

NEUTRAL VERSUS IONIC EXCITED STATES OF CONJUGATED SYSTEMS ; THEIR
ROLE IN PHOTOISOMERIZATIONS

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Abstract - VB theory introduces a qualitative distinction between neutral and ionic states according to the instantaneous content of the wave functions. The importance of this distinction is exemplified on the case of linear polyenes, and helps to understand the existence of a low lying $^1A_g^*$ neutral singlet excited state. The neutral and ionic states of the linear polyenes twisted around a double bond are interpreted in terms of neutral $A\cdot B\cdot$ ground state diradicals, neutral $A^+B\cdot$ ($A^+B^{\cdot\cdot}$) excited state diradicals or A^-B^+ (A^-B^-) zwitterions. It is argued that the ionic twisted excited states lie too high in energy to be accessible from the $^1A_g \rightarrow ^1B_u$ vertical absorption and that the photoisomerization should proceed through the neutral $A^+B\cdot$ twisted excited state, which is connected to the $^1A_g^*$ hidden state, whatever the $^1A_g^*/^1B_u$ vertical excitation ordering.

DECEIVING PREDICTIBILITY OF AB-INITIO CI RESULTS, AS EXAMPLIFIED ON
BUTADIENE

This section illustrates the difficulty to obtain accurate values of excited state energies in a small conjugated polyene from quantum chemical calculations, and to understand the mechanism of the cis-trans photoisomerization. Table 1 reproduces a few ab-initio results concerning the vertical transition energies. All methods agree for the triplet states, while the $^1A_g^*$

TABLE 1. Vertical transition energies of butadiene (kcal/mole)

state	3B_u	3A_g	1B_u	$^1A_g^*$
exp (ref. 1-5)	74	113	136	163 ^c
BSP (ref. 6)	76	114	177	162
H et al. (ref. 7)	80	116	194	156
NG (ref. 8)	77	117		163
B-K (et al. (ref. 9)	80	120	177	230
This work ^a	83	123	163	200
HEH (ref. 10) ^b	70	122		167

^a double dzeta basis set, second order CI from multireference wave functions

^b non-empirical Heisenberg Effective Hamiltonian calculations (for neutral states only)

^c uncertain

excited state exhibit large dispersion ; notice the overestimation of the ionic 1B_u excited state energy.

The strong electronic differences of the various states are underlined by the optimized geometries (Table 2), which are very different from one state to another. These geometry optimizations may become crucial in the energy lowering of the excited states since they stabilize the lowest triplet 3B_u by

13 kcal/mole ⁽¹⁰⁾ and the excited neutral

TABLE 2. Optimized bond lengths of planar conformations of butadiene in various states (in Å)

	exp ¹¹	¹ A _g ^{HEH} 10	SCF ¹²	³ B _u ^{HEH} 10	PPP* ¹³	¹ A _g ^{HEH} 10
C=C	1.343	1.351	1.465	1.452	1.387	1.390
C-C	1.467	1.445	1.329	1.364	1.396	1.383

¹A_g* state by 28 kcal/mole ⁽¹⁰⁾. Since these optimizations are difficult to perform in ab-initio-CI calculations, the calculated energies suffer a major uncertainty.

Although most ab-initio calculations predict an ¹B_u < ¹A_g* ordering, the doubt about the energies of the twisted conformation excited state is much larger. Three types of calculations are reported in Table 3, with several large CI's by the same authors⁽⁹⁾ which change the ordering of states according to the extrapolation techniques or the MO's used in the CI. One should notice that

TABLE 3. Calculated energies of various states of butadiene in its 90° twisted conformation around a C=C bond (with respect to the planar Ground State, in kcal/mole) ; A stand for Allyl like and M for Methyl like orthogonal fragments

State	¹ A ⁺ M ⁻ *	³ A ⁻ M ⁻ *	³ A ⁻ *M ⁻ *	¹ A ⁻ *M ⁻ *	¹ A ⁺ M ⁻	¹ A ⁻ M ⁺
BK (ref. 9) π CI	58	59		140	170	190
large CI	57		138	160	142	160
NO CI	60			152	130	150
Thiw work ^a (and ref. 14)	57	59	130	132	149	152
HEH (ref. 10)	51	52	130	131		

^a double dzeta basis set and 2nd order CI from multireference wave functions using adapted MO's for the different states.

some MO-CI calculations give a neutral A⁻*M⁻* < ionic A⁺M⁻ energy ordering, while others reverse this ordering. This is a problem of major photochemical importance since if the ionic A⁺M⁻ singlet state is the lower twisted singlet, and if it lies below the ¹B_u vertical excited state, the reaction may proceed on the ionic surface state connecting the ¹B_u vertical excited state to the polar twisted minimum. Both conditions are satisfied in one calculation of ref. (9), even if one refers to the experimental vertical transition energy. The works from our group, both through MO-CI approaches and through a non-empirical Heisenberg Effective Hamiltonian, support on the contrary the A⁻*M⁻* < A⁺M⁻ energy ordering. In such a case the neutral A⁻*M⁻* singlet twisted conformation might act as a funnel in the ionic surface as originally suggested by an early VB semi-empirical work of Oosterhoff for a different process (photocyclization butadiene→cyclobutene)⁽¹⁵⁾. One should notice again that the geometries of these twisted conformations are very different according to Table 4.

