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THROUGH-SPACE INTERACTION IN NON-CONJUGATED ACYCLIC DIENES STUDIED BY PHOTOELECTRON SPECTROSCOPY

J. C. BÜNZLI, A. J. BURAK and D. C. FROST*

The Chemistry Department, The University of British Columbia, Vancouver 8, British Columbia, Canada

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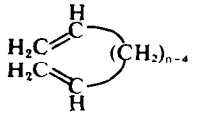
Abstract—The He (I) PE-spectra of the non-conjugated acyclic dienes **1** (n), n = 5, 6, 7, 8, 9 are reported. The π-level splitting in the molecules amounts respectively to 0·34, 0·46 (or 0·31), 0·41, 0·21 and 0·14 eV. Arguments based on the observed fine structure of the first two bands suggest there is no crossing of the π-levels, and EHT calculations on different conformations of **1** (5) and **1** (6), as well as comparisons with other available data, indicate a through-space dominated interaction throughout the series **1** (n).

INTRODUCTION

There has been considerable interest recently in studying the interactions of non-conjugated functional groups[1,2] (localized orbitals) and Hoffman[3] has presented evidence for the existence of two competing symmetry-controlled interaction mechanisms: (i) homoconjugation (through-space interaction) and (ii) hyperconjugation (through-bond interaction). Photoelectron spectroscopy (PES) allows one to study the extent of such an interaction by measuring the magnitude of the one-electron energy level splitting. Studies of the interaction among double bonds in cyclo- and bicyclo-alkenes[2,4,5] have been reported and recently Schmidt and Wilkins[6] have discussed the mechanistic consequence of the level ordering, as determined by PES, in tetracyclo-[5.3.0.$0^{2,6}$.$0^{3,10}$]-deca-4,8-diene. With the exception of 3,3-dimethylpenta-1,4-diene,[7] little is known about the π-level splitting in non-conjugated acyclic dienes, and in this communication we present the PE-spectra of **1** (n), n = 5, 6, 7, 8, 9 and discuss the



1 (n)

observed π-level splitting in terms of through-space and through-bond contributions and on the basis of Extended Hückel MO calculations (EHT) for **1** (5) and **1** (6).

EXPERIMENTAL

The He (I) spectra were obtained using spectrometers previously described.[8,9] They were calibrated by inclusion of small amounts of xenon or MeI ($^2E_{3/2}$,$^2E_{1/2}$ doublet at 9·538 and 10·165 eV[10]).

Compounds **1** (5), **1** (7) and **1** (9) were purchased from Chemical Samples Co., Columbus, Ohio. **1** (6) and **1** (8) were supplied by Aldrich Chemical Co., and the 1-pentene by K and K Laboratories. All compounds were found to be at least 99% pure (gas chromatography, IR or NMR).

RESULTS

The PE-spectra of the five dienes studied all closely resemble one another. In the region between 9 and 10·5 eV they are characterized by two overlapping bands which correspond to ionization from the π-type orbitals. The higher ionization potentials (IP's), associated with the removal of electrons which are in σ-type bonding orbitals, give rise to diffuse and overlapping bands of onset usually ~ 1 eV higher than the second vertical π IP. The first two bands for compounds **1** (5) to **1** (9) are shown in Fig 1, and Table 1 summarizes the experimentally determined IP's; data for 1-pentene have been added because they give a good estimate of the $\pi_{C=C}$ level energy before interaction. Our first IP's (first vibrational peak) compare favorably with previous determinations by electron impact or photoionization: 9·58 eV for **1** (5), 9·51 eV for **1** (6) and 9·50 eV for 1-pentene.[11]

Provided Koopmans' theorem[12] holds for the systems studied, the energy separation between the two π-levels can be expressed by:

$$\epsilon_\pi(1) - \epsilon_\pi(2) = -(IP_1 - IP_2) = \Delta IP$$

where IP_1 and IP_2 are the observed *vertical* IP's. The main difficulty is to measure IP_1 according to the definition that the vertical IP corresponds to the transition which has the highest Franck-Condon factor, that is to the most intense vibrational peak. In our spectra the first bands all show two resolved vibrational peaks and in all but one case, **1** (7), the

