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Geometries of Excited States of Small Polyenes

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The behaviour under rotations around one or two double bonds of the first (π) singlet and triplet states of small conjugated molecules have been investigated using localized Molecular Orbitals. The results obtained with a ($\sigma+\pi$) excitonic matrix are in agreement with previous results obtained with delocalized Molecular Orbitals: 1. the rotation around one double bond is more favorable than two symmetrical rotations around two double bonds, 2. the rotation occurs around one inner double bond rather than around a terminal bond. This work shows the role played by the ($\sigma-\pi$) mixing in the stabilization of the twisted conformations. A further optimization of the bond lengths in the excited singlet and triplet states of butadiene shows that the preferred geometry is a non symmetrical twisted geometry with different lengths for the two C=C double bonds. This "symmetry instability" suggests to introduce a vibronic wave-function in which the various locally excited electronic wave functions are multiplied by different vibrational wave functions corresponding to local deformations of the nuclear skeleton.

Key words: Butadiene – Hexatriene

Introduction

It is well known that molecules change their equilibrium geometry upon excitation: diatomic molecules elongate (for instance in the oxygen molecule, the bond length increases from 1.207 Å in the ground state to 1.604 Å [1]), triatomic molecules can bend (HCN for instance [1]), ammonia becomes planar in it lowest excited state [2] etc. Such deformations occur in organic unsaturated and conjugated systems: formaldehyde is pyramidal in both the singlet and triplet ($n\rightarrow\pi^*$) states [3], the lowest singlet of acetylene is trans bent [4]. Theoretical considerations by Mulliken [5] led to the conclusion that the first excited states of ethylene (singlet and triplet) prefer a non planar conformation presumably twisted to a D_{2d} geometry; furthermore different interpretations of the vibrational structure of the $\pi\rightarrow\pi^*$ spectra of ethylene in the region 1600–2200 Å have been made, and they have led to the following interpretations 1. the C–C bond length in the excited singlet state is increased [6], 2. the two CH_2 groups of ethylene are twisted relative to each others [7], 3. the equilibrium geometry of the singlet excited states is assumed to have the two CH_2 groups twisted by 90° relative two each other, and a C–C bond of 1.44 Å [8]. Numerous empirical [9, 10] and non empirical [11–14] calculations have been endeavored and these calculations also conclude to a preferred perpendicular conformation. As one proceeds to larger molecules, it seems that the increasing delocalization of the excitation would prevent major geometrical distorsions; but an extended Hückel calculation [15] suggests that butadiene and hexatriene, in the first singlet excited state, twist respectively around one terminal double bond and the central double bond.

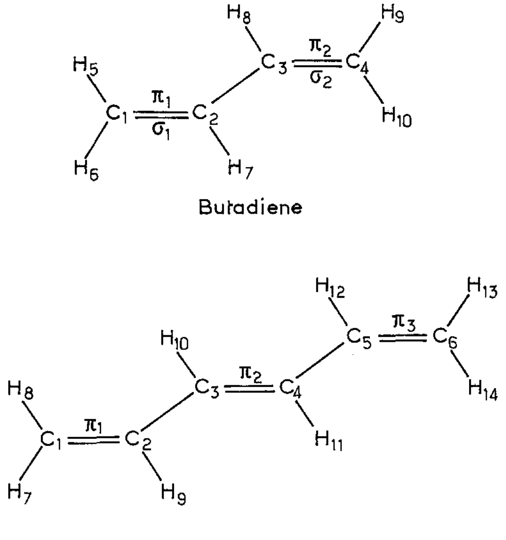


Fig. 1. Butadiene and hexatriene with the numbering of atoms and of π bonds

But a similar study [15] for *trans-trans* 1, 3, 5, 7 octatetraene, finds a preference for retention of planarity in the first singlet state. Baird and West [9] with a variant of their π semi-empirical NNDO method have also shown a preference of triplet states to twist about an (internal) C=C double bond in butadiene, hexatriene, isohexatriene and octatetraene. Recently Shih, Buenker, and Peyerimhoff [16] with *ab initio* SCF and CI calculations have investigated the CH_2 twisting motion of butadiene, maintaining the C_2 symmetry, and they have shown that the energy of the ^1Bu (^1B) state is lowered by 0.2 eV upon a 30° rotation angle.

All these calculations used delocalized MO's. The excitonic methods [17–19] provide qualitatively different descriptions of excited states. So it seems interesting to follow the behaviour under a double bond twisting of the excited states of small conjugated molecules using localized orbitals. In a first paper [20] we have discussed the possibility of building a zeroth order wave function describing the $\binom{\pi^*}{\pi}$ excited states with localized MO's, in the scope of building a PCILO method for excited states. Two possibilities appear: 1. a $(\sigma+\pi)$ excitonic wave function involving all singly excited determinants; 2. a purely (π) excitonic wave function with the $(\pi\rightarrow\pi^*, \sigma\rightarrow\sigma^*)$ coupling and $(\sigma-\pi)$ mixing treated as a perturbation. We had shown [20] that in planar polyenic systems the $(\sigma-\pi)$ coupling has strong effects on the wave function (especially on the ionic character and charge fluctuation in the π system), but as concerns energy, the $(\sigma-\pi)$ mixing may be actually considered as a perturbation. So it will be also interesting to test whether the $(\sigma-\pi)$ mixing can be considered as a perturbation in polyenic systems twisted about a double bond and to analyze the role of $(\sigma-\pi)$ mixing in excited state geometries. We have made calculations upon ethylene, butadiene and hexatriene (Fig. 1), using the CNDO/2 parametrization [21].