TABLE 4. Optimized bond lengths of the 90° twisted butadiene, in various states (in Å) (from ref. 10, except for the last column)

State	¹ A ⁺ M ⁻ * or ³ A ⁻ M ⁻ *	³ A ⁻ *M ⁻ * or ¹ A ⁻ *M ⁻ *	¹ A ⁺ M ⁻ a
C=C	1.389	1.481	1.35
C-C	1.389	1.481	1.45
C≡C	1.464	1.464	1.47

^a from ref. 16, closed shell SCF-MO geometry optimization

From that brief preliminary review one might get the discouraging feeling that ab-initio techniques are not yet able to bring reliable information on the excited potential surfaces, and will be of poor help for photochemists, and this feeling is, alas ! largely grounded. The following sections try to move back to basic qualitative concepts and models of the excited states, and

tempts to a) explain the specified difficulties in the correct representation of the various excited states by their physical heterogeneity and b) predict a certain number of behaviours of the excited states and excited surfaces, which are essentially obtained from qualitative arguments and reach a sufficient likelihood.

QUALITATIVE DIFFERENCES BETWEEN NEUTRAL AND IONIC STATES IN HOMOGENEOUS SYSTEMS

Distinction between neutral and ionic states

Valence Bond theory has introduced a qualitative distinction between the states of an homonuclear system, according to the instantaneous content of the wave-function. For a two-centre problem, such as the ethylene π system, reduced first to two valence atomic orbitals a and b on each center, one may establish directly, from symmetry considerations (with respect to the plane orthogonal to the A-B bond), the form of the four eigenstates either in the MO-CI approach or in the VB language. The former handles symmetric bonding (say π) and antisymmetric antibonding (say π^*) MO ;

$$\pi = (a+b)/\sqrt{2} \qquad \pi^* = (a-b)/\sqrt{2}$$

where a and b are two local orthogonal functions (with essential weights on the $2p_z$ AO's of the two carbon atoms and hyperconjugative tails) which will be used to build the determinants in the VB approach. The symmetry content of the Ground State, valence triplet state, and two valence singlet excited states may be explicitly given in either the MO or VB languages, using a single parameter λ

State (Mulliken's notation).Symmetry	MO-CI	VB
$N(^1A_g)$	$\lambda \pi\bar{\pi} - \mu \pi^*\bar{\pi}^* $	$((\lambda+\mu)/2)(a\bar{b} + b\bar{a}) - ((\lambda-\mu)/2)(a\bar{a} + b\bar{b})$
$T(^3B_u)$	$ \pi\bar{\pi}^* , \bar{\pi}\pi^* , (\pi\bar{\pi}^* - \bar{\pi}\pi^*)/\sqrt{2}$	$ ab , \bar{a}\bar{b} , (a\bar{b} - b\bar{a})/\sqrt{2}$
$V(^1B_u)$	$(\pi\bar{\pi}^* + \bar{\pi}\pi^*)/\sqrt{2}$	$(a\bar{a} - b\bar{b})/\sqrt{2}$
$Z(^1A_g)$	$\lambda \pi^*\bar{\pi}^* + \mu \pi\bar{\pi} $	$((\lambda+\mu)/2)(a\bar{a} + b\bar{b}) - ((\lambda-\mu)/2)(a\bar{b} + b\bar{a})$

with $\lambda^2 + \mu^2 = 1$, $\lambda > \mu > 0$, $\lambda \rightarrow 1/\sqrt{2}$ when $R \rightarrow \infty$

The preceding expressions simply express the fact that the $|\pi\bar{\pi}^*|$ and $|\bar{\pi}\pi^*|$ determinants are antisymmetric while the $|\pi\bar{\pi}|$ and $|\pi^*\bar{\pi}^*|$ determinants are symmetric with respect to the above mentioned plane of symmetry. The usual SCF or Hartree-Fock description of the ground state is $\phi_0 = |\pi\bar{\pi}|$, but CI mixes this determinant with the doubly excited determinant $|\pi^*\bar{\pi}^*|$ of higher energy ; the mixing is out of phase, since the interaction $\langle \pi\bar{\pi} | H | \pi^*\bar{\pi}^* \rangle$ is a $K_{\pi\pi^*}$ positive exchange integral. This remark insures the relationship $\lambda > \mu > 0$. The symmetric singlet excited state Z is the orthogonal combination of $|\pi\bar{\pi}|$ and $|\pi^*\bar{\pi}^*|$, while the $|\pi\bar{\pi}^*|$ and $|\bar{\pi}\pi^*|$ singly excited determinants generate the antisymmetric singlet excited state and the ($S_z=0$) triplet state component. The VB description (immediately obtained from a^z and b) gives an alternative equivalent description in terms of local instantaneous situations. While the determinants $|a\bar{b}|$ and $|b\bar{a}|$ are said to be neutral (since both atoms bear one electron), the $|a\bar{a}|$ and $|b\bar{b}|$ determinants are called ionic. They correspond respectively to A^-B^+ and A^+B^- zwitterionic instantaneous situations, in which one atom bears two π electrons, while the other is ionized. Two major points must be underlined there ;

- the neutral determinants, have lower mean energy than ionic situations

$$\langle a\bar{b} | H | a\bar{b} \rangle < \langle a\bar{a} | H | a\bar{a} \rangle$$

As a consequence the lowest eigenstates of the problem have their largest components on the neutral situations ; for instance here the ground state has a $(\lambda+\mu)/2$ component on the neutral situations, while a $(\lambda-\mu)/2$ component on the ionic situations. Similarly one will have a lower energy for the triplet $\pi\pi^*$ state (which is neutral) than for the $\pi\bar{\pi}^*$ singlet state (which is ionic). - the MO apparent similarity between the singlet and triplet $\pi\pi^*$ singly excited states is completely misleading since the instantaneous physical contents are completely different for these states ; the triplet state is purely neutral each atom having always one electron while in the singlet excited state V the overall neutral static character of the wave-function (no dipole moment) is the result of a charge fluctuation between ionic situations, the two electrons jumping from A to B and vice-versa.

