type being developed by Blumen and co-workers,[64–66] in concert with additional experimental data should clarify the matter soon.

The diffusion lengths attained here are interestingly large but are insufficient for the ultimate purpose of efficiently collecting photonic energy for supply to a reaction center. Distances greater than 200 Å will probably be needed. In order to achieve diffusion coefficients that would lead to such distances, one must find systems giving greater resonance interactions between antenna chromophores. This study has highlighted the desirability of large oscillator strength in the relevant transition and rigidity in the molecule. In addition, we have called upon steric aspects of molecular structure to minimize the formation of dimeric traps in the cast films. All these elements should be preserved in any new system. Equation 4 suggests additionally that the resonance interaction could be improved substantially by going to a chromophore with a much redder transition. This is probably the most fruitful change that could be made to improve the diffusion coefficient.

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Diradicalar or Ionic Twisted Excited States in the Singlet Cis–Trans Isomerization of Polyenes?

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Abstract: Ab initio extensive CI's are performed on singlet excited states of butadiene, hexatriene, and styrene in their planar and twisted geometries. Size dependance of both ionic and diradicalar excited states is studied. The π conjugation and proper geometrical distortions allow some stabilization of the ionic twisted minima, but these minima remain rather high in energy (above 110 kcal/mol) and twisted diradicalar excited states are always present (for more than two conjugated double bonds) *below* the ionic minima. Since the vertical absorption energy decreases when the dimension of the conjugated system increases, for large enough polyenes, the cis–trans isomerization from the "ionic" absorbing state must proceed through an internal conversion to the lower diradicalar excited surfaces.

I. Introduction

The ${}^1B_u$ absorbing state of linear polyenes is known to correspond to the homo → lumo transition[1] and to be "ionic" in nature when treated in the VB approach. The size dependence of the vertical transition energy follows the empirical law[2]

$$\Delta E = A + B/2n$$

(n being the number of double bonds), which received partial theoretical demonstrations.[3] Recent theoretical[4] treatments and experimental evidences[5,6] support the possible existence of lower ${}^1A_g$ excited states. These excited states are "neutral" in the sense of VB theory and have important components on the (homo → lumo)^2 doubly excited determinant. Experience fails to see such a neutral (forbidden) state below the lowest ${}^1B_u$ state in butadiene[7] and hexatriene,[8] but an ${}^1A_g$ neutral state is definitely found 0.5 eV below the ${}^1B_u$ state in octatetraene,[5,6] and this should be the rule[9] for larger polyenes.

Twisted singlet excited states of polyenes have received much attention. For ethylene the twisted excited singlet is much lower in energy than the vertical $\pi \rightarrow \pi^*$ absorption, and further pyramidalization of one carbon stabilizes the excited state and breaks the symmetry in favor of one of the M^+M^- resonant ionic components of the wave function, allowing an important dipole to appear ("sudden" polarization phenomenon[10]). The resulting minimum has been located at 5.81 eV above the ground state planar energy by accurate extensive CI calculations;[11,12] this funnel in the ionic singlet surface is supposed to play the main role in the cis–trans isomerization. Such ionic minima may be supposed to occur in polyenes, whatever the twisted bond, and are usually supposed to be responsible for the cis–trans isomerization after the vertical allowed transition to the ionic ${}^1B_u$ state. A lot of efforts have been devoted to the problem of the polarization of these twisted minima. For butadiene and terminally twisted polyenes, it is well established now that an important dipole moment occurs in the ionic excited state minimum.[13,14] Controversy has taken

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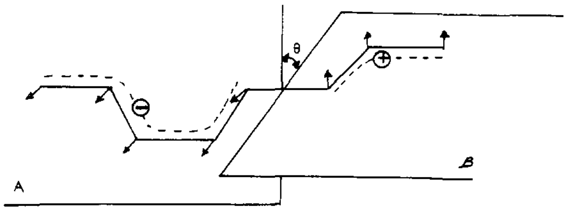
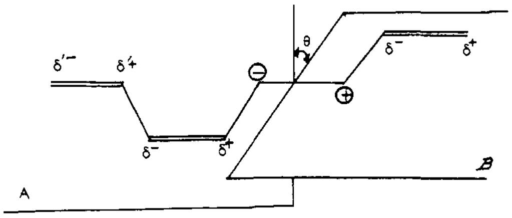
place concerning the existence of such polarizations for internally twisted polyenes,[15] although it seems likely that stabilizing symmetry breakings and pyramidalizations allow the appearance of polar minima in all cases.[16]

