72. Photoelectron-Spectroscopic Characterization of 3,4-Dimethyl-2,4-hexadienes

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Summary

The He(Iα) photoelectron (PE) spectra of the (*E,E*)-, (*E,Z*)- and (*Z,Z*)-isomers of the title compound have been recorded to obtain information about their conformation in the gas phase. For a valid correlation with the PE data of other dienes it is necessary to take the potentials $V(\varphi)$ for internal rotation and the corresponding conformer population densities $P(\varphi)$ into account, as well as the rather complicated way in which the π^{-1} ionization energy gap $\Delta I(\varphi)$ depends on the direct π-orbital interaction and the long-range 'through-space' interaction between the semi-localized methyl-group orbitals and the π-orbitals. These factors being taken into account, the mean twist angles, $\bar{\varphi}$, compatible with the PE-spectroscopic results are $\bar{\varphi}$ (*E,E*) $\approx 0° \pm 30°$, $\bar{\varphi}$ (*E,Z*) $\approx 80°$ or 110° within ±15°, and $\bar{\varphi}$ (*Z,Z*) $\approx 85°$ to 105°. These results are in rough agreement with electron diffraction data by *Traetteberg* [15], other spectroscopic results and, for the (*E,E*)- and (*Z,Z*)-isomers, internal rotation potentials $V(\varphi)$ previously calculated by *Roth* [17]. On the other hand the potential $V(\varphi)$ proposed for the (*E,Z*)-isomer does not seem to be compatible with our findings.

Introduction. – Although UV-PE spectroscopy is in general not the method of choice for the investigation of conformational equilibria, it has been applied with success in particular cases, *e.g.* by *Maier & Turner* for the study of the conformations of biphenyls [1], by *Nelsen et al.* [2] and by *Rademacher* [3], who investigated the conformers of cyclic and acyclic hydrazines, and by *Brundle & Robin* [4], who proved that octafluorobutadiene assumes a twisted, *gauche*-conformation. All these systems consist of two self-contained, identical moieties, R and S (either π-systems or lone pairs), interacting across a bond about which they can be twisted through an angle φ out of coplanarity ($\varphi = 0$). If $A_R = A_S = A$ is the energy of the HOMO basis orbitals, ψ_R and

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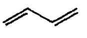
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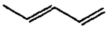
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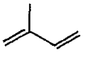
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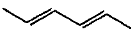
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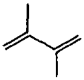
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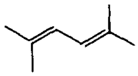
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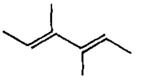
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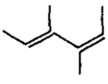
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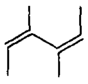
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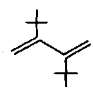
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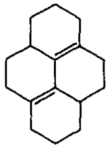
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ψ_S, of R and S, then in a first-order approximation the highest orbital energies of the compound system R–S are $\varepsilon_+ = A + B^0_{\pi\pi}\cos\varphi$ and $\varepsilon_- = A - B^0_{\pi\pi}\cos\varphi$, with $B_{\pi\pi}(0^0) = B^0_{\pi\pi} = \langle\psi_R|\hat{H}|\psi_S\rangle$ for $\varphi = 0$. Accordingly, the ionization difference $\Delta I = I_+ - I_- = \varepsilon_- - \varepsilon_+$ satisfies the condition $\Delta I = -2B^0_{\pi\pi}\cos\varphi$ (assuming *Koopmans'* theorem) and is thus a measure of the twist angle φ.

Based on a previous investigation of the methyl-substituted butadienes **1**–**6** [5], we now use essentially the above technique to obtain information about the mean conformations of the title compounds **7** [6].

Experimental Results and Preliminary Survey. – In *Fig. 1* are shown the He(I*a*) PE spectra of **7**(*E*,*E*), **7**(*E*,*Z*) and **7**(*Z*,*Z*), while the spectrum of **8** is shown in *Fig. 2*. The π-ionization energies I^m_1 and I^m_2, listed in the legends to the figures refer to the positions of the respective π-band maxima and are thus close to the vertical ionization energies (see also [5]). For convenience, the labels $b_g(\pi)$ and $a_u(\pi)$, used for the π-orbitals of the dienes **1**–**9**, are borrowed from the parent compound butadiene (**1**) in its anti-planar C_{2h}-conformation ($\varphi = 0°$). Concerning the PE spectra of the butadienes **1**–**6**, *cf.* previous publications: **1** [4][7][8], **2**–**4** [5][9], **5**, **6** [5].

The preferred *mean* conformation of the hydrocarbons **1**–**7**(*E*,*E*) is that with $\bar{\varphi} \approx 0°$, *i.e.* with an anti-periplanar butadiene moiety of local (almost) C_{2h}-symmetry. This is supported by the results of electron diffraction studies for **1** [10], **5** [11] and **7**(*E*,*E*) [12], of ^{1}H-NMR spectroscopy [13] and of electronic spectroscopy [14] (*cf.* the discussion in [5]). In contrast, steric interference of the 1,3-positioned methyl groups in **7**(*E*,*Z*) and of the 1,3- and 2,4-positioned ones in **7**(*Z*,*Z*) leads to conformations in which the mean twist angle $\bar{\varphi}$ of the two double-bond planes are close to 90° [15], *i.e.* **7**(*E*,*Z*), $\bar{\varphi} \approx 114°$; **7**(*Z*,*Z*), $\bar{\varphi} \approx 113°$, according to the electron diffraction data, as compared to $\bar{\varphi} \approx 23°$ for **7**(*E*,*E*) [12]. Previous to this work, no experimental determination of the structure of **8** [16] was available, but molecular models show that $\bar{\varphi}$ must also be close to 90°.