Generality of this distinction

This opposition between neutral and ionic states is general for non-polar systems, such as conjugated hydrocarbons, where the static charge displacements are very weak. All states are non-polar (no static charge, no large dipole moment) but some of them are dominated by the neutral instantaneous situations (they are said to be neutral), while others are essentially ionic since their largest components are on ionic instantaneous situations. As an example we give the VB physical content of the lowest states of butadiene (Table 5).

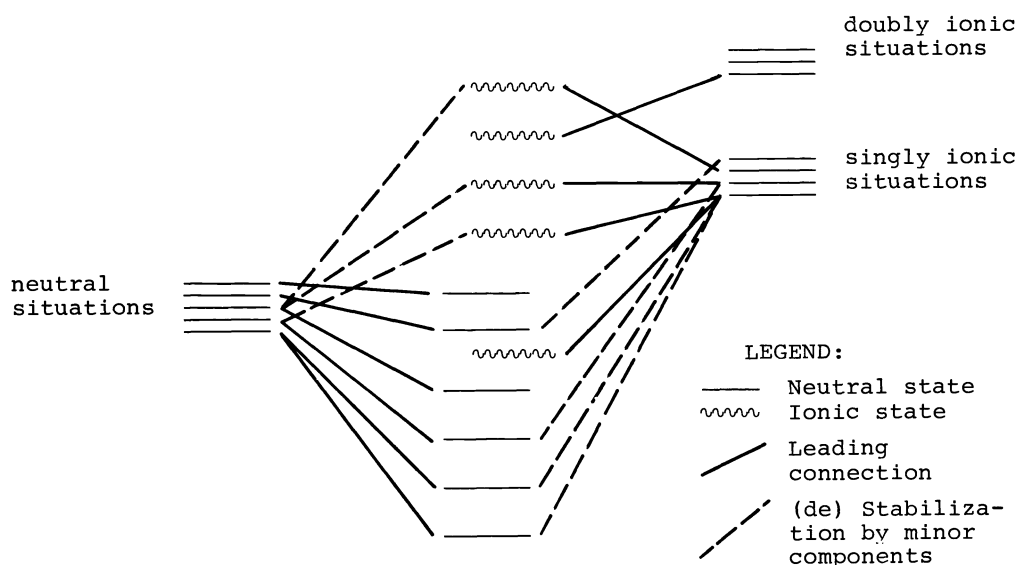
TABLE 5. VB content of the lowest states of butadiene π system

VB nature	Neut.	Neut.	Neut.	Neut.	Ion.	Neut.	Ion.
Symmetry	1A_g	3B_u	3A_g	$^1A_g^*$	1B_u	3B_u	1A_g
Total weights on neutral det.	40.0	47.8	40.4	48.7	0.	43.2	11.4
Singly ionic det.	51.8	52.2	59.6	46.9	76.8	56.8	63.3
Diionic det.	8.2	0.	0.	4.4	23.2	0.	25.3

Largest coefficients (a, d, u, b of them)	0.357 (2)	0.420 (2)	0.449 (2)	0.392 (2)	0.339 (2)	0.418 (2)	0.279 (1)

One should notice that the lowest singlet and triplet states have both their largest components on spin waves, while the singlet hidden state $^1A_g^*$ is a product of $S_z = -1$ and $S_z = 1$ triplet states on the two double bonds. The lowest ionic state 1B_u of butadiene has its largest component on charge waves (However, for larger polyenes the 1B_u state could be seen preferably as resulting from resonance between moving zwitterionic structures).

As a general statement one may say that the lowest states are neutral with important components on the ionic situations, since their stabilization to low energies results from the interaction with the higher lying ionic situations. The lowest ionic states are strongly ionic, they have weak components on the neutral situations, since the interaction with low lying determinants would higher their energy. As a consequence, the distinction between neutral and ionic states is not arbitrary, it does not vanish for large systems (see schema).



One should of course mention that

- some neutral states (these having weak coupling with ionic determinants) lie higher in energy than the lowest ionic states ; the neutral < ionic ordering is not perfect, it is only true for the lowest states of each category, but a zone exists where the neutral and ionic spectra overlap.

- the neutral \rightarrow neutral excitations are dipole forbidden. So, the transition to neutral excited singlet states will be forbidden from the ground state. The lowest ionic excited states, on the contrary, are these which keep the maximum dipolar allowance since they are essentially zwitterionic in nature. From that view-point one may say that a chiasma occurs between the way the MO and VB descriptions think the various states. In the MO approach the ground state is usually well defined and its filling of orbitals stands for a reference ; then the excited states are thought in terms of elementary electron jump from a bonding MO i into an antibonding one j^* , and the corresponding $i \rightarrow j^*$ triplet and singlet states are supposed to be strongly related, simply differing by a spin reversion and an exchange integral $K_{ij^*} (\times 2)$. Actually the physical content of these MO-connected states are completely different, as exemplified above (cf. Table 5), and the VB description makes a close connection (see Fig. 1) between the ground state and the lowest triplet state than with any other state (since they both may be seen as resulting from the in-phase and out of phase combination of two spin waves, cf. Table 5).