This peculiar problem seems of minor interest for the cis–trans isomerization mechanism. Malrieu et al.[14,17] have demonstrated that the correct qualitative description of the ionic states is not given by the delocalized SCF description



which does not take into account the σ and π repolarization effects. The attraction of the excess charges on both fragments localizes them on the twisted bond edges, resulting in a localized picture



where the vicinal π bonds and σ clouds are polarized by the local π field and diminish the dipole.

It is evident from such a qualitative picture that the ionic excited state minimum energy will rapidly reach an asymptote when the dimension of the conjugated orthogonal subsystems tends to infinity. Where may this asymptote be in view of the calculated first members of the series (ethylene, 5.81 eV;[11,12] butadiene, 5.62 eV[14])?

If these polar minima are not low enough in energy they well not be accessible from the vertical transition for large enough polyenes such as retinal analogues (octatetraene ...) and another mechanism must be invoked.

The present paper tries to answer this question by evaluating the delocalization stabilization of a twisted ionic state in the series of linear polyenes (n = 1, 2, 3). The answer is that these polar minima cannot go to lower energies than 110 kcal/mol.

If these ionic excited state minima can be ruled out as being too high above the vertical transition, one must turn to other diradicalar twisted excited states to interpret the cis–trans isomerization of large polyenes; the present paper represents a search of the lowest excited states for twisted geometries; these states may be connected to the ^1A_g neutral excited state of the planar conformation. The calculations show that in butadiene already a neutral state is present in the region of the twisted ionic minimum; delocalization strongly stabilizes these twisted neutral excited states, which will always remain below the vertical transition, and may therefore play a role in the cis–trans isomerizations, provided that internal conversion takes place from the ionic to these neutral excited surfaces. Little attention has been paid to these neutral excited states; as an exception one may quote an early suggestion by Bendazzoli et al.[18] that the lowest excited state of styrene in its twisted conformation would be diradicalar. An alternate mechanism has been proposed by Bruni et al.,[19] resting on the opposite hypothesis that the lowest twisted excited state is zwitterionic. The problem of cis-trans isomerization of styrene deserves a special discussion and the results concerning this molecule are only reported here to illustrate the delocalization dependance of the various twisted excited state energies.

II. Method

The calculations reported in this paper have been carried out with minimal basis sets for all molecules. Butadiene has also been calculated by using a second set of rather diffuse 2p orbitals (ζ = 0.08) on each carbon atom.

For planar geometries all CI calculations are performed from the closed shell SCF MO's. For twisted geometries, the radicalar states were calculated from open shell MO's obtained through the Nesbet–Fock operator;[20] the ionic states are approached first through specific closed shell SCF procedures which localize the "π" charges on separate fragments and introduce the σ and π repolarization effects.

The SCF calculations are always followed by extensive CI's carried out through the CIPSI[21] algorithm. A variational zeroth order wave function is built for each state, including the main determinants, i.e., those which have a component larger than 0.1 in the wave function (the selection is performed through a few preliminary perturbative explorations); let us call S the set of these main determinants and P_S the corresponding projector. For the state m,

$$\mathbf{P}_S H \mathbf{P}_S \Psi_m^{\,0} = E_m \Psi_m^{\,0} \tag{1}$$

$$\Psi_m^{\,0} = \sum_{K\in S} C_{mK}|K\rangle \tag{2}$$

The effect of all of the determinants $|I\rangle$ external to S is treated through a second order perturbation

$$\epsilon_m^{\,2} = \sum_{I\notin S} \frac{|\langle I|H|\Psi_m^{\,0}\rangle|^2}{E_m^{\,0} - E_I^{\,0}} \tag{3}$$

S usually implied (besides the ground state when necessary) most $\pi\pi^*$ singly excited determinants and a few doubly excited determinants; the dimension of the set S varies from 10 to 30 determinants, while the number of generated determinants I frequently exceeds 10^6. No restriction is imposed in the double substitutions.