Although a more detailed discussion of the preferred conformations of **7**(*E*,*E*), **7**(*E*,*Z*), **7**(*Z*,*Z*) and **8** will be found in [6], some remarks are needed, in view of the subsequent analysis of the PE spectra.

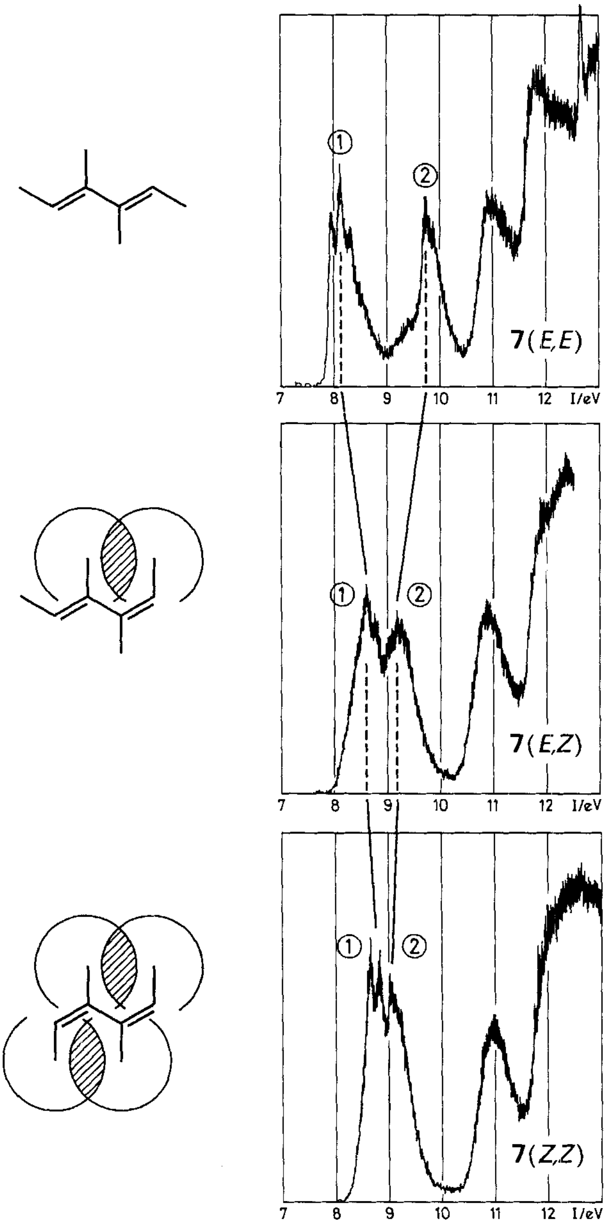

Fig. 1. *He(Iα) PE spectra of the title compounds* 7 (*E,E*), 7 (*E,Z*) *and* 7 (*Z,Z*)
Band positions I^m/eV:

Band	7 (*E,E*)	7 (*E,Z*)	7 (*Z,Z*)	Orbital
①	8.1_0	8.6_0	8.7_5	$b_g(\pi)$
②	9.7_5	9.2_0	9.0_5	$a_u(\pi)$

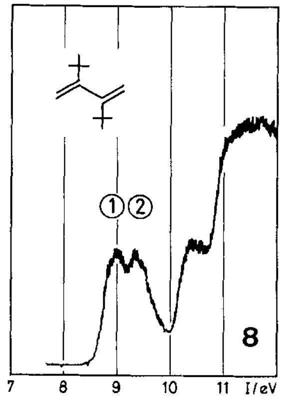

Fig. 2. *He(Iα) PE spectrum of 2,3-di(*tert*-butyl)butadiene* (**8**).
Band positions: ① ($b_g(\pi)$): 9.0_0 eV; ② ($a_u(\pi)$): 9.3_5 eV.

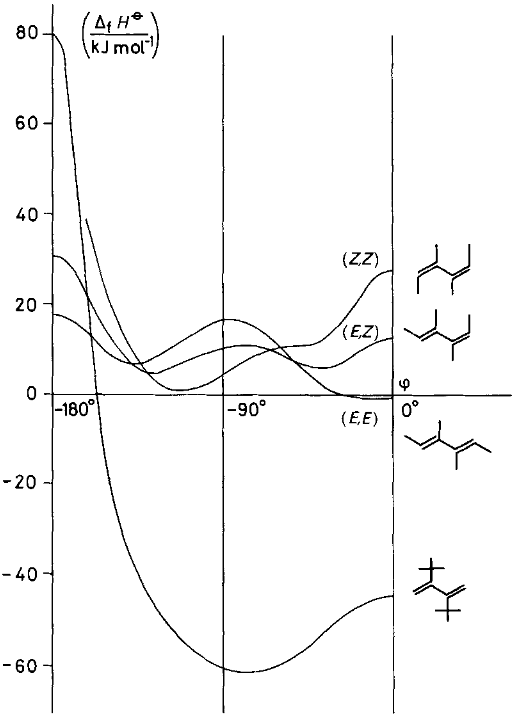

Fig. 3. *Angular dependence of the molar enthalpies of formation of the compounds* **7** *(E,E),* **7** *(E,Z),* **7** *(Z,Z) and* **8** *according to a combination of force field calculations, thermochemical data and* ab initio *results* [17]

A judicious combination of thermochemical data, force field calculations and *ab initio* results [17] yields the angular dependence of the enthalpies of formation $\Delta_f H^{\ominus}$ (298 K)[2]) of the compounds **7** and **8** displayed graphically in *Fig. 3*. Apart from a

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[2]) These enthalpies of formation were kindly provided by Prof. *W. Roth* (Ruhr Universität, Bochum) prior to their publications, see also [17].