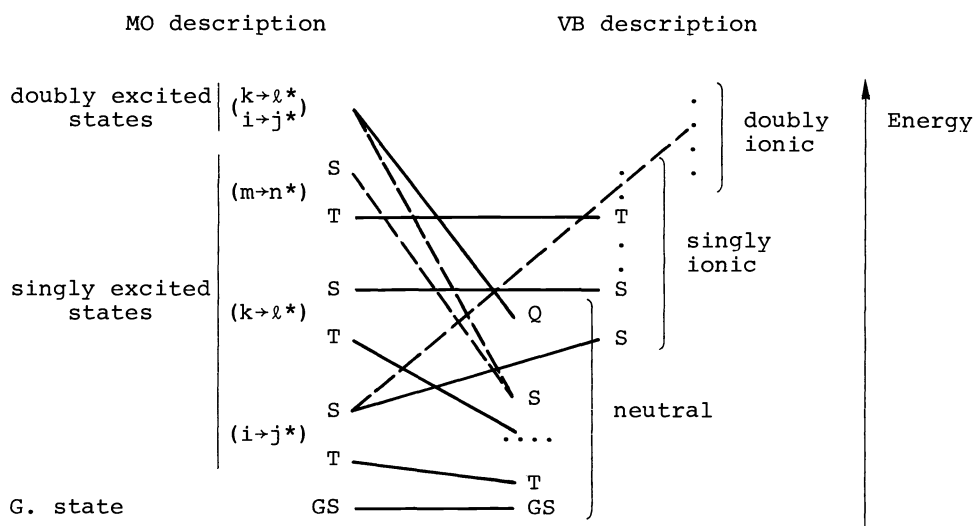
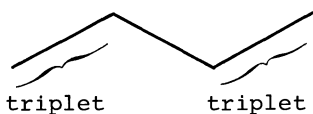


Fig. 1. The MO-VB chiasma in the excited states representation.

Photochemists should remember that point, of major significance. The description in terms of single excitations, bonding to antibonding electron jumps, is very easy since it is static and uses the now very popular MO description. But one should remember that the underlying nature of these states, in terms of fluctuating charge repartition, may be completely different and the MO description, already made rather approximate by the extent of CI effects in excited states, may become useless.

As an example one may quote the famous hidden singlet state ${}^1A_g^{(-)}$ or ${}^1A_g^*$ of conjugated polyenes. This state is a mixture of single (homo \rightarrow (lumo+1), (homo-1) \rightarrow lumo) excitations and double (homo \rightarrow lumo)² excitation in the MO approach and for this reason it seems to lead to some embarrassing feelings. Its status in the VB approach is more evident ; considering butadiene for instance, this state appears as a product of triplet states on both double bonds as appears from Table 1.

$$ab\bar{c}\bar{d} + \overline{a}bcd =$$



Origin of the difficulties in correct predictions of excited states energies
 For the present time we do not enter the polemic about the ${}^1A_g^*$ (hidden neutral singlet) versus 1B_u (ionic allowed singlet) energy ordering, g which received so many contradictory contributions (5,17,28). The discussion is made difficult by the highly forbidden character of the ${}^1A_g \rightarrow {}^1A_g^*$ excitation. From our numerical experience we would be tempted to say g that g for the lowest members of the series (butadiene and hexatriene) the ${}^1A_g > {}^1B_u$ ordering is likely, but the ${}^1A_g < {}^1B_u$ ordering must necessarily prevail g for u large enough systems. This g discussion is usually limited to the vertical excitation, except for a few papers who tried to estimate the relaxed geometry of the excited state (13,10). We would like to point out that this ordering is not of major importance for the cis-trans photoisomerization problem which will be discussed below.

One should also point out that the ionic states are much more difficult to treat accurately in ab-initio calculations than are the neutral states. Due to the ionic character, CI must involve large σ - π correlation effects representing the instantaneous repolarization of the σ cores, the basis set must involve diffuse orbitals to stabilize the negative centers (Rydbergization) and polarization orbitals to correlate angularly the instantaneous electron pairs on the same atom (for a review see ref. 29). Actually σ - π correlation (30), diffuse and polarization orbitals are verified to act more significantly on the ionic states. This is the reason why the obtention of correct ab-initio estimates of the 1B_u states of polyenes are so rare (cf. Table 1), while the ${}^1A_g^*$ state should be u obtained more easily (7,8,10). This remark concerning the difficulty to have a good ${}^1A_g \rightarrow {}^1B_u$ transition energy (28) does not prove that the calculated ${}^1A_g \rightarrow {}^1A_g^*$ theoretical estimates are wrong.

The physical content of neutral excited states as revealed by their relaxed geometries

Using a non-empirical Heisenberg Hamiltonian (10), we have been able to study the relaxed planar geometries of the excited states of linear polyenes, deriving their asymptotic behaviour. The results are very clear for the lowest triplet state, which appears to have a soliton-pair structure ; the soliton



is an impaired electron and the associated semidelocalized nuclear deformation : this concept has been made popular by the works of physicists (31) in the polyacetylene problem and its electrical conductivity properties. The two solitons are located at the first and third fourth of the chain length. One should notice that in the central region, between the two solitons, the bond alternation is reversed with respect to the ground state structure, the double bonds become single bonds and vice-versa. For that geometry the ground and the lowest triplet states are nearly degenerate since the spin coupling between the two impaired electrons, which are far from each other, is very weak. This is a region of touching of the ground and lowest triplet states potential surfaces. This region corresponds to a real minimum of the lowest triplet (except for butadiene and hexatriene) and it is not high in energy : the asymptotic limit of the non-vertical ground state to lowest triplet state transition energy should be 10.5 kcal/mole

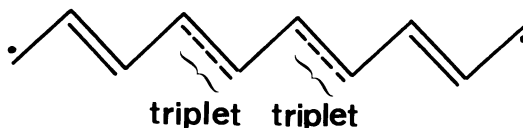
$$\Delta E({}^1A_g \rightarrow {}^3B_u) (0-0) \approx 10-11 \text{ kcal/mole, when } N \rightarrow \infty \quad (1)$$

while the vertical transition should be twice larger

$$\Delta E^V({}^1A_g \rightarrow {}^3B_u) = 20 \text{ kcal/mole when } N \rightarrow \infty \quad (2)$$

If one remembers that the corresponding excitation for ethylene is about 97 kcal/mole, 74 kcal/mole for butadiene, (1) and 60 kcal/mole for hexatriene (32), one notices that the rapid decrease of the lowest triplet state surfaces is confirmed experimentally.

