[13] *D. A. MacInnes*, The Principle of Electrochemistry, Dover, New York 1961; N. Lakshminarayanaiah, Transport Phenomena in Membranes, Acad. Press, New York & London 1969.

[14] *P. Henderson*, Z. physikal. Chem. *59*, 118 (1907); *P. Henderson*, Z. physikal. Chem. *63*, 325 (1908).

[15] *K. Schwabe*, pH-Messtechnik, 3. Aufl., Th. Steinkopff, Dresden und Leipzig 1963; *R. G. Bates*, Determination of pH, Theory and Practice, Wiley, New York 1964.

[16] *I. Feldman*, Analyt. Chemistry *28*, 1859 (1956); *G. Milazzo*, Elektrochemie, Springer-Verlag, Wien 1952; *W. Simon & D. Wegmann*, Helv. *41*, 2308 (1958).

[17] *R. Huston & J. N. Butler*, Analyt. Chemistry *41*, 200 (1969); *K. Srinivasan & G. A. Rechnitz*, Analyt. Chemistry *41*, 1203 (1969); *G. J. Moody, R. B. Oke & J. D. R. Thomas*, Analyst *95*, 910 (1970); *M. Whitfield & J. V. Leyendekkers*, Analyt. Chemistry *42*, 444 (1970).

[18] *G. H. Griffiths, G. J. Moody & J. D. R. Thomas*, Analyst. *97*, 420 (1972).

[19] *A. H. Truesdell & C. L. Christ*, in *op. cit.* in [2].

[20] *R. P. Scholer & W. Simon*, Helv. *55*, 1801 (1972).

[21] *W. K. Lutz, H.-K. Wipf & W. Simon*, Helv. *53*, 1741 (1970).

[22] *W. Simon, W. E. Morf & P. Ch. Meier*, Structure and Bonding (1973), im Druck.

[23] *Z. Štefanac & W. Simon*, Chimia *20*, 436 (1966); Microchem. J. *12*, 125 (1967).

[24] *W. E. Morf & W. Simon*, Helv. *54*, 2683 (1971).

[25] *E. Munoz, F. Garcia-Ferrandiz & D. Vazquez*, Eds., Symposium on Molecular Mechanisms of Antibiotic Action on Protein Biosynthesis and Membranes, Granada/Spanien 1971, Elsevier Publishing Co., Amsterdam 1972; *H. K. Frensdorff*, J. Amer. chem. Soc. *93*, 600 (1971); *R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore & J. J. Christensen*, J. Amer. chem. Soc. *93*, 1619 (1971).

[26] *R. P. Scholer*, Dissertation ETH, Zürich 1972.

[27] *E. Eyal & G. A. Rechnitz*, Analyt. Chemistry *43*, 1090 (1971).

[28] *G. A. Rechnitz & E. Eyal*, Analyt. Chemistry *44*, 370 (1972).

[29] *D. Bright & M. R. Truter*, Nature *225*, 176 (1970); J. chem. Soc. (B) *1970*, 1544.

[30] *E. Koch & C. Wagner*, Z. physikal. Chem. (B) *38*, 295 (1937).

[31] *R. P. Buck*, Analyt. Chemistry *40*, 1432 (1968).

[32] *E. Pungor & K. Toth*, Analyst *95*, 625 (1970).

[33] *G. J. Moody & J. D. R. Thomas*, Selective Ion Sensitive Electrodes, Merrow Publishing Co., Watford, Herts, England 1971.

[34] *G. Kahr, W. E. Morf & W. Simon*, Helv. *56*, (1973), in Vorbereitung.

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97. The Ionization Potentials of Butadiene, Hexatriene, and their Methyl Derivatives: Evidence for Through Space Interaction between Double Bond π-Orbitals and Non-Bonded Pseudo-π Orbitals of Methyl Groups?¹)

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(12. II. 73)

Summary. It is shown that the correlation of the π-ionization potentials of ethylene (**1**), butadiene (**2**) and *trans*-1,3,5-hexatriene (**4**) favours the orbital sequence **π, π, σ** in butadiene and **π, π, σ, π** in the hexatriene in excellent agreement with the results of SPINDO calculations. Within the experimental error the π-ionization potentials of *cis*-1,3,5-hexatriene (**3**) and *trans*-

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¹) Part 48 of 'Applications of Photoelectron Spectroscopy' and Part XX of 'Photoelectron Spectra and Molecular Properties'. Parts 47 and XIX: [1].

1,3,5-hexatriene (**4**) are the same. Methyl-substitution of **2** lowers the π-ionization potentials $I_1(\pi)$ and $I_2(\pi)$. For 1 and/or 4 substitution the difference $I_2(\pi)-I_1(\pi)$ remains constant ($\approx$ 2.5 eV). On the other hand 2 and/or 3 substitution leads to a smaller gap of $I_2(\pi) - I_1(\pi) \approx$ 1.6 to 2.0 eV without changing the mean π-ionization potential $\overline{I}(\pi)$ relative to the corresponding 1,4 substituted derivatives. This result is rationalized in terms of a through space interaction between double bond π-orbitals and non-bonded pseudo-π-orbitals of the substituting methyl groups.

The reduced split $I_2(\pi) - I_1(\pi)$ in cyclopentadiene is attributed to hyperconjugation across the methylene group.

It is well established that the first band in the photoelectron (PE.) spectrum of ethylene (**1**) is due to the ejection of an electron from the π-orbital $\mathbf{1b_{1u}}(\pi)$; $I(\pi)$ 2) = 10.51 eV [2a, 3]. For butadiene (**2**) the assignment is perhaps not as uniquely determined as for **1**, but the majority of the evidence indicates that the first two PE.-bands correspond to an ionization process in which the photoelectron vacates one of the π-orbitals $\mathbf{1b_g}(\pi)$ or $\mathbf{1a_u}(\pi)$ ($I_1(\pi)$ = 9.03 eV; $I_2(\pi)$ = 11.46 eV 3) [2b, 4, 5, 6]). The analysis of the vibrational fine structure of the bands in the PE.-spectrum of **2** is not fully conclusive, but suggests the assumed orbital sequence $\boldsymbol{\pi, \pi, \sigma}$ [2b]. A study of the PE.-spectra of fluorinated derivatives of **2** [5] was originally thought to indicate the sequence $\boldsymbol{\pi, \sigma, \pi}$ but a reexamination seems also to favour $\boldsymbol{\pi, \pi, \sigma}$ [7]. *Ab initio* calculations of the electronic structure of **2** clearly indicate the sequence $\boldsymbol{\pi, \pi, \sigma}$ [8], in contrast to semi-empirical SCF-treatments (such as MINDO/2 [9]), which yield $\boldsymbol{\pi, \sigma, \pi}$. However, the latter type of model has been parametrized to reproduce thermochemical properties (*i.e.* all-electron properties) of neutral molecules and is known to predict systematically σ-orbitals lying too high. Consequently the relative orbital sequence of π- und σ-orbitals derived from such models is of little relevance. On the other hand, the SPINDO-model proposed by *Fridh, Åsbrink & Lindholm* [10], which has been parametrized to reproduce PE.-spectroscopic ionization potentials, gives the sequence $\boldsymbol{\pi, \pi, \sigma}$ [11] in agreement with the *ab initio* results. In our opinion, the strongest support for the correctness of the sequence $\boldsymbol{\pi, \pi, \sigma}$ is derived from the correlation of the band positions $I_1(\pi)$, $I_2(\pi)$ of **2** with those observed for the π-bands in the PE.-spectra of other π-systems (*e.g.* [12]) in particular with those of *cis*- and *trans*-1,3,5-hexatriene (**3**, **4**, see below).

In the present paper we shall be concerned with three problems:

a) the interpretation of the PE.-spectra of *cis*- and *trans*-1,3,5-hexatriene and of *all-trans*-1,3,5-heptatriene;

b) the influence of methyl substitution on the π-band positions in the PE.-spectrum of butadiene, and

c) the PE.-spectrum of cyclopentadiene.

Problem b) has recently been discussed by *Sustmann & Schubert* [6]. While we agree with them as far as the experimental data are concerned, our theoretical interpretation of the results differs sufficiently from theirs to justify the present reexamination.

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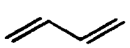
2) All ionization potentials I mentioned in the text refer to the position of the PE. band maximum. To a first approximation they are identical with the corresponding vertical ionization potential I_v (see tables).