1. Results Obtained with the $(\sigma + \pi)$ Matrix

A) *Ethylene*

In our previous calculations [20] the $B_{1g}\ \sigma \rightarrow \pi^*$ state is lower than the $\pi \rightarrow \pi^*$ state by 2.08 eV. This fact results from the CNDO parameters. But the Berry assignment of the mystery band [22] now seems an artefact in view of the recent *ab initio* calculations in non minimal basis set [23, 24] and of experimental arguments [24, 25]. This basic discrepancy diminishes the interest of an extensive study of the geometry for that molecule. One may summarize as follows the main effects of the rotation around the double bond:

– The first state energy decreases, the elementary $\pi\pi^*$ excitation goes from the second to the first excited state since they are of B_1 symmetry for intermediate torsion angle.

– The second excited state increases under rotation. In such a Berry type situation the $\pi\pi^*$ excitation would be a non vertical excitation towards the first twisted excited state. The vertical (with respect to the angle) excitation towards the second excited state $(\pi\pi^*)$ would be allowed and one should suppose it to be immerged in the Rydberg excitation. Recently, Buenker *et al.* [14] have found with both SCF and SCF CI calculations that the lowest B_1 state obtained in twisted ethylene, because of the non crossing rule, correlates with the $B_{1g}\ \pi \rightarrow 3py$ states (Rydberg species) rather to the $\pi - \pi^*\ {}^1Bu$ state, and they have concluded that the maximum in the $N \rightarrow V$ band corresponds to a non vertical transition. Although they have different origins, the ${}^1B_{1g}$ low-lying excited state leads to the same qualitative problems in the PCILO-CNDO and in the *ab-initio* SCF + CI calculation of Buenker *et al.* [14].

The $B_{1g}\ \pi \rightarrow \sigma^*_{\mathrm{CH}}$ excited state which is commonly considered as a Rydberg excited state [26] has an energy minimum for a value of $\varphi(\mathrm{H_1C_1C_2},\ \mathrm{C_1C_2H_3})$ equal to 30°, in good agreement with other estimations [5, 26].

B) *Butadiene*

Several series of calculations have been made upon the butadiene molecule:

a) rotations around one double bond (the π_1 bond).

b) symmetrical rotations around the two double bonds, maintaining the C_{2v} symmetry.

c) an investigation of bond lengths in the first singlet and triplet states, for planar and twisted conformations.

a) Rotations Around one Double Bond

Figure 2a shows the evolution of the energy of the first singlet and triplet states obtained with a $(\sigma + \pi)$ matrix under rotation around one double bond (the π_1 bond):

– The first triplet and singlet states are stabilized by a rotation around one double bond. The minimum of energy is obtained for the values of $(\mathrm{H_1C_1C_2},\ \mathrm{C_1C_2C_3})$ equal to 60° and 50° respectively.

– The energy gain obtained by this torsion in these two first excited states is respectively 1.08 eV and 1.35 eV.

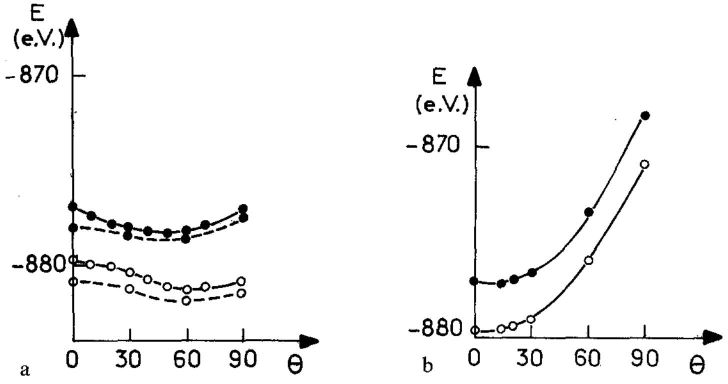


Fig. 2. Evolution of the energy (in eV) of the first singlet ●—● and of the first triplet state ○—○ of butadiene with one rotation a around the $C_1{=}C_2$ bond, without any change of C–C bond lengths (plain lines ——) and after minimization of the C_1–C_2, C_2–C_3, and C_3–C_4 bond lengths (dotted lines - - - - —○—). Results obtained with the $(\sigma+\pi)$ excitonic matrix

Fig. 2a. Evolution of the energy (in eV) of the first singlet •—• and of the first triplet ○—○ of butadiene after two symmetrical rotations around the $C_1{=}C_2$ bond $(+\theta)$ and the $C_3{=}C_4$ bond $(-\theta)$. Results obtained with the $(\sigma+\pi)$ excitonic matrix

The shape of the potential curve of the first triplet of butadiene is not in exact agreement with the one calculated by Baird *et al.* [9] since 1. these authors have found a preference for the 90° twisted conformation, 2. the energy gain we have calculated in twisting a terminal C=C is much higher than the one they have calculated with the NNDO method, or the one they have estimated by perturbation theory 3. no intermediate barriers to twisting have been found.