The planar relaxed geometry of the so called ${}^1A_g^*$ singlet excited state is less easy to guess from numerical calculation (or from intuitive grounds) with two impaired electrons located at the extremities of the chain, and a couple of triplet excited double bonds in the central region.



The asymptotic limits to the $S_0 \rightarrow {}^1A_g^{(-)}$ vertical transition energy have been extrapolated (10) and give

$$\Delta E^V({}^1A_g \rightarrow {}^1A_g^*) = 1.35 \text{ eV} \quad \text{when } N \rightarrow \infty \quad (3)$$

while the corresponding (0-0) adiabatic transition would be

$$\Delta E({}^1A_g \rightarrow {}^1A_g^*)_{(0-0)} = 0.47 \text{ eV, when } N \rightarrow \infty \quad (4)$$

These values should be compared to the asymptotic limit (3-4,33) of the allowed transition energy

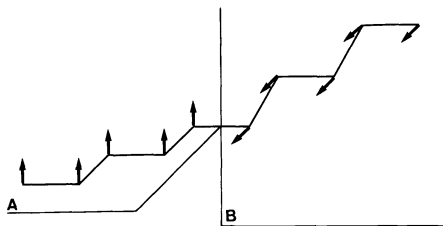
$$\Delta E({}^1A_g \rightarrow {}^1B_u) = 1.8 \text{ eV, when } N \rightarrow \infty \quad (5)$$

These tendencies show that the ${}^1A_g^* < {}^1B_u$ ordering, already experimentally verified for octatetraene (34) and decapentene (35) should be confirmed for larger polyenic systems.

THE CIS-TRANS PHOTOISOMERIZATION OF LINEAR POLYENES (AND OTHER CONJUGATED HYDROCARBONS)

General situation of the problem ; the competing excited states

The cis-trans isomerization of a double bond necessarily proceeds through a 90° twisting of this bond, defining a conformation in which two previously conjugated systems A and B come out to become orthogonal subsystems, with a vanishing conjugation between them. Although hyperconjugation plays a numerically important role, the two π systems of A and B have a very weak (and sometimes zero) overlap (through the overlap between atoms separated by three bonds at least). Both systems A and B have now an odd number of carbon atoms if one starts from a closed shell system, with $2p+1$ carbon atoms in system A, and $2q-1$ carbon atoms in B respectively,



Now in this twisted conformation, two types of electron distributions may be considered, some of them being ionic, the others being diradicalar in character. For the elucidation of the mechanism of the photoisomerization, it is a crucial point to clearly visualize the qualitative nature of the various states under competition in the 90° conformation. One should remember first that for a π system with an odd number of carbons, in the MO picture, the cationic (A^+), neutral (A^\cdot) and anionic (A^-) ground states differ by the zero, half and complete filling of a "non-bonding" MO, ψ_A (Fig. 2). One should also

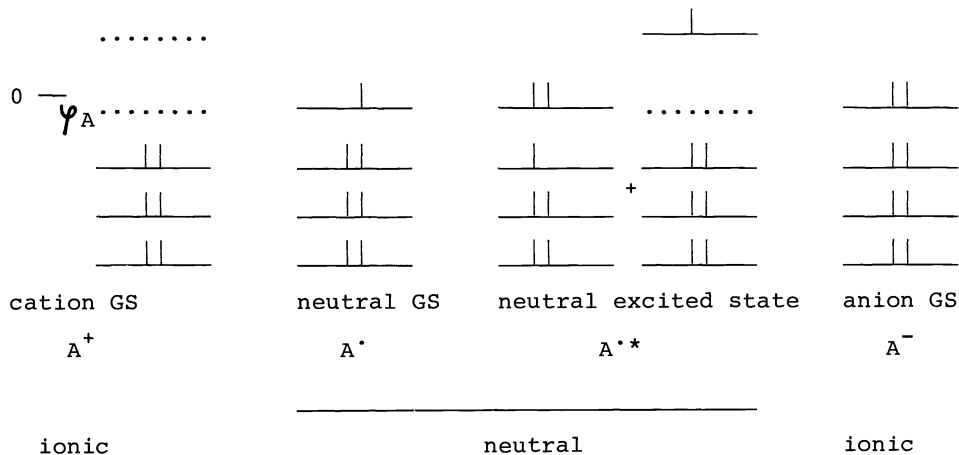


Fig. 2. MO filling of a π system with $2p+1$ carbon atoms, in ionic and neutral states.

consider the neutral excited state A^*B^* , which is a linear combination of determinants where the unpaired electron occupies bonding or virtual MO's (cf. Fig. 2).

Then it is easy to give a qualitative picture of the various states of a 90° twisted polyene, since they result from the five possible combinations A^+B^- , A^-B^+ , A^*B^* , A^*B^* and A^*B^* . The lowest states of the $A-B$ system are necessarily neutral with both A^\cdot and B^\cdot in their ground state. They are of $A^\cdot B^\cdot$ character; these are the twisted singlet ground state and the lowest triplet state, which are almost degenerate for this twisted conformation (Fig. 3). Then one may consider two types of excited states of the $A-B$ system. The ionic states are built from A^-B^+ and A^+B^- situations, they are necessarily singlet (since closed shell in nature) and they generate a couple of eigenstates S_1 and S_2 . The neutral states are built from A^*B^* and A^*B^* situations, they are of biradicalar type but one of the radicals is excited. These open shell situations generate both triplet states (T_2 and T_3) and singlet neutral excited states (labelled S_1^* and S_2^*).