3) For internal consistency all values quoted are those determined in the course of this work. They only differ marginally from values obtained by other authors.

The PE.-Spectra of *cis*- and *trans*-1,3,5-Hexatriene. Fig. 1a, 1b and 2 show the PE.-spectra of *cis*-1,3,5-hexatriene (**3**), *trans*-1,3,5-hexatriene (**4**) and of *all-trans*-1,3,5-heptatriene (**5**)[4]. The relevant data are assembled in Tab. 1.

$H_2C{=}CH_2$

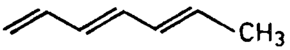
1



2

3

4



5

No doubt, the most striking feature is that the first pair of bands in the PE.-spectra of **3** and **4**, which are associated respectively with electron ejection from $\mathbf{2b_1}(\pi)$ and $\mathbf{1a_2}(\pi)$ of **3** (symmetry C_{2v}) or $\mathbf{2a_u}(\pi)$ and $\mathbf{1b_g}(\pi)$ of **4** (symmetry C_{2h}), are almost identical, both with respect to position and to vibrational fine structure, within the limits of error of measurement.

For this reason the samples of **3** and **4** used in our experiments have been carefully identified by their IR.- and UV.-spectra, which are in complete agreement with those given in the literature

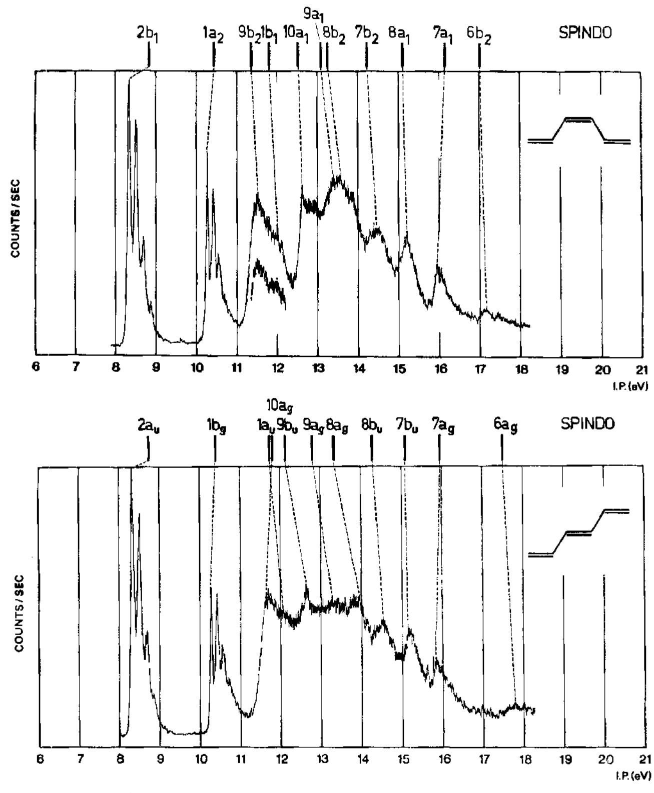


Fig. 1. *PE.-spectra of* cis-*1,3,5-hexatriene* (**3**) *and* trans-*1,3,5-hexatriene* (**4**). The vertical bars above the spectra correspond to the ionization potentials calculated by the SPINDO-method [10].

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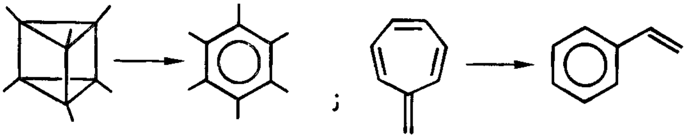
[4] We wish to thank *Dr. K. Egger* (Monsanto Research, Zürich) for the gift of a sample.

for pure **3** and **4** [13]. Furthermore, the gas-chromatograms of our samples indicate that the sample of **3** does not contain more than 0.9% of **4** and the sample of **4** not more than 1.1% of **3**.

In this connection it should be borne in mind that under the conditions prevailing in the spectrometer, **3** could in principle isomerize to the more stable **4**. Indeed, we have observed such isomerizations in previous instances, the most striking being the isomerization of hexamethylprismane to hexamethylbenzene and that of heptafulvene to styrene [14]:



However, we do not believe that such is the case in our experiment and we are convinced that the PE.-spectra shown in Fig. 1 are indeed those of pure **3** and **4**. This is supported by the observation that using different samples at different times the spectra are fully reproducible, within the limits of error, in particular in the range above 12 eV, where they strongly differ. Finally, the results of the SPINDO [10] calculations for **3** and **4**, which will be discussed below, are essentially in complete agreement with observation, as indicated in Fig. 1.

The position of the third band corresponding to the ejection of an electron from the lowest π-orbital $\mathbf{1b_1}(\pi)$ of **3** or $\mathbf{1a_u}(\pi)$ of **4** is uncertain, as it coincides with the onset of the band system associated with the σ-orbitals. From the analysis to be

Table 1. *Vertical ionization potentials* $I_{v,J}$ *of* cis-*1,3,5-hexatriene* (**3**), trans-*1,3,5-hexatriene* (**4**) *and* all-trans-*1,3,5-heptatriene* (**5**)

All values are given in eV. ψ_J: molecular orbitals .The assignment of the σ-orbitals of **3** and **4** is that obtained from the SPINDO calculation [10], as shown in Fig. 1. ε_J: SPINDO orbital energies.

	3 (C_{2v})			**4** (C_{2h})			**5**	
	ψ_J	$I_{v,J}$	$-\varepsilon_J$	ψ_J	$I_{v,J}$	$-\varepsilon_J$	$I_{v,J}$	J a)
π	$2\mathbf{b}_1$	8.32	8.88	$2\mathbf{a}_u$	8.29	8.89	8.07	①
π	$1\mathbf{a}_2$	10.27	10.51	$1\mathbf{b}_g$	10.26	10.55	10.07	②
	$9\mathbf{b}_2$	11.5	11.43	$10\mathbf{a}_g$	11.6	11.86 c)	?	
π	$1\mathbf{b}_1$	(11.9) b)	11.81	$1\mathbf{a}_u$	(11.9) b)	11.81 c)	11.56	③
	$10\mathbf{a}_1$	12.6	12.61	$9\mathbf{b}_u$	12.6	12.23	12.4	④
	$9\mathbf{a}_1$	13.4	13.18	$9\mathbf{a}_g$	13.3	12.93	13.0	⑤
	$8\mathbf{b}_2$	13.5	13.38	$8\mathbf{a}_g$	13.9	13.58	14.1	⑥
	$7\mathbf{b}_2$	14.5	14.29	$8\mathbf{b}_u$	14.5	14.38	15.5	⑦
	$8\mathbf{a}_1$	15.2	15.17	$7\mathbf{b}_u$	15.2	15.18	17.8	⑧
	$7\mathbf{a}_1$	16.0	16.29	$7\mathbf{a}_g$	15.9	16.12		
	$6\mathbf{b}_2$	17.2	16.98	$6\mathbf{a}_g$	17.8	17.60		
			d)			e)		

a) Number of PE.-band in Fig. 2.

b) Value uncertain, due to overlapping bands (see Fig. 1).

c) These orbital energies are interchanged, relative to the corresponding band positions (see Fig. 1).

d) Further orbitals: $6\mathbf{a}_1$, 18.75; $5\mathbf{b}_2$, 19.20; $5\mathbf{a}_1$, 22.49; $4\mathbf{b}_2$, 23.90; $4\mathbf{a}_1$, 25.21.

e) Further orbitals: $6\mathbf{b}_u$, 18.12; $5\mathbf{b}_u$, 19.36; $5\mathbf{a}_g$, 22.46; $4\mathbf{b}_u$, 24.05; $4\mathbf{a}_g$, 24.12.

described below we situate the third π-band in both cases near 11.9 eV. This means that the orbital sequence in **3** and **4** is π, π, σ, π (counting from the HOMO downwards) in analogy with what has been observed for fulvene [15] and for benzene [16], where the two highest occupied orbitals are degenerate.

In view of the similarity in the π-band positions observed for **3** and **4** we shall restrict the following discussion to **4**. The same arguments apply to **3**, except for a trivial change in the symmetry labels. The orbital correlation diagram for **1**, **2** and **4** is shown in Fig. 3.