Table 1a shows the weight of the $\Phi\binom{\pi_i^*}{\pi_i}$ and $\Phi\binom{\pi_j^*}{\pi_i}$ polarization and delocalization configurations in the first singlet and triplet states. During the torsion around the π_1 bond the weight of the $\Phi\binom{\pi_1^*}{\pi_1}$ polarization configuration increases and the weights of the $\Phi\binom{\pi_2^*}{\pi_2}$ and $\Phi\binom{\pi_2^*}{\pi_1}$ $\left(\text{or } \Phi\binom{\pi_1^*}{\pi_2}\right)$ decrease. The total weight of the polarization configurations decreases from the planar conformation to the 30° twisted conformation, then it increases: so the 90° conformation, in both triplet and singlet states, has a little more pronounced neutral character than the planar conformation. The total weight of the delocalization configurations decreases with the rotation around the π_1 double bond. In the 90° twisted conformation, the excitation is mostly localized in the double bond we have turned around.

The difference between 1 and the total weight of the $\Phi\binom{\pi^*}{\pi}$ and $\Phi\binom{\pi^*}{\pi'}$ polarization and delocalization configurations gives an estimation of the $(\sigma-\pi)$ mixing. Table 1a shows that: 1. for any rotation angle, the $(\sigma-\pi)$ mixing is less important in the first triplet state than in the first singlet one; 2. the $(\sigma-\pi)$ mixing increases during the torsion around a double bond, it reaches a maximum in the 30° twisted conformation then it decreases, but it is always more important in the 90° twisted conformation than in the planar conformation; 3. for twisted conformations in both states the $(\sigma-\pi)$ mixing is mainly due to the $\Phi\begin{pmatrix}\pi_1^*\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ and $\Phi\begin{pmatrix}\pi_1^*\\ \sigma_{\mathrm{CC}}\end{pmatrix}$ delocalization configurations (with CH and CC adjacent to the π_1 bond). The $\Phi\begin{pmatrix}\sigma_{\mathrm{CH}}^*\\ \pi_1\end{pmatrix}$ delocalization have a less important weight. If σ_1 is the $\mathrm{C}-\mathrm{C}$ σ bond involved in the double bond we have turned around, and σ_2 the σ bond involved in the other double bond, the weight of the $\Phi\begin{pmatrix}\sigma_1^*\\ \sigma_1\end{pmatrix}$ configuration is nearly constant during the rotation around the first double bond and the weight of the $\Phi\begin{pmatrix}\sigma_2^*\\ \sigma_2\end{pmatrix}$ configuration decreases.

b) Symmetrical Rotations Around the two Double Bonds

Figure 2b shows the potential curves obtained for the first singlet and triplet states for the symmetrical rotations around the two double bonds. Our calculation shows that the first triplet state is not stabilized at all by the two symmetrical rotations, whereas the first singlet state is lowered by 0.084 eV upon a value of ± 15° for the two torsion angles. This result is nearly in agreement with the calculations of Shih *et al.* [16] so at this step of calculation, it appears then the two first singlet and triplet states of butadiene prefer a *non symmetrical* conformation twisted about *one* double bond.

Table 1b shows that for any rotation angle, the excitation is of course equally localized on the two bonds we have turned around, and, furthermore, we have obtained a small *diminution* of the total weight of the polarization configurations. The total weight of the delocalization configurations also decreases but not to so large an extent than when twisting about one double bond. Furthermore the $(\sigma-\pi)$ mixing calculated with *two* symmetrical rotations is always less important than the $(\sigma-\pi)$ mixing calculated with *one* rotation.

c) Bond Lengths in the First π Singlet and Triplet States

In this work we have just considered the variation of the bond lengths in the two first (π) excited states of the molecule, when twisting about one double bond since the symmetrical rotations seems far less favored. The lengths of the two double bonds C=C have been investigated from 1.34–1.51 Å and the length of the single bond C–C from 1.38–1.50 Å. All these calculations have been made minimizing these three bond lengths. The $\widehat{\mathrm{HCH}}$ and $\widehat{\mathrm{CCC}}$ bond angles were kept fixed to 120° and no variation of these angles has been considered: Kirby *et al.* [10] have found that the value of the C=C distance which minimizes the energy of the excited singlet and triplet states of ethylene is unchanged by the improvement of the $\widehat{\mathrm{HCH}}$ bond angle. These conclusions are confirmed by calculations of Warshel and Karplus on the hexatriene molecule [27]. Table 2 gives the bond lengths we have calculated in the first singlet and triplet states of the planar and twisted conformations.