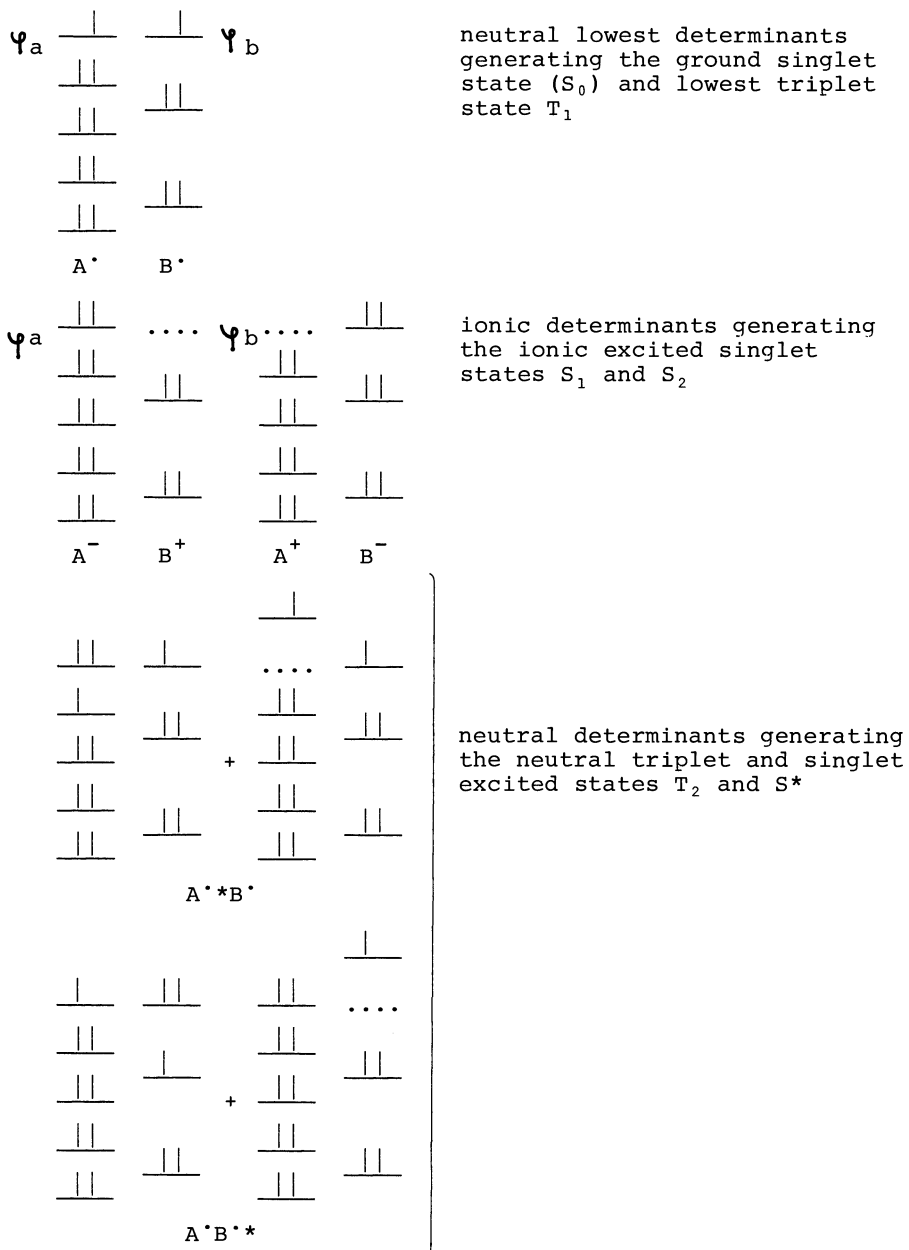


Fig. 3. MO content of the various states appearing in the 90° twisted double bond conformation of a conjugated hydrocarbon.

the chain length increases

- its asymptotic value for $N \rightarrow \infty$ is 18 kcal/mole
- the highest rotational barrier concerns the most external double bonds; it remains approximately equal to the corresponding value for butadiene (53 kcal/mole) since the asymptotic limit is about 40 kcal/mole (37)
- In view of the calculated evolution of the vertical 3B_u excitation energy (10) one may conclude that starting from this vertical excitation:
- The rotation around the external double bond of a linear polyene becomes impossible for decapentene and larger conjugated systems
- The rotation around the most internal double bond of a linear polyene is always possible ($E^V({}^3B_u) > E^I(A^*B^*)$) if the A-B bond is internal.

Twisted neutral excited states (S^* and second triplet) : $\mu(A^*B^*) + \nu(A^*B^*)$.

The two main components of these wavefunctions, A^*B^* and A^*B^* , are not of the same energy if A and B are different; the excitation energy of a radical decreases with the number of conjugated atoms; $E(A^*B^*) < E(A^*B^*)$ if A is larger than B. The interaction between these two components is very weak; turning back to Fig. 3 one sees that the determinants of A^*B^* differ at least by two spin orbitals and interact at most through integrals of the type $(i_a \psi_a, i_b \psi_b)$ where i_a and i_b are doubly occupied or virtual MO's of A and B, and these dipole-dipole interactions should decrease as $(0.5R)^{-3}$ when the size of the system increases, R being the chain length (since the ψ_a and ψ_b distributions are located in the centre of the A and B subsystems). As a consequence, the neutral excited singlet in the twisted conformation should represent an A^*B^* situation, i.e. an excitation located on the largest radical. One should have the approximate relation

$$E^I(S_1^*) = E^I(A^*B^*) + \Delta E^V(A \rightarrow A^*)$$

or

$$E^I(S_1^*) - E(GS) = R_{AB} + \Delta E^V(A \rightarrow A^*) \quad (6)$$

i.e. the neutral excited singlet lies above the ground state rotational barrier R_{AB} at an energy equal to the vertical transition energy of the largest radical fragment.