Molecular Orbital Model. For qualitative or semiquantitative discussions it is of advantage to use simple molecular orbital models of the *Hückel*-type, such as the LCAO approximation

$$\psi = \sum_{\mu=1}^{2N} c_{\mu}\, \phi_{\mu} \tag{1}$$

N being the number of double bonds in the polyene. An alternative but completely equivalent way equivalent way of writing orbital (1) is

$$\psi = \sum_{j=1}^{N} (C_j \pi_j + C_j^* \pi_j^*) \tag{2}$$

where π_j and π_j^* are the bonding and antibonding two-centre π-orbitals associated with the double bond j:

$$\begin{aligned} \pi_j &= \frac{1}{\sqrt{2}} (\phi_{2j-1} + \phi_{2j}), \\ \pi_j^* &= \frac{1}{\sqrt{2}} (\phi_{2j-1} - \phi_{2j}). \end{aligned} \tag{3}$$

It is a well known fact that the *Hückel* LCAO approximation (1) exaggerates electron delocalization in polyenic systems, which in terms of (2) corresponds to an overemphasis of the contribution of the antibonding two-centre π-orbitals π_j^*. An obvious consequence of this is that the mean orbital energy

$$\bar{\varepsilon} = \frac{1}{N} \sum_{J=1}^{N} \varepsilon_J. \tag{4}$$

of the N bonding molecular orbitals $\psi_1, \psi_2 \ldots \psi_N$ is stabilized, *i.e.* shifts to lower (more negative) values, as N increases. Making use of *Koopmans'* theorem, *i.e.*

$$\begin{aligned} \varepsilon_J &= -I_J(\pi) \\ \bar{\varepsilon} &= \frac{-1}{N} \sum_{J=1}^{N} I_J(\pi) = \overline{-I(\pi)} \end{aligned} \tag{5}$$

we therefore expect that the mean ionization potential $\overline{I(\pi)}$ increases with increasing N. However, as shown for **1**, **2** and **4**, this is not the case ($\Delta\overline{I(\pi)}$ = change in $\overline{I(\pi)}$):

	N	$\bar{\varepsilon}$	$\overline{\Delta I(\pi)}_{\text{pred.}}$ [a]	$\overline{\Delta I(\pi)}_{\text{obs.}}$	
1	1	$\alpha + 1.000\beta$	0.00 eV	0.00 eV	
2	2	$\alpha + 1.118\beta$	+0.32 eV	−0.27 eV	(6)
4	3	$\alpha + 1.165\beta$	+0.45 eV	−0.36 eV	

[a] Calculated with $\beta = -2.70$ eV, obtained from a regressional analysis of PE.-data *vs.* HMO orbital energies.

Indeed the observed trend of $\overline{I(\pi)}$ has the opposite sign from that demanded by an LCAO treatment. Within the chosen model (2), the best approximation of the observed behaviour is obtained by neglecting the interaction with antibonding π_j^*-orbitals, *i.e.* setting $C_j^* = 0$ in expression (2). This leads to the LCBO model characterized by

$$\psi = \sum_{j=1}^{N} C_j \pi_j \tag{7}$$

which makes $\overline{I(\pi)}$ independent of N. To apply the LCBO model (7) in practice we have to define the following matrix elements with respect to the hamiltonian $\mathcal{H}$ of the polyene π-system:

$$A_j = \langle \pi_j | \mathcal{H} | \pi_j \rangle \qquad B_{ij} = \langle \pi_i | \mathcal{H} | \pi_j \rangle \tag{8}$$

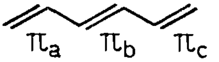
The model is easy to parametrize (*e.g.* [17]), if one uses experimentally observed π-ionization potentials $I_J(\pi)$ of reference systems and *Koopmans'* theorem (5).

LCBO-Model of Ethylene, Butadiene and Hexatriene. From the PE.-spectrum of **1** we obtain $A = -10.51$ eV, *i.e.* the π-orbital energy of a single 'unperturbed' π-bond. In **2**, the two π-orbitals π_a and π_b are symmetry equivalent, which demands $A_a = A_b = -\overline{I(\pi)} = -10.24_5$ eV. Thus, replacing a CH- by a CC-σ-orbital has lead to a destabilization of $A_a - A = \delta A = +0.26_5$ eV. The energy split $\varepsilon_1 - \varepsilon_2 = I_2(\pi) - I_1(\pi)$ between the orbital energies associated with the two LCBO-molecular orbitals

$$\psi_1 = \frac{1}{\sqrt{2}} (\pi_a - \pi_b) \qquad \psi_2 = \frac{1}{\sqrt{2}} (\pi_a + \pi_b) \tag{9}$$

is found to be 2.43 eV. As $\varepsilon_1 = A_a - B_{ab}$ and $\varepsilon_2 = A_a + B_{ab}$ we obtain $B_{ab} = -1.21_5$ eV, the negative sign corresponding to overlap controlled through-space interaction.

The usefulness of this very simple approximation can be demonstrated by calculating expectation values for *trans*-1,3,5-hexatriene (**4**) and by comparing them to those observed. We number the π-orbitals in **4** as follows:



(10)

The orbital energies $A_a = A_c$ of the terminal π-orbitals π_a and π_c should be equal to those in **2**, *i.e.* $A_a = A_c = -10.25$ eV. On the other hand, we expect A_b to be destabilized roughly by $2 \cdot \delta A = 0.52$ eV relative to $A = -10.51$ eV in **1**, which leads to $A_b = -9.99$ eV. The interaction elements $B_{ab} = B_{bc} = -1.21_5$ eV are postulated to be the same as in **2** and we shall furthermore assume $B_{ac} = 0$. Solving the third order secular problem defined by (7) with N = 3 yields the following result:

$$\begin{aligned}
\psi_1 &= 0.481\,\pi_a - 0.733\,\pi_b + 0.481\,\pi_c;\ \varepsilon_1 = -\ 8.40\ \text{eV};\ I_1(\pi) = \ 8.29\ \text{eV}\\
\psi_2 &= 0.707\,\pi_a \qquad\qquad\quad\ - 0.707\,\pi_c;\ \varepsilon_2 = -10.25\ \text{eV};\ I_2(\pi) = 10.26\ \text{eV}\\
\psi_3 &= 0.519\,\pi_a + 0.680\,\pi_b + 0.519\,\pi_c;\ \varepsilon_3 = -11.84\ \text{eV};\ I_3(\pi) = 11.9\ \ \text{eV}
\end{aligned} \tag{11}$$

A comparison of ε_J with the observed π-ionization potentials $I_J(\pi)$ shows that the agreement is as good as can reasonably be expected.

SPINDO-Model of *cis*- and *trans*-1,3,5-Hexatriene. The assignment (11) of the bands at positions 8.3, 10.3 and 11.9 eV in the PE.-spectrum of **4** (and thus in the spectrum of **3**) to the three π-orbitals is convincingly supported by the results of a SPINDO calculation [10] for **3** and **4**. The structure parameters used for **4** are those derived by *Haugen* & *Traetteberg* from electron diffraction experiments [18]: R(C(1)=C(2)) = R(C(3)=C(4)) = 1.345 Å; R(C(2)–C(3)) = 1.450 Å; ∢(C(1)C(2)C(3)) = ∢(C(2)C(3)C(4)) = 124°; ∢(HC=C) = 118°; Symmetry C_{2h}. Furthermore we have assumed R(C–H) = 1.09 Å. The model parameters are those given in [10]. The same interatomic distances and bond angles have been used for **3**, imposing strict C_{2v} symmetry. Note that this structure may be slightly in error because of the forced closeness of the hydrogen atoms in positions 2 and 5.

The *Koopmans* ionization potentials derived in this way for **3** and **4** are given in Tab. 1 and displayed graphically in Fig. 1. The striking agreement between calculated and observed band positions leaves little doubt that our assignment (see Fig. 1 and (11)) is reasonable. At the same time it confirms that the SPINDO model is a reliable tool for the interpretation of PE.-spectra, at least of planar unsaturated molecules.