Our results have shown that 1. the planar conformation is symmetrical in both singlet and triplet states. The two double bonds C=C have been lengthened

Table 1a–d. Weight of the excitonic wave function on the local excitations (in %), in function the rotation angle θ. The number on line i and column j gives the weight on the i–j^* process. The table also gives the value of the $(\sigma-\pi)$ mixing, of the total weight of the polarization and delocalization configurations calculated with the $(\sigma+\pi)$ excitonic matrix. These values are given for the first singlet S_1 and the first triplet T_1 excited states of: 1a *butadiene* when twisting about *one* terminal double bond; 1b *butadiene* with *two* symmetrical rotations around the two double bonds; 1c *hexatriene* when twisting about the *central* bond; 1*d hexatriene* with rotation around one terminal bond. In Table 1a the values between parenthesis indicate the weight we have calculated for the optimized bond lengths

(%)		$\theta=0$		$\theta=30$		$\theta=60$		$\theta=90$	
1a		1	2	1	2	1	2	1	2
S_1	2–	16.0 (17.4)	30.2 (30.0)	6.8 (10.3)	5.3 (8.1)	4.4 (5.9)	1.4 (1.9)	3.6 (4.7)	0.6 (0.9)
	1–	30.2 (30.0)	16.0 (17.4)	34.8 (39.9)	6.8 (10.3)	50.4 (54.1)	4.4 (5.3)	67.2 (68.1)	3.6 (4.1)
$(\sigma-\pi)$ mixing		7.5	(5.2)	46.4	(30.9)	39.3	(32.8)	24.9	(22.1)
Polarization		60.5		40.1		51.8		67.9	
Delocalization		32.0		13.5		8.8		7.2	
		1	2	1	2	1	2	1	2
T_1	2–	10.5 (10.5)	39.5 (39.5)	6.8 (7.3)	10.9 (4.1)	3.6 (3.9)	0.6 (0.7)	1.2 (2.7)	0.1 (0.2)
	1–	39.5 (39.5)	10.5 (10.5)	64.0 (73.4)	4.8 (4.5)	70.6 (76.6)	2.6 (2.6)	81.0 (84.1)	1.8 (1.9)
$(\sigma-\pi)$ mixing		0		13.5	(10.7)	22.6	(22.2)	15.9	(11.0)
Polarization		79.0		74.9		71.2		81.2	
Delocalization		21.0		11.6		6.2		6.9	
1b		1	2	1	2	1	2	1	2
S_1	2–	16.0 (17.4)	30.2 (30.0)	10.0	24.9	11.5	25.9	14.2	24.5
	1–	30.2 (30.0)	16.0 (17.4)	24.9	10.9	25.9	11.5	24.5	14.2
$(\sigma-\pi)$ mixing		7.5	(5.2)	28.4		125.2		22.6	
Polarization		60.5		49.9		51.9		49.1	
Delocalization		32.0		21.7		22.9		28.3	
		1	2	1	2	1	2	1	2
T_1	2–	10.5 (10.5)	39.5 (39.5)	7.8	35.3	7.1	34.7	8.8	33.3
	1–	39.5 (39.5)	10.5 (20.5)	35.3	7.8	34.7	7.1	33.3	8.8
$(\sigma-\pi)$ mixing		0		13.8		16.4		15.7	
Polarization		79.0		70.6		69.4		66.6	
Delocalization		21.0		15.6		14.2		17.6	

Table 1 (continued)

(%)		$\theta=0$			$\theta=30$			$\theta=60$			$\theta=90$		
1c		1	2	3	1	2	3	1	2	3	1	2	3
	S_1 3–	1.4	10.2	9.6	0.6	5.8	3.2	0.4	4.1	1.2	0.2	3.2	0.6
	2–	8.4	36.0	8.4	5.8	37.2	5.8	4.0	50.4	4.0	3.2	64.3	3.2
	1–	9.6	10.2	1.4	3.2	5.0	0.6	1.2	4.0	0.4	0.6	3.2	0.2
$(\sigma-\pi)$ mixing		4.6			31.9			30.4			21.1		
Polarization		55.2			43.7			52.8			65.6		
Delocalization		40.2			24.3			16.8			13.3		
		1	2	3	1	2	3	1	2	3	1	2	3
	T_1 3–	0.6	7.9	10.2	0.4	5.4	2.8	0.2	3.3	0.5	0.1	2.2	0.2
	2–	5.3	51.8	5.3	3.6	60.4	3.6	2.3	68.9	2.3	1.8	78.4	1.8
	1–	10.2	7.9	0.6	2.8	5.4	0.4	0.5	3.3	0.2	0.2	2.2	0.1
$(\sigma-\pi)$ mixing		0			15.2			18.6			13.2		
Polarization		72.3			66.0			69.9			78.7		
Delocalization		27.7			18.7			11.4			8.2		
1d		1	2	3	1	2	3	1	2	3	1	2	3
	S_1 3–	1.4	10.2	9.6	0.6	2.7	1.7	0.4	0.2	0.1	0.2	0.0	0.0
	2–	8.4	36.0	8.4	8.4	12.9	1.7	5.8	2.2	0.1	4.4	0.8	0.0
	1–	9.6	10.2	1.4	28.1	9.6	0.6	49.0	5.3	0.2	65.6	4.0	0.1
$(\sigma-\pi)$mixing		4.6			33.7			36.8			24.7		
Polarization		55.2			42.7			51.3			66.4		
Delocalization		40.0			23.5			11.8			8.8		
		1	2	3	1	2	3	1	2	3	1	2	3
	T_1 3–	0.6	7.9	10.2	0.6	1.7	1.0	0.2	0.0	0.8	0.1	0.0	0.0
	2–	5.3	51.8	5.3	7.8	13.7	0.8	4.0	1.0	0.0	2.7	0.2	0.0
	1–	10.2	7.9	0.6	51,8	6.2	0.2	70.6	2.9	0.0	81.0	1.9	0.0
$(\sigma-\pi)$ mixing		0			15.9			20.5			14.1		
Polarization		72.3			66.5			72.4			81.3		
Delocalization		27.7			17.5			7.2			4.6		