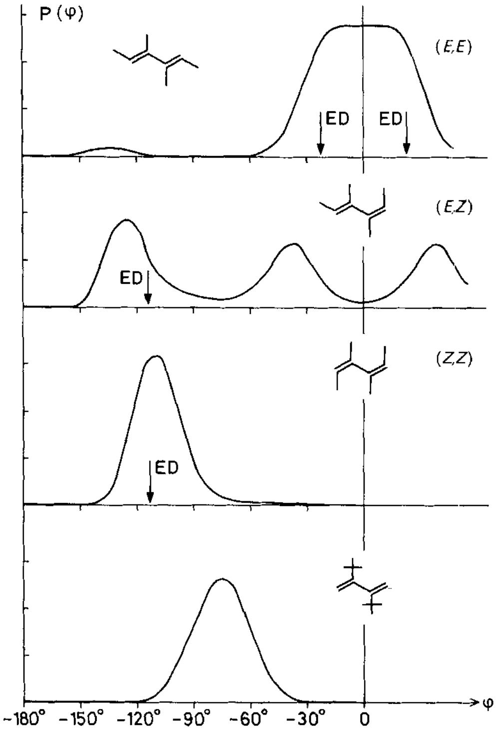


Fig. 4. *Conformer population densities P(φ) at T = 300 K for the compounds* **7** (*E,E*), **7** (*E,Z*), **7** (*Z,Z*) *and* **8**. The P(φ) are defined in such a way that dw = P(φ)dφ is the probability of finding a conformer in the interval dφ at position φ. The P(φ) are normalized to yield $\int_0^{2\pi} P(\varphi)d\varphi = 1$.

trivial, arbitrary shift along the ordinate, these are the rotational potentials, $V(\varphi)$, needed to compute the conformer population densities, P(φ), shown in *Fig. 4* for $T = 300$ K, *i.e.* the temperature at which the PE spectra were recorded. Thus the probability dw of finding a conformer in the interval dφ at position φ is given by dw = P(φ)dφ. It should be borne in mind that the $V(\varphi)$ of *Fig. 3* are at best first approximations of the true, as yet unknown potential functions (*cf.* [17]), reproducing probably only their general character. As we shall see the PE-spectroscopic results suggest some changes of a quantitative nature, at least for $V(\varphi)$ of **7**(*E,Z*).

If the potentials $V(\varphi)$ are taken at face value, we would deduce from *Fig. 4* that the preferred conformations of the molecules **7** and **8** span a rather wide range of angles φ. Thus, **7**(*E,E*) shows an almost constant population, P(φ), in the range $-30° < \varphi < +30°$; *i.e.* over almost 60°. It is immediately obvious that the value obtained by electron diffraction, $\varphi \approx 23°$ [12] (arrow ED in *Fig. 4*), does not correspond to the mean value $\bar{\varphi} = 0°$ of the symmetrical population distribution P(φ) around 0°, but, because of the well-known 'shrinkage effect' in electron diffraction data [18], to a weighted mean of the deviations $|\varphi|$ from $\varphi = 0°$. Note that 23° is in the expected range suggested by the calculated $P(\varphi)$ for **7**(E,E). In the case of **7**(Z,Z), the value $\bar{\varphi} \approx 113°$ found by electron diffraction should correspond to the mean of $P(\varphi)$ in the range $90° < \varphi < 120°$. As indicated in *Fig. 4* by the arrow labeled ED, this is indeed the case, but it is again obvious that the conformers expected to be present in the gas phase at 300 K range with comparable probability over more than 30°. The same is true for **8** were a mean value $\bar{\varphi} \approx 75°$ is expected on the basis of $P(\varphi)$.

The molecule **7**(E,Z) seems to be a special case. Although the mean twist angle $\bar{\varphi} \approx 114°$ found by electron diffraction [15] is practically identical to that of **7**(Z,Z) ($\bar{\varphi} \approx 113°$), the population densities, $P(\varphi)$, derived from the potential $V(\varphi)$ and tentatively proposed for **7**(E,Z) and **7**(Z,Z) suggest that the two distributions of conformers are vastly different. Indeed, if the potential $V(\varphi)$ for **7**(E,Z) were to be trusted, this molecule should exhibit two well-separated groups of conformers (of given chirality), namely one in the interval $20° < \varphi < 60°$ and another in the interval $105° < \varphi < 140°$. The corresponding mean values are $\bar{\varphi} \approx 35°$ and $\bar{\varphi} \approx 125°$, respectively. Both intervals are predicted to be populated to roughly the same extent. As we shall see, this picture is difficult to reconcile with the PE-spectroscopic results, and also with those of the electron diffraction studies.