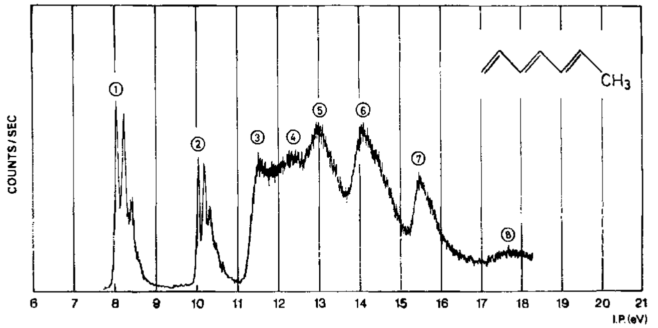


Fig. 2. *PE.-spectrum of* all-trans-*1,3,5-heptatriene* (**5**)

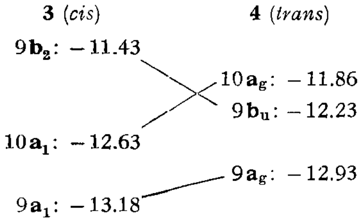
An important conclusion derived from the SPINDO-model is that the observed insensitivity of the π-orbital energies on *cis-trans* isomerism is indeed what would have been expected:

SPINDO-π-orbital energies (in eV):

3 (*cis*)	$2b_1$: −8.88	$1a_2$: −10.51	$1b_1$: −11.81	(12)
4 (*trans*)	$2a_u$: −8.89	$1b_g$: −10.55	$1a_u$: −11.81	

In contrast, the highest occupied σ-orbitals of **3** and **4** differ noticeably in energy. Again the calculated orbital energies reflect the observed changes in the envelope of the σ-band systems of **3** and **4**, especially in the critical region around 12 eV to 14 eV (see Fig. 1). Consider in particular the upper three σ-orbitals of **3** and **4**. (Note that *cis-trans* isomerisation will transform orbitals $\mathbf{a}_1$ into $\mathbf{a}_g$ and $\mathbf{b}_2$ into $\mathbf{b}_u$).

SPINDO-σ-orbital energies (in eV)



(13)

In **3** these orbitals are widely spaced (gaps of 1.20 eV and 0.55 eV respectively), while they are close together in **4** (gaps of 0.37 eV and 0.70 eV). This explains nicely the characteristic difference observed in the envelopes of the corresponding σ-band systems, in particular the large minimum near 12 eV in the PE.-spectrum of **3**, which is absent in that of **4**. Looking at the SPINDO linear combinations of **3**, which belong to the irreducible representations A_1 and B_2 of C_{2v} one notices that the reasons

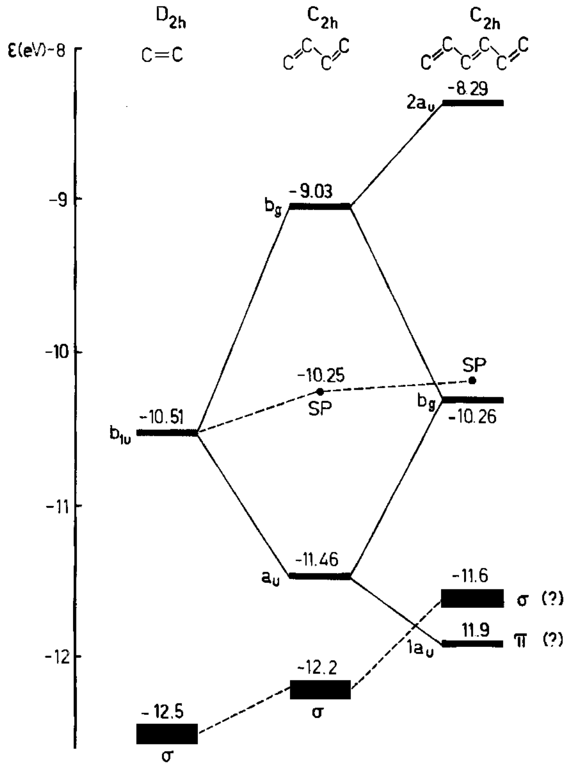
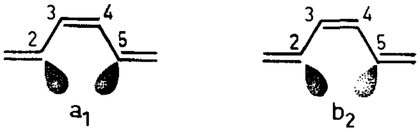


Fig. 3. *Correlation diagram for the π-orbitals of ethylene* (**1**), *butadiene* (**2**) *and* trans-*1,3,5-hexatriene* (**4**)

for the observed shifts are the through space interactions of the orbitals σ-C(2)H(2) and/or σ-C(2)C(3) with σ-C(5)H(5) and/or σ-C(4)C(5) in **3**, which stabilize all $\mathbf{a_1}$ and destabilize the $\mathbf{b_2}$ orbitals relative to their $\mathbf{a_g}$ or $\mathbf{b_u}$ counter parts in **4**, e.g.:



(14)

This is shown in more detail in the diagram of Fig. 4.

Dependence of π-Ionization Potentials on Methyl-Substitution. Methyl-substitution of a π-system shifts the π-ionization potentials towards lower values. Typical examples are the methyl derivatives of **1** [19] and of benzene [20], which have been extensively investigated both experimentally and theoretically. A recent investigation of the PE.-spectra of 6-alkyl-substituted fulvenes [21] has shown that a true understanding of the electronic mechanism, which leads to the lowering of the π-ionization potentials in alkyl-substituted, unsaturated hydrocarbons, can only be gained by means of a many electron treatment. In addition it is necessary to treat separately the case of the neutral π-system M and that of the radical cation M^+ in the electronic state resulting by photoejection of an electron from the orbital ψ_J, *i.e.*

$$M + h\nu \rightarrow M^+ (\psi_J^{-1}) + e^-, \qquad (15)$$

in particular if ψ_J is localized in a part of the molecule M remote from the point of substitution. However, if ψ_J extends over the whole molecule M, *i.e.* if the positive charge in the radical cation $M^+(\psi_J^{-1})$ is not localized in one part of the system only, then the influence of a methyl substituent may be treated as an inductive and/or hyperconjugative perturbation in the framework of an independent electron model of the *Hückel* type.

We assign to a methyl group a pair of degenerate pseudo-π-orbitals, using the CH-σ-orbitals as a basis:

$$\begin{aligned} \pi'(CH_3) &= \frac{1}{\sqrt{2}} (\sigma_1 - \sigma_2), \\ \pi''(CH_3) &= \frac{1}{\sqrt{6}} (\sigma_1 + \sigma_2 - 2\sigma_3). \end{aligned} \qquad (16)$$

Their orbital energy is A_{CH_3}. Depending on the conformation of the methyl group relative to the substituted π-system, a linear combination of $\pi'(CH_3)$ and $\pi''(CH_3)$, which we shall abbreviate by $\pi(CH_3)$, will interact with the LCBO-molecular orbitals ψ_J of the polyene. If $\mathcal{H}$ is the hamiltonian of the unsubstituted polyene and $\mathcal{H}' = \mathcal{H} + \mathfrak{h}$ that of the substituted one, then the perturbation of the orbital energy ε_J of ψ_J is determined by two effects, namely

a) the inductive effect

$$\delta\varepsilon_J(\text{ind.}) = \langle\psi_J|\mathfrak{h}|\psi_J\rangle = C_{Jk}^2\langle\pi_k|\mathfrak{h}|\pi_k\rangle \qquad (17)$$