Of course there is nearly no experimental information about the transition energies of such radical systems. The calculations (10) predict that

- the $E^I(S_1^*)$ energies decrease linearly as N^{-1}
- for small and intermediate polyenes (up to $N=16$) $E^I(S_1^*)$ is lower when the twisting concerns the external bond,
- for large enough polyenes ($N > 16$), the lowest energy twisted conformation of the neutral excited state implies the most internal double bond
- if one focuses on the rotation around the most internal double bond, the following relation is satisfied :

$$E^{\text{Relaxed}}({}^1A_g^*) < E^I(S_1^*) < E^V({}^1A_g^*) \quad (7)$$

The rotation around the most central double bond would be always possible for a vertical excitation of the hidden singlet state. If one accepts that for large enough polyenes ($N > 8$), the hidden state (${}^1A_g^*$) is lower in energy than the vertical (1B_u) state,

$$E^V({}^1A_g^*) < E({}^1B_u) \implies E^I(S_1^*) < E^V({}^1B_u) \quad (8)$$

The rotation around an internal double bond would be always possible from the vertical allowed transition, at least by a change from the ionic surface 1B_u to the neutral ${}^1A_g^*$ surface. More precisely it seems that the variation of the $E^V({}^1B_u)$ vertical absorption is slow enough to insure $E^I(S_1^*) < E^V({}^1B_u)$ for all double bonds (10).

Ionic twisted excited singlets : $\alpha(A^-B^+) + \beta(A^+B^-)$. The two main components of the wave-function are weakly interacting. Assuming that they simply differ by the position of the highest energy filled MO (which is a crude approximation due to large repolarization effects), their mutual interaction is given by an exchange integral between the non-bonding MO's of the systems A and B ($\langle \phi_{A-B+} | H | \phi_{A+B-} \rangle \approx K \psi_a \psi_b$). This integral is very small since the overlap distributions $\psi_a \psi_b$ are almost vanishing. When the energy difference between the polar situations A^+B^- and A^-B^+ is larger than this weak interaction, the ionic state appears as polar, with a non negligible dipole moment; if $\langle \phi_{A+B-} | H | \phi_{A+B-} \rangle - \langle \phi_{A-B+} | H | \phi_{A-B+} \rangle > \langle \phi_{A+B+} | H | \phi_{A+B-} \rangle$ the lowest ionic state

is dominated by the lower energy ϕ_{A-B^+} distribution

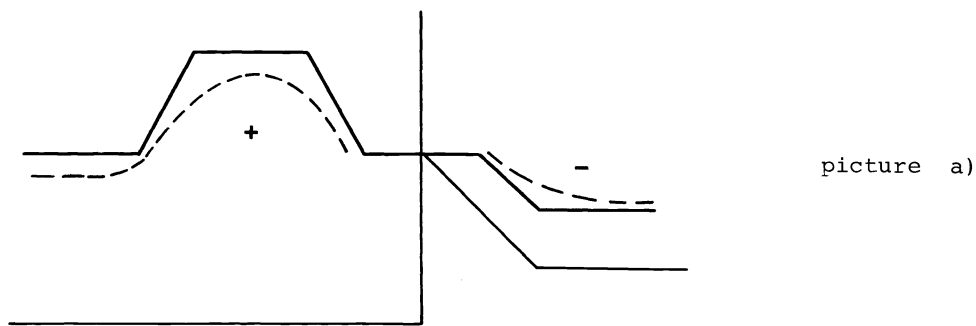
$$\psi_{\text{ionic}} = \phi_{A-B^+} + \epsilon \phi_{A^+B^-}$$

$$\langle \psi_{\text{ionic}} | \vec{\mu} | \psi_{\text{ionic}} \rangle \cong \langle \phi_{A-B^+} | \vec{\mu} | \phi_{A-B^+} \rangle$$

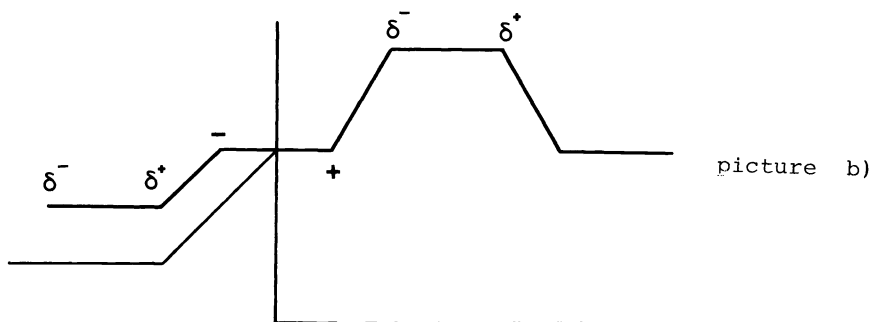
(and vice-versa if $\phi_{A^+B^-}$ is of lower energy). The so-called "sudden polarization effect" noticed first by Salem *et al.* (38) pointed out the fact that for 90° twisted conformations, the ionic eigenstates are not an equal mixture of A^+B^- and A^-B^+ situations, one of the situations prevails when the twisting destroys the conjugation and weakens the resonance between the ionic situations which insured a non polar character of the ionic states when the conjugation was large.

- as a second general fact one should mention that the positive charge will tend to locate on the larger subsystem ; if $2p+1 > 2q-1$ (A longer than B), the lowest energy ionic situation is A^+B^- . This is a direct consequence of the larger sensitivity of the ionization potential to the chain length ; the electroaffinity is a small quantity which cannot vary significantly when the conjugated chain increases.