The qualitative analysis of the PE spectra presented in *Fig. 1* and *2* relies on correlation with the reference compounds **1**–**6** [5], aided by simple orbital arguments using localized molecular orbitals (LMO). Thus, the π-orbitals of the parent compound **1** will be described in a first approximation as

$$\begin{aligned} b_g(\pi) &= (\pi_a - \pi_b)/\sqrt{2} \\ a_u(\pi) &= (\pi_a + \pi_b)/\sqrt{2} \end{aligned} \qquad (1)$$

where π_a and π_b are the π-LMO's of bonds 1, 2 and 3, 4, respectively. In principle π_a and π_b can be obtained from the canonical orbitals stemming from a many-electron treatment of **1** (*e.g.* the STO-3G model [19]) through a unitary localization transformation (*e.g.* the *Foster-Boys* transformation [20]). Description *(1)* of the butadiene π-orbitals is both simpler and more appropriate than a standard *Hückel* representation (*cf.* [5]) because the latter grossly exaggerates the coupling between π_a and π_b. It is also more consistent with the thermal data discussed in [6]. Assuming the validity of *Koopmans'* theorem it is a simple matter to calibrate model *(1)* using the PE data for **1**, **2**, **4** and **6** (*cf.* references given above):

	I_1^m/eV $b_g(\pi)^{-1}$	I_2^m/eV $a_u(\pi)^{-1}$	$\bar{I}^m$/eV	ΔI^m/eV
1	9.03	11.46	10.25	2.43
2	8.61	11.10	9.86	2.49
4	8.22	10.7	9.46	2.48
6	7.65	10.12	8.89	2.47

(2)

We note that ΔI^m is the same for all four compounds within the limits of error, indicating that the empirical crossterm for $\varphi = 0°$, namely

$$B^0_{\pi\pi} = \langle \pi_a | \hat{H} | \pi_b \rangle = -\frac{\Delta I^m}{2} = -1.24\ \text{eV} \qquad (3)$$

is the same. This shows that all four compounds have presumably the same conformation, *i.e.* $\varphi \approx 0°$, and that $B_{\pi\pi}(0°)$ is not changed significantly by methyl substitution, in contrast to I^m, which is reduced. Obviously the self-energy of a π basis orbital in **1** is

$$A_\pi = \langle\pi_a|\hat{\mathrm{H}}|\pi_a\rangle = \langle\pi_b|\hat{\mathrm{H}}|\pi_b\rangle = -\overline{I^m} = -10.25 \text{ eV} \tag{4}$$

This value suffers, in the mean, a shift of $\delta A = 0.8$ eV per single methyl group, or $\delta A = 1.3$ eV per pair of geminal methyl groups in positions 1 or 4. from the data reported in [5] it is obvious that changing the configuration of a single terminal methyl group from (*Z*) to (*E*) has only a marginal influence on δA.

We now compare the π^{-1} ionization energies of the compounds **3**, **5** and **7**:

	I_1^m/eV $b_g(\pi)^{-1}$	I_2^m/eV $a_u(\pi)^{-1}$	$\overline{I^m}$/eV	ΔI^m/eV
3 [5]	8.85	10.9	9.88	2.05
5 [5]	8.62	10.2	9.41	1.58
7 (*E,E*)	8.1_0	9.7_5	8.93	1.65
7 (*E,Z*)	8.6_0	9.2_0	8.90	0.60
7 (*Z,Z*)	8.7_5	9.0_5	8.90	0.30

(5)

For clarity, and in view of the ensuing discussion, the data (*5*) are graphically displayed in the correlation diagram of *Fig. 5*.

First of all one notices that the $\overline{I^m}$ values of **3** and **5** agree within the limits of error with those of **2** and **4**, respectively (see (*2*)). Furthermore $\overline{I^m}$ is the same for **7**(*E,E*), **7**(*E,Z*) and **7**(*Z,Z*) indicating once more that δA is insensitive towards configurational changes. In addition the value is close to that of **6** (*cf.* (2)).

As pointed out previously [5], it is a remarkable fact that ΔI^m decreases along the series **1**(2.43 eV)→**3**(2.05 eV)→**5**(1.58 eV) in the absence of any significant out-of-plane distortion ($\varphi \approx 0$) and can therefore not be explained by a change of the cross-term according to $B_{\pi\pi}(\varphi) = B^{\circ}_{\pi\pi}\cos\varphi$. (The value $\Delta I^m = 1.58$ eV for **5** is in pleasing agreement with $\Delta I^m = 1.65$ eV for **7**(*E,E*) known to be essentially planar). In addition, as can be seen from the correlation diagram of *Fig. 5*, this decrease of the split ΔI^m results from a stabilization of $b_g(\pi)$ and a destabilization of $a_u(\pi)$, both these shifts being about equal in absolute size, *i.e.* $\delta\varepsilon(b_g(\pi)) \approx -\delta\varepsilon(a_u(\pi))$. The reason for this curious result can be found in the 'through-space homo-hyperconjugation' of the methyl group pseudo π-orbitals, π_μ(a), in position $\mu = 2(3)$ with the vicinal basis π-orbitals, $\pi_b(\pi_a)$, shown schematically in the following diagram.

This effect was predicted by *Hoffmann et al.* [21]. For a detailed discussion of this long-range effect *cf.* [5].