to 1.410 Å and 1.430 Å respectively. The central single bond has been shortened to 1.435 Å and 1.450 Å respectively. The value 1.47 Å calculated for the two double bonds of butadiene in the first triplet state is little shorter than the one calculated by Baird with the NNDO method (1.45 Å) [9], but these authors have found a very short length of the single bond (1.373 Å). So from the results of these authors, in the first triplet states, the butadiene molecule has a structure with the two double and single bonds inverted relative to the ground state structure. This inverted structure has a lower energy than the ground state structure in the *ab initio* SCF + CI calculations of Shih *et al.* [16], who did not perform a systematic

optimization. On the contrary, our calculations show a tendency in the planar conformation of the two first π excited states to equalize the lengths of the three C – C bonds. 2. When twisting about a double bond, the symmetry of the molecule is destroyed, the two double bonds, in any twisted conformation have not the same length in both singlet and triplet states. With respect to the planar (singlet or triplet) excited conformation, during the twisting about one double bond, the length of the double bond we have turned around has increased by a small amount (0.02 Å for a 90° rotation angle value) and the other double bond has decreased (respectively 0.05 Å and 0.07 Å); while the single central bond is lengthened slightly. These results are in qualitative but not quantitative agreement with the conclusions found by Baird *et al.* [9]. The smaller changes of the central bond length in the excitonic calculation might be understood as due to a location of the excitation on the double bonds. It has been shown elsewhere [28] that CI and excitonic treatments in some sense "relocalize" the excitation. Furthermore an investigation of the geometry of the ground state has shown that, when considering only the zeroth order localized energy calculated for the ground state, the PCILO method gives double bonds lengths which are nearly in agreement with the experimental one's (1.35 Å instead of 1.34 Å) but the lengths of the single bonds are a little larger than the experimental ones (1.51 Å instead of 1.472 Å). 3. The energy gain obtained by changing the bond lengths in the planar conformation is smaller than the energy gain obtained by a rotation around one double bond (0.879 eV and 0.977 eV versus 1.080 eV and 1.350 eV respectively in the first singlet and first triplet states).

Furthermore the energy gain obtained by changing the lengths of the bonds is more important in the planar than in any twisted conformation. The values between parenthes which are in Table 1a shows, for any twisted conformation, the weights of the polarization and delocalization configurations obtained with the minimized bond lengths. We can notice that the localization of the excitation in the double bond we have turned around is increased. Furthermore as the weight of the others configurations is also increased, the $(\sigma - \pi)$ mixing we have calculated is decreased.

C) *Hexatriene*

We have just considered the effect of one rotation which can occur either in the central bond or in one terminal bond. Our calculations (Fig. 3a and 3b) in agreement with those of Hoffmann [15] and Baird [9], show that the twisting occurs about the central bond; a rotation around the terminal bond destabilizes the first singlet state and stabilizes the first triplet state, but in this latter case, the energy gained by twisting the terminal bond is much smaller than by twisting the central bond (0.4 eV instead of 0.8 eV). Furthermore, an intermediate barrier (peaking at 20°) occurs in the first triplet state, during the rotation around the terminal bond. The minimum of energy obtained with a rotation around the central double bond occurs for the same rotation angle value than in the butadiene molecule.

The energy gain obtained by the rotation around the central bond of hexatriene is smaller than the one obtained by a torsion around one terminal bond of butadiene.