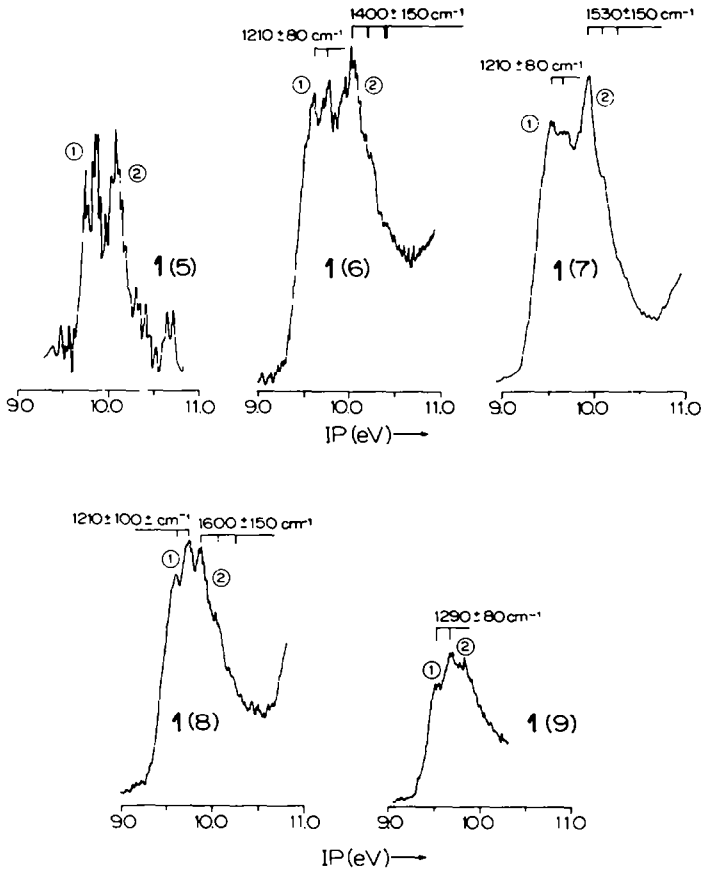


Fig 1.

Table 1. Experimental IP's, main vibrational intervals ν_{av}, ΔIP's and average IP's for the π-levels of the non-conjugated acyclic dienes

Compound	First band 1st vibr.	First band 2nd vibr.	ν_{av}	Second band IP_2[a]	Second band ν_{av}	ΔIP	IP_{av}
1 (5)	9·62 eV	9·78* eV	1,300 cm^{-1}	10·12 eV	1,400 cm^{-1}	0·34 eV	9·95 eV
1 (6)[b]	9·59*	9·74*	1,200	10·05	1,400	0·46 or 0·31	9·82 or 9·89
1 (7)	9·52*	9·67	1,200	9·93	1,500	0·41	9·72
1 (8)	9·52	9·67*	1,200	9·88	1,600	0·21	9·77
1 (9)	9·51	9·67*	1,300	9·81	—	0·14	9·74
1-pentene	9·54	9·71*	1,370	—	—	—	(9·71)

[a] Vertical IP.
[b] The assignment of the vertical IP is not certain (see text).
All values are ± 0·02 eV; * denotes the apparent highest vibrational peak (vertical ionization potential IP_1).

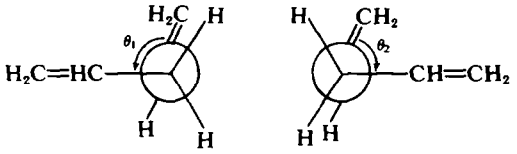
second is the more intense. However, the intensity of this peak may well be enhanced by overlap with the second band (IP_2). We feel that this effect is generally not large enough to reverse the relative intensity of the two peaks, except possibly for 1 (6) where they have the same intensity. The measured values for ΔIP and $IP_{av} = \frac{1}{2}(IP_1 + IP_2)$ are also reported in Table 1.

For four of the non-conjugated dienes, vibrational structure is also observed in the second π-band; however its complexity is greater than in the first band, resulting in poorly resolved peaks, al-

though a main vibrational interval could still be measured (*cf* Table 1). One can point out that (i) the main vibrational interval ν_{av} for the second band is systematically larger than ν_{av} for the first band and (ii) ν_{av} for 1-pentene (1370 cm^{-1}) is essentially similar to the value observed for cyclopentene (1290 cm^{-1}).[13]