From *Fig. 5* it is immediately apparent that the increasing steric interference of the methyl groups in the anti-planar conformation along the series **7**(*E,E*)→**7**(*E,Z*)→**7**(*Z,Z*) leads to an increase of the twist angle φ and thus to a reduction of the gap

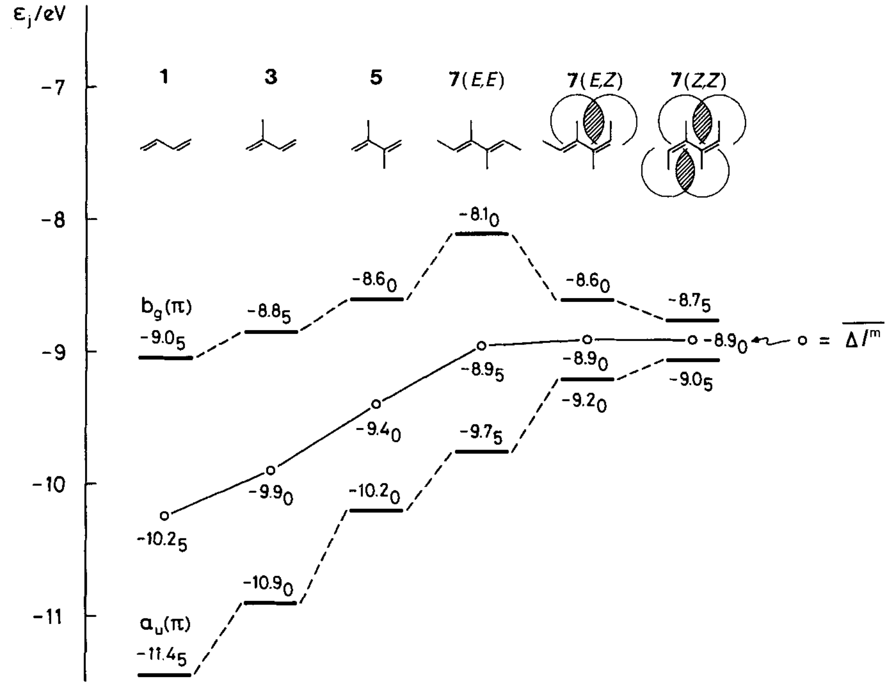
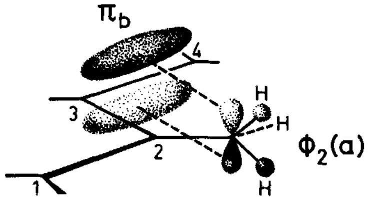


Fig. 5. *Correlation diagram of the 'experimental' π-orbital energies* $\varepsilon(b_g(\varphi))$ *and* $\varepsilon(a_u(\pi))$ *of the series* **1**, **3**, **5**, **7** (*E,E*), **7** (*E,Z*), **7** (*Z,Z*) *assuming the validity of* Koopmans' *theorem*



ΔI. Although, qualitatively, this seems to be a text-book example for the validity of the naive orbital picture described above, the true situation is slightly more complicated, as will be shown in the next section.

The Conformational Dependence of ΔI. – We shall now investigate in somewhat more detail how the π-ionization energy difference ΔI depends on the twist angle φ in the molecules **6**, **7**(*E,E*), **7**(*E,Z*) and **7**(*Z,Z*). To this end we use a *Hückel*-type equivalent bond orbital (EBO) model based on localized molecular orbitals λ_j, (LMO) derived from *ab initio* calculations. This model has been discussed in detail in previous contributions [22][23]. It is important to emphasize that the aim of this exercise is only to provide a heuristically useful scheme for a transparent rationalization of the observed data, and that it should *not* be taken as a valid substitute for more sophisticated and rigorous treatments. However, it has the great advantage of drawing attention to the important factors governing the angular dependence of ΔI in terms of qualitative concepts that can easily be extrapolated to other, similar situations.

According to the simple argument given in the previous chapter, twisting **1** through $\varphi \approx 90°$ should reduce the gap ΔI to zero. This is supported by a STO-3G calculation of the conformers of **1** with $\varphi = 0°, 45°, 90°$ but otherwise standard geometries, which yields,

φ	$\frac{V(\varphi)}{\text{kJ mol}^{-1}}$	$-\varepsilon_j$/eV		$-\bar{\varepsilon}$/eV	ΔI/eV
		$b_g(\pi)$	$a_u(\pi)$		
0°	0	7.08	10.76	8.92	3.68
45°	15.3	7.44	9.88	8.66	2.44
90°	27.9	8.45	8.49	8.47	0.04

(7)

The above *ab initio* calculation exaggerates the split $\Delta I(0°)$ by a factor of 1.5, the experimental value being only 2.4 eV (see the data collected in (*2*)). The height of the rotational barrier is predicted to be $V(90°) = 27.9$ kJ mol^{-1}, which is a fair guess of the accepted value (*cf.* references quoted in [6]) as the geometries have not been energy-minimized and because of the use of a minimal basis set.

With respect to the title compounds **7** the situation is more complex. Using the data displayed in *Fig. 5*, and summarized in (*5*), at face value, one is tempted to use the naive model to account for the symmetrical closing up of the gap $\Delta I^m = 1.65$ eV$\rightarrow$0.60 eV$\rightarrow$0.30 eV along the series **7**(*E,E*)$\rightarrow$**7**(*E,Z*) **7**(*Z,Z*) by assuming an *ad hoc* value $B^{\circ}_{\pi\pi} \approx -0.82_5$ eV to simulate the net interaction of π_a, π_b in **7**(*E,E*) at $\varphi \approx 0°$. From this one would deduce that $\varphi(E,Z) \approx 70°$ or 110° and $\varphi(Z,Z) \approx 80°$ or 100°, as compared to the electron diffraction values of 114° and 113°, respectively. (Note that at this level PE spectroscopy can not differentiate between φ and $180°-\varphi$).