In some cases, in order to avoid the defects of poor convergence and to reach more reliable results a third (intermediate) class of determinants M has been defined; the effect of these determinants, selected for the importance of their energetic contribution, is calculated variationally (i.e., to all orders) by solving a somewhat larger matrix $\mathbf{P}_{S+M} H \mathbf{P}_{S+M}$

$$\mathbf{P}_{S+M} = \sum_{K\in S} |K\rangle\langle K| + \sum_{K\in M} |L\rangle\langle \mathrm{L}| \tag{4}$$

leading to a new eigenvalue $E_m^{(S+M)}$. The second order effect of the determinants of M on $\Psi_m^{\,0}$ is substracted from $\epsilon_m^{\,2}$

$$\epsilon_m'^{\,2} = \epsilon_m^{\,2} - \sum_{L\in M} \frac{|\langle L|H|\Psi_m^{\,0}\rangle|^2}{E_m^{\,0} - E_L^{\,0}} \tag{5}$$

and $E_m = E_m^{(S+M)} + e_m'^{\,2}$. The class M usually implied most of the π–π^* doubly excited determinants.

III. Twisted Ionic Excited States

Table I reports the main results obtained for the nonvertical transition energies from the planar ground state to the twisted ionic excited states. Let us focus first on the size dependence of this transition energy as appears for the minimal basis set before pyramidalization. At the SCF level, the energy goes from 5.90 eV for ethylene M^+M^- to 5.46 eV in butadiene M^-A^+; the delocalization of the positive charge in the allylic system brings a 0.45 eV (10 kcal/mol) stabilization. On the contrary the delocalization of the negative charge in M^+A^- only gives a 0.17 eV (4 kcal/mol)

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Table I. Position of the Twisted Ionic Excited States with Respect to the Planar Ground State (in eV)[a]

	ethylene		butadiene				hexatriene			styrene	
	M^+M^-		M^-A^+		M^+A^-		A^+A^-	M^-P^+	M^+P^-	M^-B^+	M^+B^-
	EBS	MBS	EBS	MBS	EBS	MBS	MBS	MBS	MBS	MBS	MBS
SCF no pyramid.	5.72[b]	5.90[b]	4.95	5.46	5.59	5.73	≈5.20[b]	5.31	5.63	5.16	5.59
pyramid.	5.25	5.38	4.63		5.54		4.92[c]				
CI no pyramid.		6.87	5.98	6.45	6.81	6.61	6.42			6.47	
pyramid.	5.81		5.62		6.65		6.26[c]				

[a] M = methyl, A = allyl, P = pentadienyl, B = benzyl, EBS = extended basis set, MBS = minimal basis set. [b] Broken symmetry solutions. [c] Partial optimization of the pyramidalization angle of the internal carbon.