DISCUSSION

Through-space interaction of two semi-localized π-orbitals, φ_1 and φ_2, will place their antibonding linear combination $\Psi_- = 1/\sqrt{2}(\varphi_1 - \varphi_2)$, of energy ϵ_-, above their bonding combination $\Psi_+ = 1/\sqrt{2}(\varphi_1 + \varphi_2)$, of energy ϵ_+, while through-bond interaction in mixing high-lying σ-type orbitals can reverse this "natural order", the symmetry of the σ-orbital permitting.[3,14] When both interactive mechanisms occur, the sign of $\Delta\epsilon_\pi = \epsilon_+ - \epsilon_-$ reflects whether this "natural order" is retained or not. As experimental data give only the magnitude of the splitting ($\Delta IP = |\Delta\epsilon_\pi|$) we have performed EHT calculations[15] for **1** (5)* in order to find out the sign of $\Delta\epsilon_\pi$. The different conformations of this diene can be defined by the two dihedral angles θ_1 and θ_2 that each planar vinyl group makes with the C(2) C(3) C(4) plane.



Along C(3)–C(2) Along C(3)–C(4)

Results for seven conformations, three of them planar (*A*, *E* and *F*) are reported in Table 2. Starting from the C_{2v} conformation *A*, where the hyperconjugative effect dominates, and rotating the two vinyl groups "in phase" (that is keeping $\theta_1 = \theta_2$) one notices that through-space interaction rapidly cancels the through-bond effect and dominates the overall interaction for angles smaller than 120°. The total energy E_t goes through a maximum when the two π-levels are almost degenerate (120°) as a result of mutual cancellation of both interactions, and then reaches a minimum for dihedral angles of 90°. When θ_1 and θ_2 are further decreased H . . . H repulsions give rise to less stable conformations; in particular conformation *E* is most unlikely because it has too short a distance between two of the vinylic H atoms. Thus both vinyl groups cannot freely rotate exactly "in phase", and conformations with $\theta_1 \neq \theta_2$ will always be less favorable for π-level interaction. This is verified by calculations on conformations *F* and *G* for which $|\Delta\epsilon_\pi|$ is predicted smaller than in conformations *A* and *C* respectively, while the sign of $\Delta\epsilon_\pi$ is unchanged. Clearly, the EHT calculations show that there are two minima in the potential energy surface and that in the corresponding conformations (*C* and *G*) the π-interaction is mainly homoconjugative. Although EHT calculations are not too reliable in predicting the magnitude of rotation barriers, they usually indicate quite satisfactorily which conformation is more stable.[15] We consequently feel that in **1** (5) the π-interaction is dominated by the through-space mechanism. This conclusion is supported by the photochemical results of Srinivasan and Carlough[16] who studied the mercury $^3P_1$ photosensitized cyclo-addition of some non-conjugated dienes. For **1** (5) the addition is highly selective and the ratio of cross addition, which yields bicyclo[1.1.1]pentane, to parallel addition, which leads to bicyclo[2.1.0]pentane, is found to be 0·10.[16] The suggested mechanism implies formation of the C(1)–C(5) bond as a first step, that is the lowest virtual π^* orbital must be C(1)–C(5) bonding, which is the case for conformation *C* (or *D*) where the first virtual level has a′ symmetry. It should however be mentioned that Schweig *et al.* assume a C_{2v} symmetry for 3,3-dimethyl-penta-1,4-diene (that is a conformation similar to *A*), and explain the observed splitting (0·40 eV) by a hyperconjugative

*An exponent of 1·3 was used for H atoms.

Table 2. Relative total energies E_t and π-level splitting $\Delta\epsilon_\pi$ for different conformations of 1,4-pentadiene, as given by EHT calculations

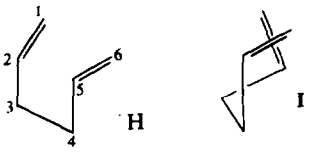
Conformation	θ_1[b]	θ_2[b]	Symmetry	E_t (kcal/mole)	$\Delta\epsilon_\pi$[a] (eV)
A	180°	180°	C_{2v}	5·8	0·34
B	120°	120°	C_s	15·2	−0·01
C	90°	90°	C_s	0·0	−0·30
D	60°	60°	C_s	12·2	−0·33
E	0°	0°	C_{2v}	207·0	−0·16
F	180°	0°	C_s	13·6	0·23
G	90°	270°	C_2	0·0	−0·27

[a] Through-bond interaction prevails when $\Delta\epsilon_\pi > 0$, through-space when $\Delta\epsilon_\pi < 0$.