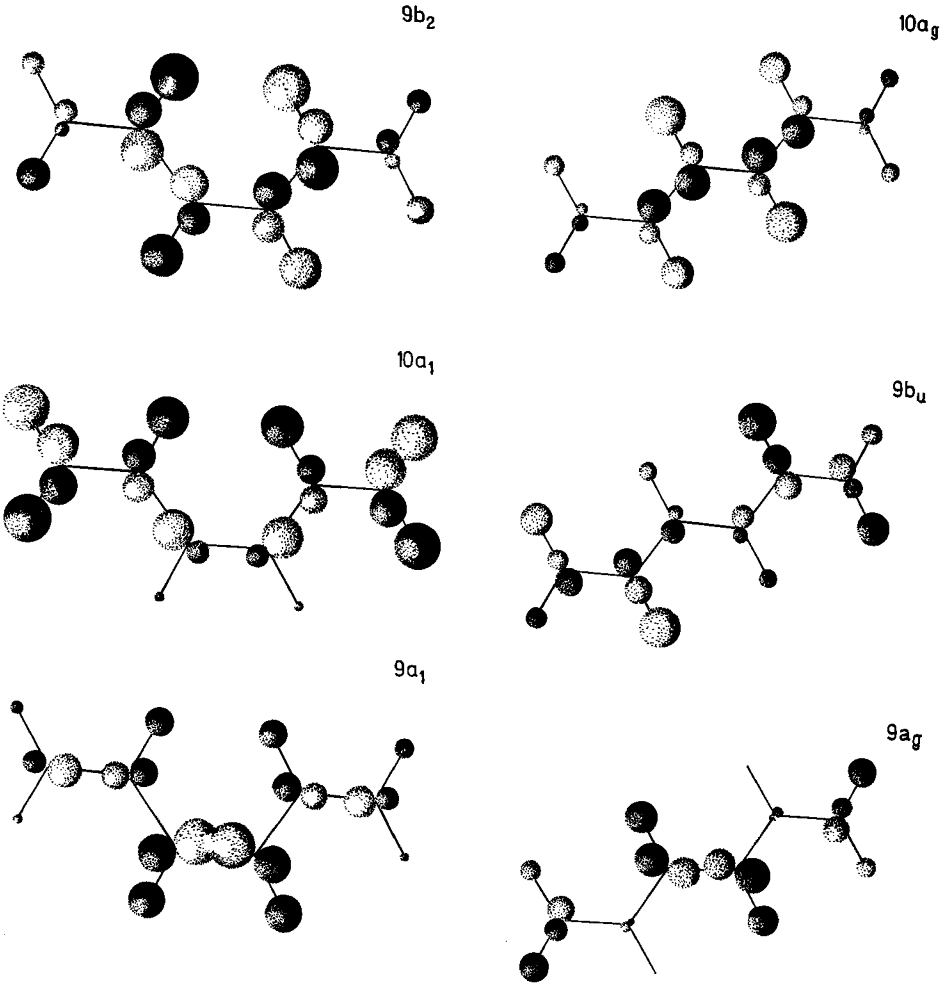


Fig. 4. *Computer drawn orbital diagrams for the three highest occupied σ-orbitals of* cis- *and* trans-*1,3,5-hexatriene* (see (13)).

b) the hyperconjugative effect

$$\delta\varepsilon_J(\text{hyper conj.}) = \frac{\langle\psi_J|\mathfrak{h}|\pi(\mathrm{CH_3})\rangle^2}{\varepsilon_J - A_{\mathrm{CH_3}}} = C_{Jk}^2\,\frac{\langle\pi_k|\mathfrak{h}|\pi(\mathrm{CH_3})\rangle^2}{\varepsilon_J - A_{\mathrm{CH_3}}}. \tag{18}$$

In (17) and (18) π_k is the two-centre π-orbital of the substituted double bond. The total perturbation is thus:

$$\delta\varepsilon_J = C_{Jk}^2\left(\langle\pi_k|\mathfrak{h}|\pi_k\rangle + \frac{\langle\pi_k|\mathfrak{h}|\pi(\mathrm{CH_3})\rangle^2}{\varepsilon_J - A_{\mathrm{CH_3}}}\right). \tag{19}$$

Within the limitations of our LCBO model we may assume that $\varepsilon_J - A_{\mathrm{CH_3}}$, and thus the expression in brackets, is practically independent of J, in which case (19) becomes

$$\delta\varepsilon_J = C_{Jk}^2 \cdot \delta A' \tag{20}$$

Thus we are not in a position to discriminate at that level of approximation between an inductive and a hyperconjugative mechanism.

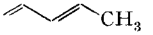
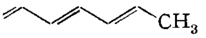
If the k-th double bond of a polyene containing N double bonds is substituted by a single methyl group, the shifts $\delta\varepsilon_J$ $(J = 1, 2 \dots N)$ given by (20), must satisfy the condition

$$\sum_{J=1}^{N} \delta\varepsilon_J = \delta A' \sum_{J=1}^{N} C_{Jk}^2 = \delta A' . \tag{21}$$

Applying *Koopmans'* theorem we expect therefore the following sum rule for the shifts $\delta I_J(\pi)$ of the N π-ionization potentials

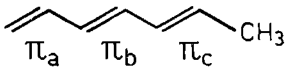
$$\sum_{J=1}^{N} \delta I_J(\pi) = -\delta A' = \text{constant}. \tag{22}$$

As the following examples show, this is what is observed (values in eV):

$CH_2{=}CH_2$	$CH_2{=}CH{-}CH_3$		
$I_1(\pi) = 10.51$	$I'_1(\pi) = 9.73$	$\delta I_1(\pi) = -0.78$	
		$\sum \delta I_J(\pi) = -0.78$	
			
$I_1(\pi) = 9.03$	$I'_1(\pi) = 8.61$	$\delta I_1(\pi) = -0.42$	
$I_2(\pi) = 11.46$	$I'_2(\pi) = 11.10$	$\delta I_2(\pi) = -0.36$	(23)
		$\sum \delta I_J(\pi) = -0.78$	
			
$I_1(\pi) = 8.29$	$I'_1(\pi) = 8.07$	$\delta I_1(\pi) = -0.22$	
$I_2(\pi) = 10.26$	$I'_2(\pi) = 10.07$	$\delta I_2(\pi) = -0.19$	
$I_3(\pi) = 11.9$	$I'_3(\pi) = 11.56$	$\delta I_3(\pi) = -0.34$	
		$\sum \delta I_J(\pi) = -0.75$	

It follows that $\delta A' = 0.8$ eV is a reasonable perturbation to be used for mono-substitution by a methyl group in the ω-position of a polyene.

With reference to the LCBO model (10) used for **4** we now assign the following basis orbital energies to an analogous model of *all-trans*-1,3,5-heptatriene (**5**):



$$\begin{aligned} A_a &= -10.25 \text{ eV} \\ A_b &= -\ \ 9.99 \text{ eV} \\ A_c &= A_a + \delta A' = -9.47 \text{ eV} \end{aligned} \tag{24}$$

The interaction matrix elements are the same as before, *i.e.* $B_{ab} = B_{bc} = -1.215$ eV, $B_{ac} = 0$. This yields the following π-orbital energies ε_J for **5**,

$$\begin{array}{ll} \varepsilon_1 = -\ \ 8.16\ \text{eV}; & I_1(\pi) = \ \ 8.07 \\ \varepsilon_2 = -\ \ 9.87\ \text{eV}; & I_2(\pi) = 10.07 \\ \varepsilon_3 = -11.69\ \text{eV}; & I_3(\pi) = 11.56 \end{array} \qquad (25)$$

in reasonable agreement with the observed π-ionization potentials $I_J(\pi)$.

Substitution by more than one methyl group at the same double bond leads to smaller perturbations $\delta A'$ per methyl group than mono-substitution. For example [19]:

$$\mathrm{H_2C{=}CH_2} \longrightarrow \left\{ \begin{array}{ll} \mathrm{CH_2 = CHMe} & \delta A' = 0.78\ \text{eV} \\ \mathrm{MeHC = CHMe} & \delta A' = 0.69\ \text{eV} \\ \textit{cis, trans} & \\ \mathrm{Me_2C = CH_2} & \delta A' = 0.64\ \text{eV} \\ \mathrm{Me_2C = CHMe} & \delta A' = 0.61\ \text{eV} \\ \mathrm{Me_2C = CMe_2} & \delta A' = 0.55\ \text{eV} \end{array} \right. \qquad (26)$$

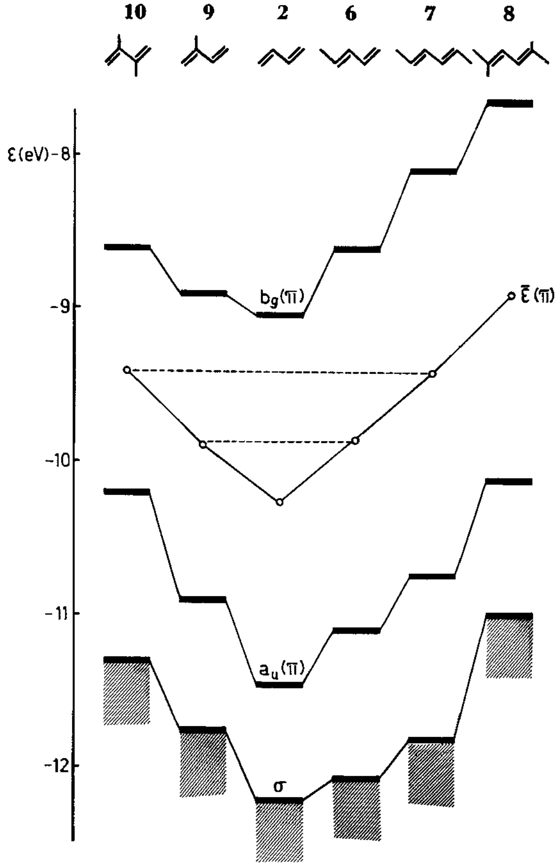


Fig. 5. *Correlation diagram for the π-orbitals in methyl-substituted butadienes.* The relevant data are taken from Table 2.