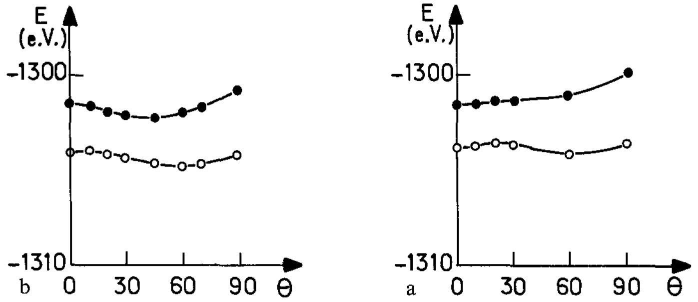


Fig. 3. Evolution of the energy (in eV) of the first singlet •—• and triplet ○—○ of hexatriene with the rotation around the central bond (Fig. 3a) or around one terminal bond (Fig. 3b). Results obtained with the $(\sigma + \pi)$ excitonic matrix

Table 1c and 1d show that a rotation around the central bond does not demand any qualitative reorganization of the molecule: In the planar conformation the excitation already tends to be localized in the central bond of the molecule, and the torsion around the central bond increases this tendency. So in agreement with Baird *et al.* [9], the excited singlet and triplet states of hexatriene are well represented by two allylic fragments, each of them containing one of the two unpaired electrons. On the contrary, rotations around the terminal bond, tend to localize the excitation on the terminal bond we have turned around, so this rotation does involve significant reorganization of the molecule.

One may understand the prefered rotation around the central bond as follows: the rotation localizes the excitation on the twisted double bond; if the excitation is located on a terminal C=C bond it looses the benefit of the possible partial delocalizations on two adjacent double bonds.

During the torsion around one double bond, the total weights of the polarization and delocalization configurations evolves qualitatively in the same way as in the butadiene molecule. If we compare the values of the $(\sigma - \pi)$ mixing calculated in the 90° twisted conformation, nearly the same values are obtained in the hexatriene twisted about the terminal bond and in butadiene (the values of the $(\sigma - \pi)$ mixing calculated for hexatriene twisted about the central bond being slightly weaker).

The large number of degrees of freedom has prevented us from optimizing the bond length in that molecule for the various angles of rotation. Turning back to Fig. 2a, one may notice that the bond length optimization in butadiene lowers more the planar form (by 0.89 eV) than the twisted one (0.29 eV). In the hexatriene molecule where the stabilizing effect of the rotation leads to a less pronounced well, the final curve of energy after bond length optimization might be very flat.

2. Discussion of the Results

One may try to analyze the origin of the striking stabilization by the rotation around a double bond. This stabilization may be due to the $(\sigma - \pi)$ mixing. In order to solve this problem, calculations have been performed using a purely π excitonic wave function. In such a calculation the σ system is involved by the field it creates, but the excitation never involves σ orbitals.

Table 2. Lowest singlet and triplet $\pi\pi^*$ excited state energies obtained from a $(\sigma + \pi)$ excitonic method (in eV); θ is the rotation angle of the first terminal $C_{(1)}H_2$ group. Two sets of results are presented, 1. the results with the ground state bond lengths, 2. the results after an optimisation of the C–C bond lengths $l_1 = C_1C_2$, $l_2 = C_2C_3$, $l_3 = C_3C_4$ (between parenthesis). These results concern the butadiene molecule

State	Bond lengths	θ 0°	30°	60°	90°
S_1	Ground state bond lengths: 1.34–1.472–1.34	−876.990	−878.000	−878.070	−876.920
	Optimized bond lengths	−877.869 (1.41–1.435–1.41)	−878.283 (1.41–1.45–1.38)	−878.363 (1.41–1.472–1.36)	−877.425 (1.43–1.472–1.36)
T_1	Ground state bond lengths	−879.720	−880.370	−881.070	−880.620
	Optimized bond lengths	−880.697 (1.43–1.45–1.43)	−881.114 (1.45–1.472–1.36)	−881.679 (1.43–1.485–1.36)	−881.334 (1.45–1.485–1.36)

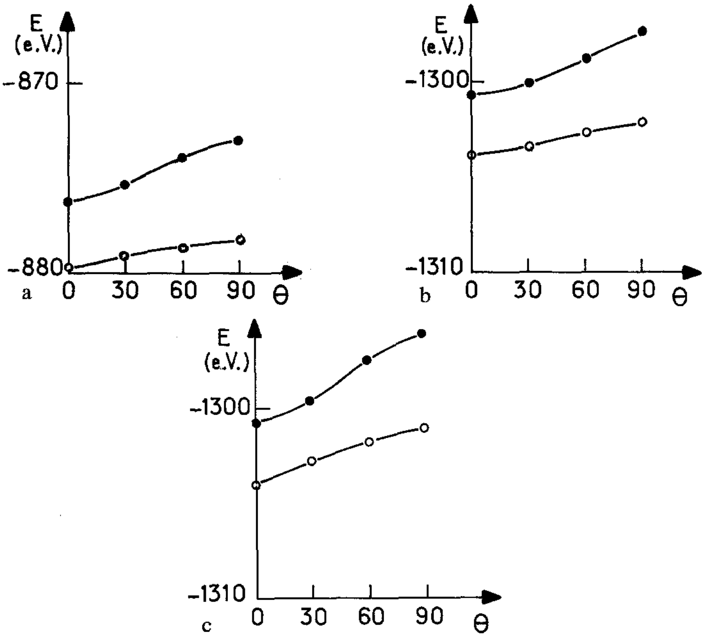
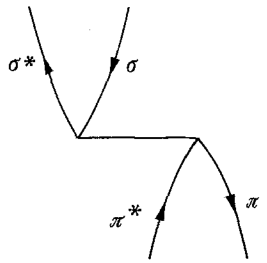