Closer to reality and as discussed above, the reduced gaps $\Delta I = 1.6$ and 1.6_5 eV of **5** and **7**(*E,E*) relative to $\Delta I = 2.4_5$ of **1** are due to the long range 'through-space' interaction of the methyl pseudo-π-orbitals, $\Phi_2(a)$ and $\Phi_2(a)$, in positions 2, 3 with the vicinal π-orbitals, π_b and π_a, respectively, as depicted in (*6*). To derive an EBO model which simulates the interaction mechanism in the hydrocarbons **5** and **7** we proceed as follows. According to the rules formulated previously [23], we first derive the basis energies $A_{\text{Me,s}} = A_{\text{Me,a}} = A_{\text{Me}} = -13.2$ eV for the two pseudo-π-orbitals, $\Phi_\mu(a)$ and $\Phi_\mu(s)$, of the methyl groups. Of these, the $\Phi_\mu(a)$ are antisymmetric and the $\Phi_\mu(s)$ are symmetric with respect to the planes containing the carbon atoms of the methyl group and those of the double bond to which the latter is attached. The diagram (*6*) shows $\Phi_2(a)$ as an example. The basis energies of the π-orbitals, π_a and π_b, $A_a = A_b = A_\pi = -10.25$ eV, calibrated by using the PE data of **1**, have already been mentioned, *cf.* (*4*). A STO-3G calculation of the conformers of **5** carried out at 30° intervals of φ and subsequent localization reveals that A_{Me} and A_π remain invariant within 0.05 eV and 0.1 eV, respectively, in the interval $0 \leqslant \varphi \leqslant 180°$. The conjugation parameter $B_{\pi\pi}$ defined in (*3*) for the anti-planar conformation of **1**, and thus of **5**, depends on φ according to

$B_{\pi\pi}(\varphi) = B^{\circ}_{\pi\pi}\cos = (-1.5 \text{ eV}) \cos\varphi$, with $B^{\circ}_{\pi\pi}$ a bit larger than the empirical value derived above. In agreement with previous experience concerning methyl-substituted ethylenes, it is found that the hyperconjugative interaction terms $B_{\pi\text{Me}} = \langle \pi_a|\hat{H}|\Phi_2(a)\rangle = \langle \pi_b|\hat{H}|\Phi_3(a)\rangle$ have the value $B_{\pi\text{Me}} = -1.5$ eV [24]. Note that $\langle \pi_a|\hat{H}|\Phi_2(s)\rangle = \langle \pi_b|\hat{H}|\Phi_3(s)\rangle = 0$ for reasons of symmetry. The angular dependence of the 'through-space' interaction matrix elements, $\tau_s = \langle \pi_a|\hat{H}|\Phi_3(s)\rangle = \langle \pi_b|\hat{H}|\Phi_2(s)\rangle$ and $\tau_a = \langle \pi_a|\hat{H}|\Phi_3(a)\rangle = \langle \pi_b|\hat{H}|\Phi_2(a)\rangle$, have been determined by carrying out STO-3G calculations for **5** at various angles φ, localizing the canonical molecular orbitals according to the procedure of *Foster & Boys* [20] and evaluating the above cross terms τ_s and τ_a using the relevant matrix elements of the *Fock* matrices $\mathbf{F}_\lambda$ in localized basis. The dependence of τ_s and τ_a on φ is displayed in *Fig. 6,* A. Whereas $\tau_s = 0$ in the anti- or syn-planar conformation ($\varphi = 0°$ or $180°$) of **5**, for reasons of symmetry, it becomes rather large when the methyl groups in position 2(3) swing out of the nodal planes of the π-orbitals $\pi_b(\pi_a)$. In contrast τ_a is largest (in absolute value) for $\varphi = 0°$, becomes zero around $\varphi \approx 70°$, and increases again, albeit with opposite sign, for $\varphi > 70°$. Thus the long range 'through-space' interaction between the methyl groups in position 2(3) with $\pi_b(\pi_a)$ is finite for all angles φ, its angular dependence being rather complicated due to the competing interaction terms τ_s and τ_a. From a comparison with experiment [5] it is found that the absolute values of τ_a and τ_s, as shown in *Fig. 6,A,* are too small by a factor of almost 2. This may be due to the choice of basis functions for the STO-3G model, which are rather compact and tend therefore to underestimate long-range interactions. For this reason we have chosen $\tau_a(\varphi = 0°) = -0.7$ eV and have scaled all other τ_a, τ_s values accordingly.

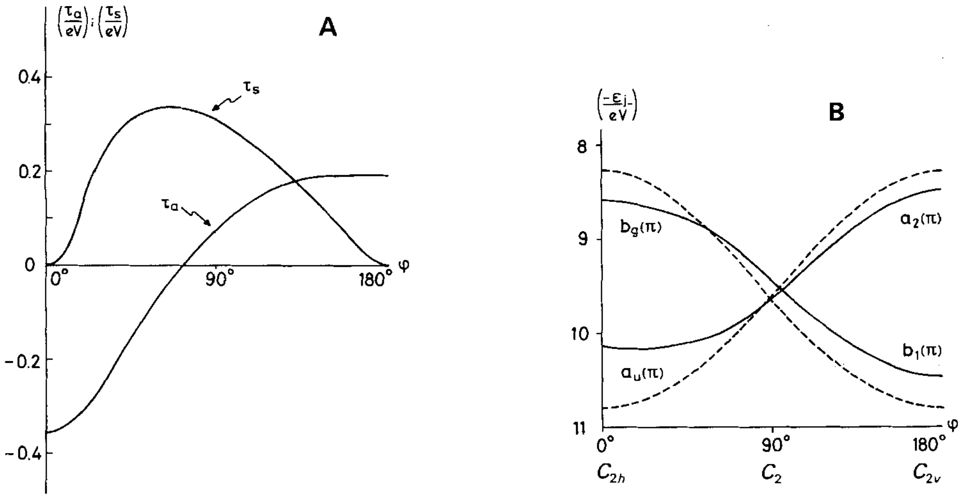
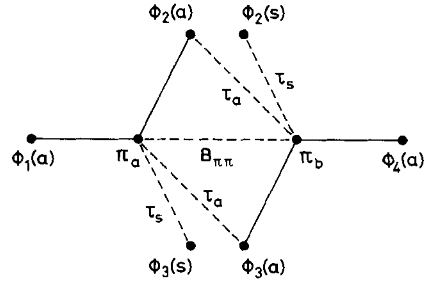