[b] See text for definitions.

mechanism,* finding a good correlation with the PE-data of tetravinyl-methane.[7] The gem-dimethyl group introduces steric complications and provides higher lying σ-type orbitals than the methylene group, which can explain the preference for a through-bond interaction.

When one more methylene group is inserted between the two double bonds, the experimental splitting ΔIP remains approximately the same (0·31 or 0·46 eV, *cf* preceding section). Among the many conformations the hexadiene can have, conformation *H*, of C_s symmetry, is particularly suitable for



H

I

both homo- and hyperconjugations. EHT calculations place Ψ_+ below Ψ_- and predict an overall splitting of − 0·47 eV. Again, the effect of through-space interaction (a splitting of − 1·15 eV is evaluated by calculation on the fragment $H_2C = CH \ldots CH = CH_2$) is largely cancelled out by the hyperconjugative destabilization of Ψ_+. Hoffmann *et al.*[2] have discussed the boat conformation of 1,5-cyclooctadiene and reached the same conclusions, but in this more rigid molecule both homo- and hyperconjugations are larger than in **1** (6): through-space interaction leads to a calculated splitting of − 1·67 eV, compared to − 1·15 eV, because the two double bonds are held more parallel to each other than in conformation *H* and through-bond interaction is roughly twice as large because of the participation of a second ethylene bridge, so that the overall split is predicted to be − 0·48 eV (experimentally $|\Delta\epsilon_\pi| < 0{\cdot}2$ eV).[2] Such an assignment (Ψ_- above Ψ_+) for **1** (6) suggests that the photochemical cyclo-addition for this molecule will essentially occur as for **1** (5). In fact it is not the case.[16] EHT calculations on conformation I, where the two double bonds are "crossed", indicate however that (i) I is slightly more stable than *H* (by 2·3 Kcal/mole), (ii) $\Delta\epsilon_\pi$ is still through-space dominated although the magnitude of the splitting is somewhat reduced (− 0·39 eV) and (iii) the lowest π^*-level is now C(1)–C(5) and C(2)–C(6) bonding.†

MO-calculations were not performed for **1** (7), the π-level splitting of which is still quite appreciable (0·41 eV); but comparisons with more rigid molecules like *cis,cis*- and *trans,trans*-1,6-cyclodecadiene ($|\Delta\epsilon_\pi| = 0{\cdot}50$ eV and 1·70 eV respectively[5]) indicate that the open-chain diene **1** (7) has some difficulty in achieving a suitable conformation for a more efficient interaction. Regarding the ordering of the π-levels in **1** (7), **1** (8) and **1** (9), the shape of the two overlapping π-bands (*cf* Fig) as well as the vibrational intervals (Table 1), as compared to **1** (5) and **1** (6), suggest that Ψ_- is still above Ψ_+. That is there is no crossing over of the levels along the series of dienes. The vibrational intervals of the first bands can be assigned to excitation of the $\nu_{C=C}$ stretching mode (~ 1,640 cm^{-1} in the neutral molecules) while the main intervals of the second bands can be assigned to a δ_{C-H} overtone (~ 1,830 cm^{-1} in the neutral molecules), which is consistent with a σ-type orbital participation in Ψ_+.

The trend of the splitting $\Delta\epsilon_\pi$ throughout the series **1** (5) to **1** (9) can be summarized as follows. Through-space interaction increases from **1** (5) to **1** (6) or **1** (7) because in these latter molecules the two double bonds can be conveniently positioned for a maximum overlap; this interaction then decreases because of the larger number of methylene groups between the two semi-localized π-systems. Through-bond interaction is likely to follow the same variations along the series but is never strong enough to overcome the homoconjugative effect although it reduces considerably the through-space splitting. This study thus suggests that the non-conjugated dienes investigated, even the long chain containing ones **1** (8) and **1** (9), have a more stable conformation in which the two double bonds face each other and interact more strongly via the homoconjugative mechanism than via the hyperconjugative one.

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*For this conformation, MINDO/2 calculations give $\Delta\epsilon_\pi = 0{\cdot}66$ eV[7] and EHT calculations $\Delta\epsilon_\pi = 0{\cdot}50$ eV (this work).

†Conclusions (ii) and (iii) are completely confirmed by CNDO/2 calculations which predict somewhat larger $|\Delta\epsilon_\pi|$ and the same stability for I and *H*.

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