Fig. 4. Evolution of the energy (in eV) of the first singlet and triplet with rotation around *one* double bond of *butadiene* (Fig. 4a), hexatriene (Fig. 4b or 4c) respectively following the rotation around the central bond or the terminal bond. Results obtained with the (π) excitonic matrix

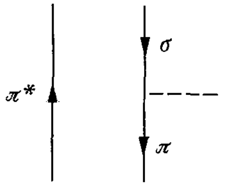
Figures 4a–c show the potential curves obtained upon one non symmetrical rotation around 1. the $C_1 = C_2$ bond of butadiene (Fig. 4a) 2. the $C_3 = C_4$ bond of hexatriene (Fig. 4b), 3. the $C_1 = C_2$ bond of hexatriene (Fig. 4c) for the first singlet and triplet states, obtained after diagonalization of the (π) excitonic matrix.

We have noticed that in these two states a planar conformation is preferred. A rotation barrier peaking at 90° occurs. This barrier is more important in the first singlet state than in the first triplet state. The same value of the height of the rotation barrier is obtained for twisting about one double bond of butadiene and the central bond of hexatriene. Torsion around the terminal bond of hexatriene requires much more energy than twisting about the central bond.

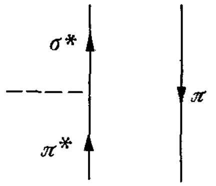
We have given in the Appendix an explanation of the behaviour of the energy of the π excitonic wave function in the CNDO hypothesis. Baird [9] has shown that the differential overlap (neglected in the CNDO hypothesis) may lead to stabilizing effects of the torsion around double bonds. Our PCILO-CNDO calculation shows that the $(\sigma-\pi)$ mixing also favors these rotations. The $(\sigma-\pi)$ mixing is simply a π transition dipole-σ transition dipole interaction in the planar form, vizualized by the diagram



In the twisted conformations one must add the $\sigma-\pi$ delocalization interactions,



and



representing a delocalization of the hole or particle in the σ sea.

The $(\sigma-\pi)$ mixing is so large for twisted conformations that it cannot be treated as a perturbation as was done for planar conjugated systems [20]. For twisted conformations it is necessary to include the σ orbitals adjacent to the twisted C–C bond into the excitonic wave-function.

Conclusions

The PCILO-CNDO calculations of the excited states geometries, although completely different in nature, leads qualitatively to the same conclusions that previous calculations by Hoffmann [15] (Extended Hückel), Baird [9] (NDDO π calculation), and Shih *et al.* [16] (*ab initio* calculations) – torsions around double bonds stabilize the energy of the lowest $\pi\pi^*$ excited states of the small conjugated polyenes (1 to 3 double bonds). For butadiene, the symmetrical torsion around the two double bonds leads to a slight minimum $(\theta_1=\theta_2=15°)$, in qualitative agreement with Shih *et al.* $(\theta_1=\theta_2=30°)$ [16]. But the non symmetrical torsion around one double bond only, which has not be studied by Shih *et al.* [16] is more favorable, even when the bond lengths are optimized. This result agrees with Hoffmann's results [15], although our optimum angle is only 50–60° instead of 90° in his calculations.

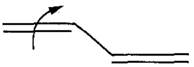
This result in favor of a non symmetrical geometry is very interesting. One may notice that this phenomenon localizes the excitation, the delocalization of which is frequently overestimated by the usual representation of the excited state wave function [28]. For the excited state of the butadiene, one finds a case of "symmetry instability" with respect to the nuclear geometry.

One may compare in some sense this instability to charge density and the spin instability (widely studied for instance by Cizek and Paldus [29]) of the wave function, or the spatial instability of the wave function shown by Prat [30] on the case of O^{--}, or to the Jahn-Teller effect [31]. Our calculation was made in the Born-Oppenheimer approximation. Although the electronic wave function ψ implied a linear combination of local excitations, the vibrational wave function χ was supposed to be the same, the total wave function keeping the form

$$\Phi = \chi(Q)\,\Psi(Q, q) \tag{1}$$

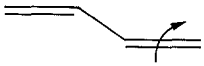
where Q and q are the coordinates of nuclei and electrons respectively. In spite of this constraint we found two non symmetrical minima, i.e. two wave functions

$$\chi_1(Q_1)\,\Psi_1(Q_1, q)$$



corresponding to a torsion around the first double bond, and

$$\chi_2(Q_2)\,\Psi_2(Q_2, q)$$



corresponding to a torsion around the second double bond. The correct wave function is necessarily a linear combination of these two wave functions

$$\Psi = N(\chi_1(Q_1)\,\Psi_1(Q_1, q) \pm \chi_2(Q_2)\,\Psi_2(Q_2, q)) \tag{2}$$

the linear combination lowering again the energy.

The question arises whether, even when there is no instability of the wave function Φ (Eq. 1), the proper representation of the excited state would not be given by Eq. (2), in which the local excitations leading to Ψ_1 and Ψ_2 are accompanied by local deformations of the nuclear geometry. This question will be analyzed formally in greater details later on.