Fig. 6. A: *Angular dependence of the long-range 'through-space' interaction matrix elements* τ_a *and* τ_s. B: *Angular dependence of the* π*-ionization energies* $-\varepsilon(b_g(\pi))$ *and* $-\varepsilon(a_u(\pi))$ *of* **5**. The solid lines correspond to the orbital energies, obtained by diagonalizing the matrices corresponding to (*8*). The dotted lines correspond to the energies obtained by neglecting the long range interaction terms τ_a und τ_s.

Another type of interaction that suggests itself is the one between the CC σ-orbitals σ_a, σ_b of the double bonds 1,2 or 3,4 with π_b or π_a, respectively, which comes into play when $\varphi \neq 0°$ or 180°. It is found that the cross terms $\langle\sigma_a|\hat{H}|\pi_b\rangle = \langle\sigma_b|\hat{H}|\pi_a\rangle$ assume sizeable values, especially for $30° < \varphi < 150°$. However, the basis energies A_σ of σ_a and σ_b are so low ($A_\sigma \approx -22$ eV [23]) that the resulting perturbation of the π-orbital energies of **5** can be neglected in a first approximation.

Using the above data, we are now in a position to construct a simple *Hückel*-type model of the molecules **5** and **7**, which is of sufficient quality to allow an analysis of our experimental data. This model can be summarized in the following labeled graph, where the edges represent the cross terms, the dotted ones depending on φ as discussed above. The vertices labeled $\Phi_1(a)$ and $\Phi_4(a)$ refer to antisymmetric pseudo-π-orbitals of the terminal methyl groups in the molecules **7**. For **5**, the two vertices $\Phi_1(a)$ and $\Phi_4(a)$, including the edges leading to them, are removed from the graph (*8*). For this reference molecule, the π-orbital energies $\varepsilon(b_g(\pi))$ and $\varepsilon(a_u(\pi))$ obtained by diagonalizing the matrices corresponding to (*8*) are plotted as a function of φ in *Fig. 6, B* (solid lines). They are compared to the energies (dotted lines) that would have been obtained if the cross terms τ_s and τ_a had been neglected, *i.e.* if the dotted edges of the graph (*8*) had been removed. The difference between the two sets of curves illustrates nicely the collective effect due to the 'through space' interaction of the methyl group orbitals with the π-orbitals defined in (*6*). It is found that the interaction due to the cross-terms τ_s, τ_a leads to a calculated reduction of ΔI from 2.52 eV to 1.55 eV, *i.e.* by 38%, if $\varphi = 0°$ and that ΔI vanishes for $\varphi = 96°$. If $\varphi = 180°$ the 'through-space' reduction of ΔI is smaller, namely from 2.52 eV to 1.99 eV, or 21%.



(8)

If the matrix corresponding to the complete graph (*8*) is diagonalized, one obtains the $\varepsilon_{b_g(\pi)}$ and $\varepsilon_{a_u(\pi)}$ values of the molecules **7** as a function of φ. The result is the same as the one shown in *Fig. 6, B* for **5**, except for an upward shift of all curves by +0.45 eV.

From the information contained in *Fig. 4* and *6, A* it is now possible to derive a rough picture of what the first two bands ① ② in the PE spectra of **7**(*E,E*), **7**(*E,Z*) and **7**(*Z,Z*) should look like, *if* the angular dependence of the enthalpies of formation $\Delta_f H^{\ominus}$ shown in *Fig. 3* is accepted. First, one calculates an ionization energy density D(I), such that D(I)dI is proportional to the number of conformers exhibiting an ionization energy in the interval $I - dI/2$ to $I + dI/2$. This function is then folded with a gaussian G(X) (standard deviation $\sigma = 0.2$ eV), as a crude approximation for the individual (smoothed) band shapes, to yield

$$i(I) = \int_{-\infty}^{+\infty} D(X)G(X-I)dX \tag{9}$$

which is the *Franck-Condon* envelope (intensity i *vs.* ionization energy I) of the PE spectrum in the ionization energy range of interest. The results are presented in *Fig. 7*, for the three compounds **7** under discussion.