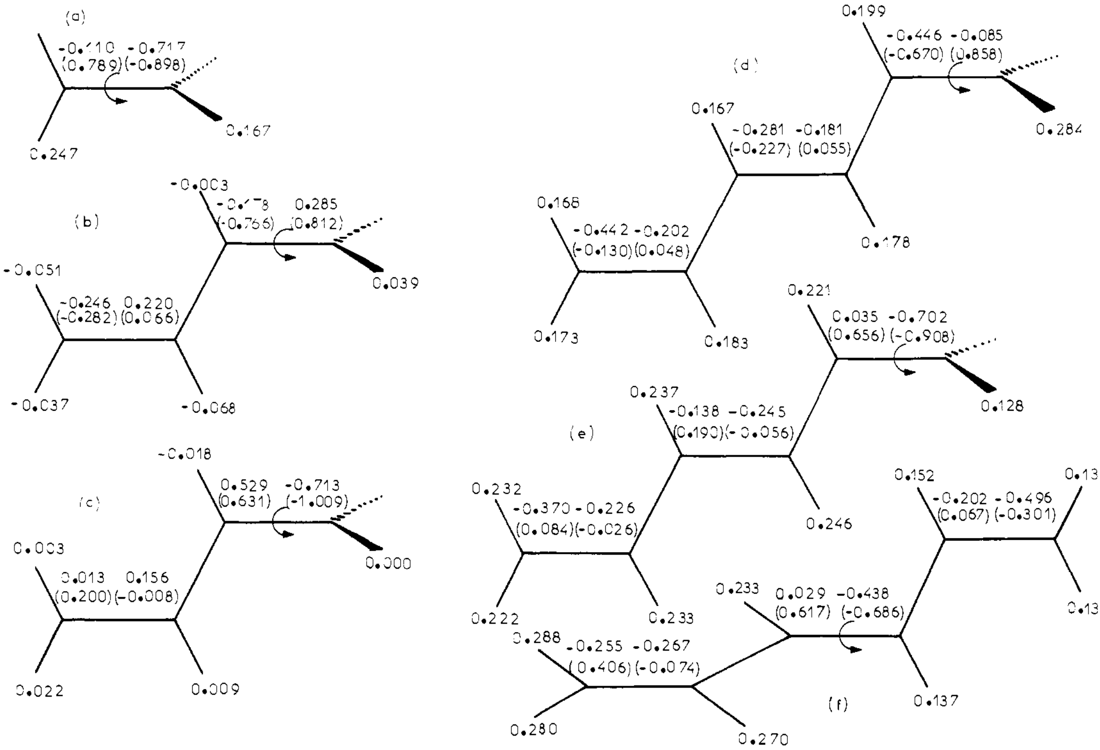

Figure 1. π (in parentheses) and total charge SCF repartition in the ionic twisted excited states of the following: (a) M^-M^+, (b) M^+A^-, (c) M^-A^+, (d) M^+P^-, (e) M^-P^+, (f) broken-symmetry A^-A^+.

stabilization (5.73 eV for M^+A^-). This difference between the positive and negative charge delocalization energies is easily explained from the nonbonding character of the allylic HOMO. Going to hexatriene twisted around the central bond (A^+A^-) one should add the positive and negative charge delocalization energies and actually get a 0.70 eV (16 kcal/mol) stabilization with respect to ethylene.

Delocalization energy in a benzyl fragment is larger for the positive charge (0.74 eV, 17 kcal/mol in B^+M^-) than for the negative one (0.31 eV, 7 kcal/mol in B^-M^+), as is easily understood from the preference of the benzene ring for six-electron occupancy ($4n + 2$ aromaticity rule).

From these few results it appears *that the positive charge tends to go into the largest of the two perpendicular fragments.* In order to estimate the possible size dependance of the delocalization energy of the excess charges, hexatriene has been twisted around its terminal bond; the extension of the positive charge to a supplementary double bond ($M^-A^+ \rightarrow M^-P^+$) only brings a 0.15 eV (3.5 kcal/mol) stabilization (instead of 10 kcal/mol for $M^-M^+ \rightarrow M^-A^+$). The corresponding stabilization of the negative charge ($M^+A^- \rightarrow M^+P^-$) is only 0.1 eV (2 kcal/mol) (instead of 4 kcal/mol for $M^+M^- \rightarrow M^+A^-$). One may estimate that delocalization on larger systems will rapidly lead to an asymptotic value for the nonvertical transition energy (especially when taking into account the loss of correlation energy as seen below).

At this step it is worthwhile to analyze the charge repartition as pictured in Figure 1. The π repartition is in much better agreement with the localized scheme 1 than with the delocalized scheme 2 (cf. the strong charge concentration on the atoms of the twisted bond, instead of equal weights on the terminal carbons of the fragment, and the important polarizations of the adjacent π bonds). The σ repolarization is very important, screening the π charge on the rotated bond and increasing the charge on the terminal atoms; surprisingly enough the final overall charge repartition is rather similar to that proposed by the crude (open shell SCF + 3 × 3 CI)[10,13] approach, which only introduces delocalized π charges and a σ neutral skeleton.