Appendix. Evolution of the Matrix Elements of the π Excitonic Matrix

Let π_r be the π bond around which the rotation occurs. One must discuss first the evolution of the ground state energy. Defining bond nuclear charges and a bond nuclear field h_{vi} for each bond i, involving two protonic charges, Daudey *et al.*

[32] have shown that the zeroth order energy of the PCILO-CNDO localized determinant is a sum of one bond and two bonds energies

$$E_0 = \sum_i \mathscr{E}_i + \sum_{i<j}\sum \mathscr{E}_{ij} \tag{3}$$

where

$$\mathscr{E}_i = 2\langle i| - V_2^2 + h_{vi}|i\rangle + J_{ii} + R_{ii}^v$$

$$\mathscr{E}_{ij} = 2\langle i| + h_{vi}|i\rangle + 2\langle j| h_{vi}|j\rangle + 4J_{ij} + R_{ij}^v .$$

In these equations R_{ij}^v represents the repulsion between the bond nuclear charges of bonds i and j, R_{ii}^v is the repulsion between the bond nuclear charges of the bond i. The terms $\mathscr{E}_{ij}$ appears as electrostatic interaction between two neutral bond distributions, each of them being built from a two electronic distribution and two protonic charges. For non polar systems as are the hydrocarbons the terms $\mathscr{E}_{ij}$ are rather small and one may neglect their total variation under the rotation. On the contrary the one bond term for the bond r will vary significantly. Expressing the bond MO r (supposed to be non polar) in terms of atomic hybrids χ_{r_1} and χ_{r_2} (cf. 33), one may see that J_{ii} is unvariant in the rotation due to the CNDO hypotheses and

$$\begin{aligned} \Delta\mathscr{E}_0 = \Delta\mathscr{E}_r &= 2\langle \chi_{r_1}| - V^2/2 + h_{vi}|\chi_{r_2}\rangle \\ &= 2\beta_0 S_{r_1 r_2} \\ &= 2\beta\cos\theta . \end{aligned} \tag{4}$$

The ground state fully localized determinant energy increases with θ as $\cos\theta$. One may demonstrate in the same way that the diagonal Fock operators for the bonding and antibonding MO's only vary for the bond r

$$\langle r|F|r\rangle = C + \beta\cos\theta$$

$$\langle r^*|F|r^*\rangle = C' - \beta\cos\theta$$

where C and C' are constants. J_{rr^*} and K_{rr^*} are also unvariant and therefore the transition energy towards the excited state determinant $\begin{pmatrix} r^* \\ r \end{pmatrix}$ varies as

$$E_T\begin{pmatrix} r^* \\ r \end{pmatrix} = C'' - 2\beta\cos\theta . \tag{5}$$

Therefore the energy of this state $\left\langle \begin{pmatrix} r^* \\ r \end{pmatrix} \middle| H \middle| \begin{pmatrix} r^* \\ r \end{pmatrix} \right\rangle = E_0 + E_T\begin{pmatrix} r^* \\ r \end{pmatrix}$ is constant.

For the other bonds $l \neq r$, $\langle l|F|l\rangle$ and $\langle l^*|F|l^*\rangle$ are constant, $E_T\begin{pmatrix} l^* \\ l \end{pmatrix}$ is constant and the energy of the determinants $\begin{pmatrix} l^* \\ l \end{pmatrix}$ varies as E_0, i.e. increases in the rotation. So are the energies of the determinants $\begin{pmatrix} k^* \\ l \end{pmatrix}$ where k and l are different from r. The energies of the delocalization determinants $\begin{pmatrix} l^* \\ r \end{pmatrix}$ or $\begin{pmatrix} r^* \\ l \end{pmatrix}$ vary as $\beta\cos\theta$. Their energy increases, by an amount which is half the variation of E_0. One sees that all the diagonal matrix elements of the excitonic matrix increase, except one, concerning the rotated bond. It is therefore not surprising that in the π excitonic model, the excited state energy increases when one rotates a double bond. A proper demonstration should consider the off-diagonal matrix elements. One may see that

$$\left\langle \begin{pmatrix} r^* \\ r \end{pmatrix} \middle| H \middle| \begin{pmatrix} l^* \\ r \end{pmatrix} \right\rangle = \langle r^* | F | l^* \rangle$$

and

$$\left\langle \begin{pmatrix} r^* \\ r \end{pmatrix} \middle| H \middle| \begin{pmatrix} r^* \\ l \end{pmatrix} \right\rangle = -\langle r | F | l \rangle$$

are the only varying off diagonal matrix elements; their variations are opposite, as easily seen by decomposing them on atomic integrals. Their variation involves non bonded atoms monoelectronic integrals, which are much smaller than the corresponding integrals between neighbourg atoms, and they cannot change significantly the conclusion obtained from the consideration of the diagonal elements.

For two equal rotations, the energy E_0 increases as $4\beta\cos\theta$; the transition energies towards locally excited determinants are unchanged and the diagonal of the excitonic matrix is more increased than in the single rotations, leading to an increased barrier.

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