Table 2. *Vertical ionization potentials $I_{v,J}$ of methyl-substituted butadienes.* All energies in eV. The assignment of orbitals to band positions for the molecules **2**, **7** and **10** of symmetry C_{2h} is based on the results of SPINDO calculations [10]; orbital energies ε_J.

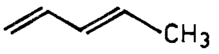
	2 (C_{2h})			**6** (C_s)		**7** (C_{2h})			**8** (C_{2h})		**9** (C_s)		**10** (C_{2h})		
	ψ_J	$I_{v,J}$	$-\varepsilon_J$ [a]	ψ_J	$I_{v,J}$	ψ_J	$I_{v,J}$	$-\varepsilon_J$	ψ_J	$I_{v,J}$	ψ_J	$I_{v,J}$	ψ_J	$I_{v,J}$	$-\varepsilon_J$
π	$1b_g$	9.03	9.41	$3a''$	8.61	$2b_g$	8.09	9.25	$3b_g$	7.83 [b]	$3a''$	8.89	$2b_g$	8.62	9.44
π	$1a_u$	11.46	11.40	$2a''$	11.10	$2a_u$	10.6	11.06	$3a_u$	10.12	$2a''$	10.9	$2a_u$	10.18	10.83
	$7a_g$	12.23	11.89		11.9	$10a_g$	11.7	11.89		11.0		11.8	$10a_g$	11.3	11.74
	$6b_u$	13.0	12.91			$9b_u$	12.0	12.62				12.9	$9a_g$	11.6	12.65
	$6a_g$	13.3	13.44			$9a_g$	12.9	12.88				15.3	$9b_u$	12.1	13.16
	$5a_g$	15.3	15.33			$8a_g$	13.1	13.36				17.1	$8a_g$		13.54
	$5b_u$	?	15.42			$8b_u$		13.72					$8b_u$		13.78
	$4b_u$	17.9	17.87			$1b_g$		14.12					$1b_g$	14.0	13.95
						$1a_u$	14.5	14.20					$1a_u$		14.43
						$7b_u$	14.8	14.81					$7a_u$		15.82
						$7a_g$	(15.7)	15.82							

[a] This work; cf. [11].

[b] $I_{a,J} = 7.65$; the adiabatic ionization potentials $I_{a,J}$ of the π-orbitals of **2**, **6**, **7**, **9**, **10** are coincident with their vertical ionization potentials $I_{v,J}$.

We shall now turn our attention to the set of methyl substituted butadienes **6** to **10**, which has already been studied by *Sustman* & *Schubert* [6]. The relevant data are assembled in Tab. 2 and displayed in the correlation diagram of Fig. 5.

As shown in (23) mono-substitution in position 1 yielded according to (22) a perturbation $\delta A' = 0.78$ eV to be applied to the energy of the basis orbital π_a. The analogous treatment of derivatives **6** to **10** yields:



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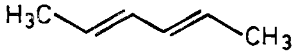

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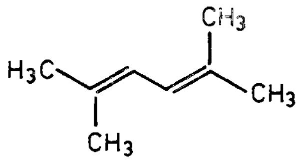

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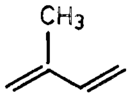

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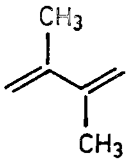


10

Compound	**6**	**7**	**8**	**9**	**10**	
$\delta A' =$	0.78	0.83	0.68	0.73	0.85 eV	(27)

Thus to a first approximation $\delta A'$ is the same for all derivatives with the exception of **8** for which a slightly smaller $\delta A'$ was expected on the basis of the trend shown in (26). As a consequence the mean π-ionization potentials (5) are the same within the limits of error of our experiment for the pairs **6**, **9** and **7**, **10** as indicated in the correlation diagram of Fig. 5.

In the series **2**, **6**, **7**, **8** *i.e.* in butadiene and derivatives carrying a methyl group in positions 1 and 4 the difference $I_2(\pi) - I_1(\pi) = \varepsilon_1 - \varepsilon_2$ and consequently the interaction parameter B_{ab} are constant:

	$I_2(\pi) - I_1(\pi)$	B_{ab}	
2	2.43 eV	−1.215 eV	
6	2.49 eV	−1.245 eV	
7	2.51 eV	−1.255 eV	(28)
8	2.47 eV	−1.235 eV	
		mean: −1.238 ± 0.015 eV	

The results summarized in (27) and (28) are exactly those predicted by the LCBO-model (9), which we had assumed to be representative for butadiene and found to be also valid for the hexatrienes **3** and **4** and the methyl derivative **5**.

The surprising result of *Sustmann* & *Schubert*'s [6] and of our investigation is that the split $I_2(\pi) - I_1(\pi)$ found for the two derivatives of **2** having methyl groups at the inner positions 2 and 3 are significantly smaller than those given in (28), notwithstanding the fact that the mean ionization potential $I(\pi)$ is the same as that found for the isomers with the substituent in positions 1 and 4:

$$\begin{array}{lll} & I_2(\pi) - I_1(\pi) & B_{\mathrm{ab}} \\ \mathbf{9} & 1.98\ \mathrm{eV} & -0.99\ \mathrm{eV} \\ \mathbf{10} & 1.56\ \mathrm{eV} & -0.78\ \mathrm{eV} \end{array} \qquad (29)$$

Assuming that the LCBO model is still valid for **9** and **10**, two explanations have to be considered.

In view of the fact that $I_1(\pi)$ and $I_2(\pi)$ of **9** and **10** lie symmetrically with respect to the mean ionization potential $\overline{I(\pi)}$ observed for **6** and **7**, the reduction in split could in principle be due to a change in conformation of the butadiene system, *i.e.* to a twist around the central single bond. If this twist angle were ω (with $\omega = 0$ for the planar system), we should have as a first approximation

$$B_{\mathrm{ab}}(\omega) = B_{\mathrm{ab}}(0) \cdot \cos\omega \qquad (30)$$

With $B_{\mathrm{ab}}(0) = -1.24$ eV from (25), the values given in (29) would demand twist angles of $\omega = 37°$ and $\omega = 51°$ for **9** and **10** respectively. However, such an explanation can certainly be dismissed. Electron diffraction has shown that 2,3-dimethylbutadiene (**9**) is planar within the limits $\omega = \pm 3°$ [22]. This result is supported by the electronic spectra of **2** and its methyl derivatives **6**, **7**, **9** and **10**. It is known that the intensity of the $\pi^* \leftarrow \pi$ transition at 210 ± 10 nm is strongly dependent on ω [23]. Nevertheless, the ω_{max}-values observed for **2** and the methyl derivatives mentioned above, are the same: **2**, 21,000; **6**, 23,000; **7**, 24,000; **9**, 25,000; **10**, 22,000 [24]. Furthermore the X-ray structure determination of polyenes carrying methyl substituents along the chain *e.g.* carotenoids and related compounds, yield no indication for significant deviations from planarity [25].

Sustmann & *Schubert*'s interpretation of the PE.-spectra of **6**, **7**, **9** and **10** [6] rests in the assumption that the orbital sequence is π, σ, π rather than π, π, σ. The observed shifts of the orbitals $\mathbf{b}_{\mathrm{g}}(\pi)$ and $\mathbf{a}_{\mathrm{u}}(\pi)$ are then accounted for by a simple perturbation model of the type defined in (17) or (20).