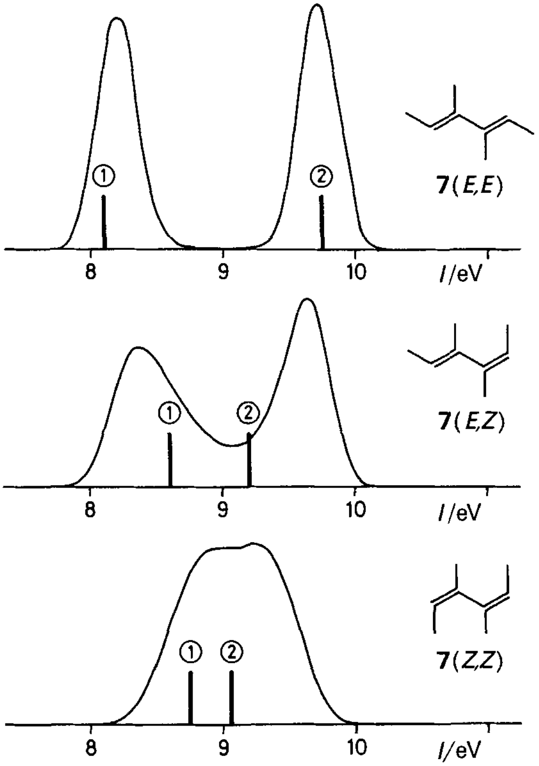


Fig. 7. *Convoluted spectra for* **7** *(E,E),* **7** *(E,Z) and* **7** *(Z,Z) based on the population curves P(φ) of* Fig. 4

It is immediately obvious that the PE spectra observed for **7**(*E,E*) and **7**(*Z,Z*) (*cf.* the vertical bars labeled ① and ② in *Fig. 7*, as well as the spectra presented in *Fig. 1*) agree very well with the results of our model. On the other hand the predicted envelope for **7**(*E,Z*) is incompatible with the observed one, which strongly suggests that the angular dependence of $\Delta_f H^{\ominus}$ *(cf. Fig. 3)*, and hence the conformer population density P(φ) *(cf. Fig. 4)*, of **7**(*E,Z*) is unreasonable. This supports the previous argument concerning the results of the electron diffraction experiment [15], which also suggest that the densities P(φ) of **7**(*E,Z*) and **7**(*Z,Z*) must be rather similar.

Conclusions. – From molecular models and the potential $V(\varphi)$ for internal rotation *(cf. Fig. 3)*, it is obvious that the preferred conformation of **8** is close to $\varphi \approx 80°$ to 90°, which agrees perfectly with the small gap of $\Delta I = 0.3_5$ eV between the bands ① and ②, as observed in its PE spectrum *(Fig. 2)*. Note that the results summarized in *Fig. 6,B* do not apply to **8**, because nothing is known about the 'through-space' coupling between a *tert*-butyl group and a π-orbital, due to the lack of relevant reference compounds. The bands ① and ② lack vibrational fine structure, as expected in view of the size of the substituents. At the other extreme, the two double bonds in **9** are held in a strictly antiplanar conformation $\varphi = 0°$ without significant deviations [24]. Although the gap ΔI is not as well defined as in the PE spectra of **1–8**, because of the overlap of the a_u (π)-band with σ-bands, one observes $\Delta I = 2.7$ eV. This is slightly larger, but close to the values found for **1**, **2**, **3** and **6** (*cf.* (*2*), [1–5]). However, the influence of the large σ-framework of **9**, in which the butadiene moiety is imbedded, is difficult to assess. Nevertheless, the ΔI values observed for the molecules **1–6** and for the pair **8**, **9** provide a safe background against which the results for **7**(*E,E*), **7**(*E,Z*) and **7**(*Z,Z*) can be evaluated:

a) From the correlation shown in *Fig. 5* and the comparison presented in *Fig. 7*, it is obvious that **7**(*E,E*) is peri-antiplanar with $\bar{\varphi} = 0°$ and, has presumably a mean amplitude of $\sim \pm 30°$. This agrees both with the structure determination by electron diffraction [12], with the electronic spectrum and also with the calculated potential $V(\varphi)$ for internal rotation (*Fig. 3* and *4*).

b) For the **7**(*Z,Z*) isomer, the PE spectroscopic data suggest a mean conformation close to that of **8**, *i.e.* $\varphi \approx 85$ to 105°, which are the values deduced from *Fig. 6,B* for $\Delta I = 0.3_5$ eV. It has been shown in *Fig. 7* that the main features of the PE spectrum expected on the basis of $V(\varphi)$ (*Fig. 3*) and thus of the population density $P(\varphi)$ (*Fig. 4*) are in rather good agreement with observation. In addition both the electronic spectrum [6] and the electron diffraction results [15] (*Fig. 4*) support the above conclusion about the preferred conformation of **7**(*Z,Z*).

c) As far as the agreement of the different data is concerned, **7**(*E,Z*) is definitely the odd-man-out. The PE-spectroscopic result that the gap between bands ① and ② is only $\Delta I = 0.6_0$ eV, strongly suggests that the conformation of this compound is much closer to that of **7**(*Z,Z*) or **8**, than of **7**(*E,E*). This is also supported by the electronic spectrum [6]. A conservative guess of the mean twist angle $\bar{\varphi}$ would be either $\approx 80°$ or 110° if ΔI is used as a measure. The latter value is compatible with the electron diffraction result, but it must be emphasized that a direct comparison is almost impossible because both types of measurement are influenced in a different manner by deviations of φ from its mean value. However, even if these uncertainties are taken into consideration, the experimental facts can not be reconciled with the potential $V(\varphi)$ for **7**(*E,Z*) shown in *Fig. 2* and the population density $P(\varphi)$ derived from it (*cf. Fig. 4*). The corrections suggested for $V(\varphi)$ consist of a lowering of the dip at $\varphi \sim > 90°$, relative to the local minimum at $\varphi \approx 45°$.

With regard to the above conclusions it should be mentioned that an analysis in terms of such a simple MO model as the one used in this work, although adequate in our opinion, must nevertheless be viewed with some caution. Concerning the difficulties that could arise the reader is referred to work by *Schweig et al.* [25], as well as to the references given therein.

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