- One may be tempted to ignore the electrostatic interaction between the two charges in an ionic situation and to delocalize the positive and negative charges on A and B respectively, as they would be in isolated A^+ and B^- system ; then the center of gravity of the + and - charges would be on the



centres of the A and B subsystems at distances $R/2$, resulting in a huge dipole moment (39). This picture has been criticized (40) since the electrostatic interaction will bring the two charges as close as possible, on the two sides of the twisted bond with polarization effects on the π (and σ) bonds of both



A and B. This relocation of the charge leads to a much lower (and almost constant) dipole moment. The question of the sudden character of the polarization has been relativized by the study of the specific distortions of the ionic minima (41,42). The asymptotic energy of picture a) would be

$$E^{\perp}(S_1) - E(\text{GS}) = R_{AB} + PI_A - EA_B - N\ell^{-1} \quad (9)$$

while that of picture b) will be deduced from the (0-0) ΔE ($N \rightarrow V$) transition energy of ethylene (134 kcal/mole) (41-43)

$$E(S_1) - E(\text{GS}) = \Delta E^{(0-0)}(S_0 \rightarrow S_1)_{\text{ethylene}} - \text{polarization effects on the adjacent bonds} \quad (10)$$

If picture a) is adopted, by comparing with eq. (6), it is evident that for large enough N , $E^{\downarrow}(S_1^*) < E^{\downarrow}(S_1)$ since the excitation energy of A is of course lower than its ionization potential. If one adopts picture b), the same conclusion may be reached since the polarization effects converge rapidly (as $\sum_{n=1}^N \frac{1}{n^4}$) toward a limit.

A first general conclusion is then the following : for twisted conformations the neutral excited singlet state (A^*B^{\cdot}) should be lower in energy than the ionic singlet state (A^+B^-). This conclusion is confirmed by our numerical calculations (14, see however ref. 9) for butadiene.

A second conclusion is obtained from the fact that the vertical allowed transition energy $\Delta E^V(^1A_g \rightarrow ^1B_u)$ is rapidly decreasing (linearly with N^{-1}) to a limit estimated to be about 2 eV (33). Then if $E^{\downarrow}(S_1) - E(\text{GS})$ tend toward 100 kcal/mole (as suggested by ref. 14), the cis-trans photoisomerization cannot proceed on the singlet excited ionic surface connected with the vertically excited 1B_u state (see above inequality I') when the vertical transition energy $\Delta E^V(^1A_g \rightarrow ^1B_u)$ becomes lower than 100 kcal/mole (i.e. for octatetraene and larger polyenes).

On the contrary the rapid decrease of the neutral excited singlet state energy of the twisted conformation insures the $E^{\downarrow}(S_1^*) < E^V(^1B_u)$ (inequality II) and we are thus in case (I'+II) of the previous discussion for polyenes larger than octatetraene. If the cis-trans photoisomerization from the $^1A_g \rightarrow ^1B_u$ absorption cannot proceed on the ionic surface, it must involve lower energy surfaces. The most likely mechanism would not involve an intersystem crossing (i.e. the 3B_u state) nor the internal conversion to the ground state, but a passage to the closest surface of singlet character, i.e. the $^1A_g^*$ excited surface. The change from the 1B_u to the $^1A_g^*$ surface may occur through internal conversion, through an avoided crossing for intermediate values of θ or through a dipole allowed $^1B_u \rightarrow ^1A_g$ infrared emission. The only exceptions for these general statements are of course ethylene (for which the $^1A_g^*$ neutral excited state does not exist) and possibly butadiene (cf. ref. 9). These results are schematically summarized in fig. 4.

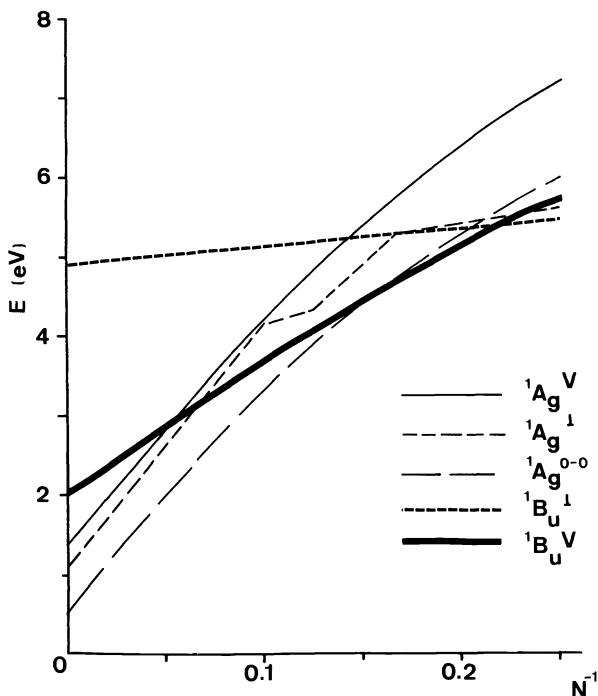


Fig. 4. Experimental (1B_u)^V and calculated (refs. 10,14) transition energy N -dependences of polyenes. The (0-0) (1B_u) energies lies ~ 0.1 eV below the vertical energies and are not included. The symbol \downarrow refers to 90° twisted polyene around the most favorable double bond. For large N the values of $E(^1B_u)^{\downarrow}$ are very estimative (14).

CONCLUDING REMARKS

This work partly supports its numerous predictions upon the calculations of neutral excited states geometries and energies through an unusual magnetic model (Heisenberg Hamiltonian) which has proved its reliability on a wide variety of ground state situations (37). Ionic excited states are more difficult to reach to the same kind of accuracy, but experimental information is larger for these states (at least in planar conformations) from absorption and emission spectra. The implication of neutral singlet excited states in photochemistry should not be limited to polyenes, it concerns of course the triplet cis-trans isomerization of styrene, stilbene and analogs, but also the singlet isomerization of styrene (as suggested early (44) and recently demonstrated (45,46)) against a mechanism which involved ionic intermediates (47).

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