If the accepted order is π, π, σ, this type of treatment leads to contradictions. An HMO-model (1) of **2**, which accounts for the bond alternation is obtained by assigning to the bonds 1, 2 and 3, 4 resonance integrale $\beta_{1,2} = \beta_{1,3} = \beta$ and a resonance integral $\beta_{2,3} = \beta' = \mathrm{m}\beta$ (m < 1) to the central bond 2, 3. The linear combinations $\mathbf{a}_{\mathrm{u}}(\pi)$, $\mathbf{b}_{\mathrm{g}}(\pi)$ and their corresponding orbital energies are

$$\begin{aligned} \mathbf{a}_{\mathrm{u}}(\pi) &= \mathrm{a}\,(\phi_1 + \phi_4) + \mathrm{b}\,(\phi_2 + \phi_3) \\ \mathbf{b}_{\mathrm{g}}(\pi) &= \mathrm{b}\,(\phi_1 - \phi_4) + \mathrm{a}\,(\phi_2 + \phi_3) \\ \varepsilon(\mathbf{a}_{\mathrm{u}}(\pi)) &= \alpha + (\sqrt{\mathrm{m}^2 + 4} + \mathrm{m})\,\beta/2 \\ \varepsilon(\mathbf{b}_{\mathrm{g}}(\pi)) &= \alpha + (\sqrt{\mathrm{m}^2 + 4} - \mathrm{m})\,\beta/2 \end{aligned} \qquad (31)$$

Depending on whether the methyl substituents are in positions 1, 4 or 2, 3 we obtain from a first order perturbation treatment

$$\frac{\delta\varepsilon(\mathbf{a}_{\mathrm{u}}(\pi))}{\delta\varepsilon(\mathbf{b}_{\mathrm{g}}(\pi))} = \begin{cases} \mathrm{a}^2/\mathrm{b}^2 & (1,4\text{-subst.}) \\ \mathrm{b}^2/\mathrm{a}^2 & (2,3\text{-subst.}) \end{cases} \qquad (32)$$

This ratio depends on m as follows:

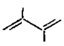
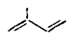
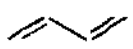
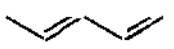
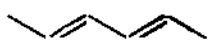
$$\begin{array}{llllll} \mathrm{m} = 0.0 & 0.1 & 0.2 & 0.3 & 0.4 & 0.5 \ldots 1.0 \\ \mathrm{a}^2/\mathrm{b}^2 = 1.00 & 1.11 & 1.22 & 1.35 & 1.49 & 1.64 \ldots 2.62 \end{array} \qquad (33)$$

The observed ratios (according to (32)) are $a^2/b^2 = 1.3$ for 1.4 substitution and $a^2/b^2 = 3.1$ for 2,3 substitution, *i.e.* they are incompatible within our model. Furthermore, the ratio $a^2/b^2 = 1.3$ demands $m \approx 0.3$ according to (33). As the orbital gap calculated from (31) is

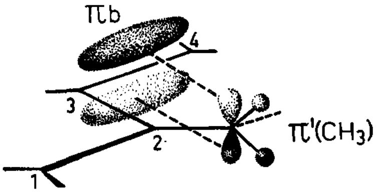
$$\Delta = \varepsilon(\mathbf{b}_g(\pi)) - \varepsilon(\mathbf{a}_u(\pi)) = -m\beta \tag{34}$$

we should have to assign a value of $\beta \approx -8$ eV to the resonance integral if we want to reproduce the observed spacing $\Delta = 2.4$ eV. Finally $a^2/b^2 = 3.1$ would lead to $m > 1$, which is absurd.

Table 3. *Results of a CNDO/2 calculation for methyl substituted butadienes*
Method and parameters as described in ref. [26].

	10 	**9** 	**2** 	**6** 	**7** 
$-\varepsilon(\mathbf{b}_g(\pi))$	10.19	10.29	10.43	10.08	9.77
$-\varepsilon(\mathbf{a}_u(\pi))$	12.47	13.02	13.59	13.23	12.84
$I_2(\pi) - I_1(\pi)$	2.28	2.73	3.16	3.15	3.07
$\overline{I(\pi)}$	11.33	11.66	12.01	11.66	11.31

A different and theoretically attractive explanation is suggested by the results of CNDO/2 [26] calculation (summarized in Tab. 3) which qualitatively reproduce the important trends observed in our spectra: same mean ionization potential $\overline{I(\pi)}$ for the pairs **6**, **9** and **7**, **10**; constant decrease of $\overline{I(\pi)}$ per methyl group relative to $\overline{I(\pi)}$ of **2**; constant split $\Delta = I_2(\pi) - I_1(\pi)$ for **2**, **6** and **7**; decreased splits Δ for **9** and **10**. An analysis of the CNDO/2 wave functions reveals that the decrease in split for **9** and **10** is due mainly to a through-space interaction of the pseudo π-orbitals, $\pi'(CH_3)$ and/or $\pi''(CH_3)$ (16), of the methyl groups in positions 2 and 3 with π-orbitals π_b and π_a respectively, as indicated for the pair $\pi'(CH_3)$ (in position 2) and π_b (bond 3,4) in the following diagram.



(35)

That such long-range interactions can be of importance has been pointed out by *Hoffmann* [27]. If this concept of through space interaction is incorporated in our LCBO model, then the correlation diagram shown in Fig. 6 is obtained, where the symmetrically substituted derivatives **7** and **10** have been chosen as examples.

The diagram is almost selfexplanatory. Both for **7** and for **10** the starting points are the orbitals (9) of butadiene, *i.e.* $\psi_1 \equiv \mathbf{b}_g(\pi)$ and $\psi_2 \equiv \mathbf{a}_u(\pi)$. As indicated in (32) we arbitrarily assume conformations of the methyl groups in positions r, s = 1,4 (**7**)

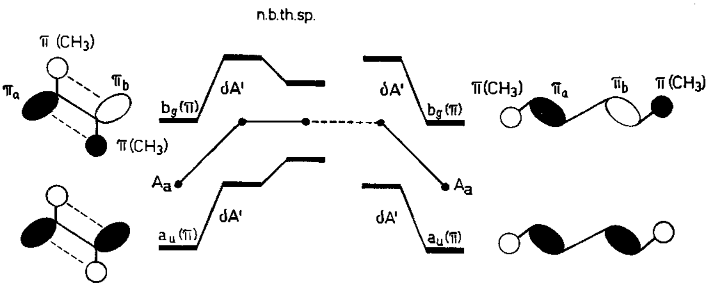


Fig. 6. *Correlation diagram showing the influence of non-bonded through space interaction* (*n. b. th. sp.*) *between the pseudo-π-orbitals* $\pi(CH_3)$ (*circles*) *and the double bond π-orbitals* π_a, π_b (*ovals*) *on the π-orbital energies of* $\mathbf{b}_g(\pi)$ *and* $\mathbf{a}_u(\pi)$ *in* **10**. The full dots denote the mean $[\varepsilon(\mathbf{b}_g(\pi))+\varepsilon(\mathbf{a}_u(\pi))]/2$. A_a is the basis orbital energy in **2** and $\delta A'$ the destabilization defined in (19) through (22).

or 2,3 (**10**), which make $\pi_r' \equiv \pi_r'$ (CH_3) antisymmetric with respect to the molecular plane. The symmetry-adapted linear combinations of these pseudo-π-orbitals are

$$\begin{aligned}\pi'(B_g) &= (\pi_r' - \pi_s')/\sqrt{2}\\ \pi'(A_u) &= (\pi_r' + \pi_s')/\sqrt{2}\end{aligned} \qquad (36)$$

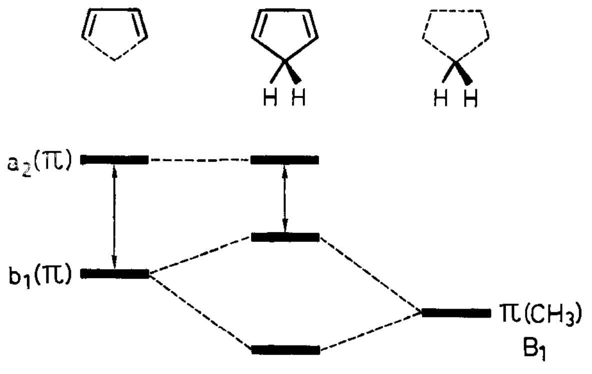
Both these linear combinations are out of phase with $\mathbf{b}_g(\pi)$ and $\mathbf{a}_u(\pi)$ respectively, thus contributing to the destabilization $\delta A'$ (see (16) and (17)), which is the same for both orbitals and for both systems **7** and **10**. In the case of **10** we have an additional interaction (indicated in Fig. 6 by dotted lines), which destabilizes the $\mathbf{a}_u(\pi)$- and stabilizes the $\mathbf{b}_g(\pi)$-orbital. This reduces the gap between these orbitals in **10** without shifting the mean orbital energy, as indicated in the correlation diagram (n. b. th. sp. = non-bonded through space interaction).

As a final example we discuss briefly the PE.-spectroscopic results for cyclopentadiene **11** (cf. [28]).

