spectrophotométrie UV. on établit les structures de 8 dérivés O-hydroxyéthylés de la quercétine obtenus par trois voies: [a]) l'hydrolyse acide de dérivés identifiés O-hydroxyéthylés de la rutine conduit aux mono-éther-4', di-éther-7,4', tri-éther-7,3',4' et tétra-éther-5,7,3',4'; [b]) l'hydroxyéthylation soit modérée de la quercétine ou du tri-éther-7,3',4', qui conduit

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