11

The most noteable feature is that the difference $I_2(\pi) - I_1(\pi) = \varepsilon(\mathbf{a}_2(\pi)) - \varepsilon(\mathbf{b}_1(\pi)) =$ 2.16 eV is noticeably smaller than for the linear dienes discussed above (2.48 ± 0.03 eV; see (28)) and for 1,3-cyclohexadiene (2.53 eV; [28]). Through space interaction between the centres 1 and 4 of the diene system in **11** would tend to increase $I_2(\pi) - I_1(\pi)$, but extrapolation of the results observed for *cis*- and *trans*-1,3,5-hexatriene suggests that this is presumably a negligible effect.

We ascribe the reduction of the π-orbital gap in **11** to the hyperconjugative interaction with the pseudo-π-orbital of the methylene bridge. This orbital belongs to the irreducible representation B_1 and can therefore interact only with the low lying π-orbital $\mathbf{b}_1(\pi)$ of the diene moiety, as shown qualitatively in the following diagramm:



(37)

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BIBLIOGRAPHY

[1] *Ch. Batich, O. Ermer, E. Heilbronner & J. R. Wiseman,* Angew. Chem., in print; *H. Stafast & H. Bock, ibid.*, in print.

[2] *D. W. Turner, C. Baker, A. D. Baker & C. R. Brundle,* 'Molecular Photoelectron Spectroscopy', Wiley-Interscience, London 1970; a: p. 166, b: p. 168.

[3] *G. R. Branton, D. C. Frost, T. Makita, C. A. McDowell & I. A. Stenhouse,* J. chem. Physics *52,* 802 (1970); *C. R. Brundle, M. B. Robin, H. Basch, M. Pinsky & A. Bond,* J. Amer. chem. Soc. *92,* 3863 (1970); *J. M. Hollas & T. A. Sutherley,* Mol. Physics *21,* 183 (1971); *C. R. Brundle & D. B. Brown,* Spectrochim. Acta *27A,* 2491 (1971).

[4] *M. J. S. Dewar & S. D. Worley,* J. chem. Physics *49,* 2454 (1968); *J. H. D. Eland,* Int. J. Mass Spectrom. Ion Physics *2,* 471 (1969).

[5] *C. R. Brundle & M. B. Robin,* J. Amer. chem. Soc. *92,* 5550 (1970); *C. R. Brundle, M. B. Robin, N. A. Kuebler & H. Basch, ibid. 94,* 1451 (1972).

[6] *R. Sustmann & R. Schubert,* Tetrahedron Letters *1972,* 2739.

[7] *M. B. Robin,* private communication.

[8] *R. J. Buenker & J. L. Whitten,* J. chem. Physics *49,* 5381 (1968); *B. Dumbacher,* Theoret. Chim. Acta *23,* 346 (1972); *G. Berthier,* private communication.

[9] *N. C. Baird & M. J. S. Dewar,* Theoret. chim. Acta *9,* 1 (1967); *S. D. Worley,* Chem. Rev. *71,* 295 (1971); *M. J. S. Dewar & S. D. Worley,* J. chem. Physics *50,* 654 (1969).

[10] *C. Fridh, L. Åsbrink & E. Lindholm,* Chem. Physics Letters *15,* 282 (1972).

[11] *L. Åsbrink, C. Fridh & E. Lindholm,* J. Amer. chem. Soc. *94,* 5501 (1972).

[12] *F. Brogli & E. Heilbronner,* Theoret. chim. Acta *26,* 289 (1972).

[13] *J. C. H. Hwa, P. L. DeBenneville & H. J. Sims,* J. Amer. chem. Soc. *82,* 2537 (1960); *H. Schuler, E. Lutz & G. Arnold,* Spectrochim. Acta *17,* 1043 (1961).

[14] Unpublished Results.

[15] *E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung & A. de Meijere,* Helv. *54,* 783 (1971).

[16] *L. Åsbrink, E. Lindholm & O. Edquist,* Chem. Phys. Letters *5,* 609 (1970).

[17] *H. Bock & W. Ensslin,* Angew. Chem. *83,* 435 (1971).

[18] *W. Haugen & M. Traetteberg,* Acta Chem. Scand. *20,* 1726 (1966).

[19] *P. A. Clark,* Theoret. chim. Acta *28,* 75 (1972).

[20] *M. Klessinger,* Angew. Chem. *84,* 544 (1972); Angew. Chem. Int. Ed. *11,* 525 (1972), and references given therein.

[21] *F. Brogli, P. A. Clark, E. Heilbronner & M. Neuenschwander,* Angew. Chem., in print.

[22] *C. F. Aten, L. Hedberg & K. Hedberg,* J. Amer. chem. Soc. *90,* 2463 (1968).

[23] *E. A. Braude & E. S. Waight,* Progress in Stereochemistry, Vol. I, p. 126 (*W. Klyne,* Edit.), Butterworth Scientific Publications, London, 1954.

[24] *A. E. Gillam & E. S. Stern*, 'An introduction to Electronic Absorption Spectroscopy in Organic Chemistry', *E. Arnold Ltd.*, London, 1955.

[25] *L. E. Sutton* (Edit.), Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publications No. 11 and 18, The Chemical Society, London 1958, 1965.

[26] *J. A. Pople & D. L. Beveridge*, 'Approximate Molecular Orbital Theory', McGraw-Hill Book Company, New York 1970; *H. Fischer & H. Kollmar*, Theoret. chim. Acta *13*, 213 (1969).

[27] *R. Hoffmann & R. A. Olofson*, J. Amer. chem. Soc. *88*, 943 (1966); *R. Hoffmann, Ch. Levin & R. A. Moss*, *ibid. 95*, 629 (1973).

[28] *P. Bischof & E. Heilbronner*, Helv. *53*, 1677 (1970).

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98. Die Cyclopropylcarbinyl-Cyclobutyl-Homoallyl-Umlagerung. I. Teil. Synthese von Tricyclo[3.2.1.$0^{2,7}$]octan-3-ol, *endo*- und *exo*-Tricyclo[3.2.1.$0^{3,6}$]octan-4-ol und *exo*-Bicyclo[3.2.1]-oct-2-en-7-ol

von **Manfred Geisel, Cyril A. Grob, Werner Santi** und **Werner Tschudi**

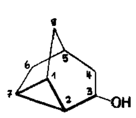
Institut für Organische Chemie der Universität Basel

(15. II. 73)

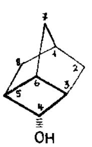
Summary. Tricyclo[3.2.1.$0^{2,7}$]octan-3-ol (**1**) and its 4-isomer **7** were obtained by hydroboration of tricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**5**). The former alcohol **1** is quantitatively converted to the isomeric alcohol *exo*-bicyclo[3.2.1]oct-2-en-7-ol (**3**) by treatment with aqueous acid.

Photolysis of 1-diazo-3-(cyclopent-3-enyl)-propan-2-one (**12c**) gave a high yield of tricyclo-[3.2.1.$0^{3,6}$]octan-4-one (**10a**). Reduction of the latter ketone produced a mixture of *endo*- and *exo*-tricyclo[3.2.1.$0^{3,6}$]octan-4-ol **2** and **9**, respectively. Oxidation of these secondary alcohols with silver carbonate in benzene furnished a mixture of the ketone **10a** and the lactone **14** of 6-hydroxy-bicyclo[2.1.1]heptane-2-carboxylic acid. The latter is thought to be formed by oxydation of the hydrate of the strained ketone **10a**.

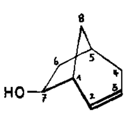
Die im Titel genannten sekundären Alkohole enthalten eine Cyclopropylcarbinyl- (**1**), eine Cyclobutyl- (**2**) oder Homoallyl-Gruppierung (**3**)[1], welche jeweils durch ein gleiches Gerüst von vier Kohlenstoffatomen fixiert ist. Wegen ihrer geometrisch definierten Struktur eignen sich Derivate dieser Alkohole besonders gut zum Studium der Umlagerungen, welche für Verbindungen dieses Strukturtyps charakteristisch sind und denen wir früher in der Bicyclo[2.2.2]octan-Reihe begegnet sind [1].



1



2



3

Nach heutiger Auffassung treten bei diesen Umlagerungen dieselben oder ähnliche kationische Zwischenstufen auf, was sich vor allem in der Bildung gleicher oder ähnlicher Produktgemische äussert. Über die Zahl und Natur dieser Zwischenstufen gehen die Meinungen freilich auseinander[2]. In Anbetracht der noch im Gange be-

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[1] In den Formeln durch dicke Striche hervorgehoben.

[2] Für Literaturübersichten vgl. [2].