The conclusions regarding the transition energy must be revised after inclusion of (i) larger basis sets, (ii) CI correlation effects (in both the ground and the ionic excited states), and (iii) specific geometry optimizations of the twisted excited state. The study of the combined effects of these three factors was beyond our capabilities for large systems. Correlation effects have been calculated in the minimal basis set for all compounds; they result in a systematic increase of the transition energy (0.97 eV in M^+M^-, 0.99 eV in M^-A^+, 0.88 eV in M^+A^-, 1.22 eV in A^+A^-, and 1.31 eV in B^+M^-); the *differential* correlation effect increases with the delocalization of the system; this may be explained by the polarization of an increasing number of bonds, since polar bonds have smaller dynamical correlation energies than nonpolar ones (this appears immediately from a study of the intrabond correlation energy with use of minimal basis sets). *The differential correlation effect seems to destroy the benefit of the excess charge delocalization in the ionic states of conjugated twisted molecules, resulting in a rather constant transition energy to these ionic minima.*

It is very difficult to assess the possible effect of basis set extension on these conclusions from the few calculations performed on ethylene and butadiene; it seems to result in a 0.51 eV decrease of the nonvertical transition energy to M^-A^+ in butadiene.

Basis set enlargement may allow correlation of the electron pair on the negative carbon atom and may compensate the loss of dynamical correlation on the polar bonds. In some sense our SCF values for the transition energies may be viewed as lower bounds and the CI values with minimal basis sets as upper bounds. As a compromise one may assume that the minimal basis set transition energies (including CI effects) are overestimated by about 0.5 eV.

As for the specific geometry optimization of the ionic excited states, the number of degrees of freedom prevents such a systematic research for anything besides ethylene,[11] where the complete optimization leads to a 13-kcal/mol stabilization, and butadiene[14] (M^-A^+), where the optimization of main geometric parameters results in a 12 kcal/mol energy lowering. Among these geometry changes one is more or less transferable, namely the bond lengthening of the twisted bond (and the previously reported calculations assume this transferability to larger systems). The pyramidalization of the carbon of a M^- fragment is important and brings most of the stabilization energy. The pyramidalization of internal carbons in a delocalized negative fragment of M^+A^- or A^+A^- gives a smaller stabilization,, due to the negative charge delocalization and to greater interfragment repulsion.

It seems reasonable to assume that the specific distortions of a twisted ionic excited state may stabilize it by an almost constant amount of say 10–15 kcal/mol. (Notice that our calculation on styrene already included an optimization of the C_v–C_α extracyclic bond length.)

The main conclusion of this exploration of the size dependance of the energy position of twisted ionic funnels is that they cannot very easily go below 4.70–5.20 eV above the ground state. Since the vertical transition ($^1A_g \rightarrow {}^1B_u$) energies of large conjugated system go far below 4.50 eV, the mechanism of cis–trans isomerizations through these ionic twisted minima seems to be unlikely for large enough systems.

IV. Twisted Radicalar Excited States

The ground state of the twisted molecules may be viewed as built from two radicalar π systems in their respective ground states, A· and B·, to give the nearly degenerate diradicalar singlet and triplet states. (In general the singlet ground state is lower than the triplet, in contradiction with Hund's rules, due to the dynamic spin polarization of the σ core, as explained by Kollmar et al. for ethylene.[22])

In these neutral states, the σ part will not receive important polarization and may be taken as a frozen core for the discussion. Let us consider the MO description of the π radicalar systems in their ground doublet state,

$$^2\Psi^0{}_{A\cdot} = |...i_A\bar{i}_A...n_A| \quad S_z = \tfrac{1}{2} \tag{6}$$

$$^2\Psi^0{}_{B\cdot} = |...j_B\bar{j}_B...\bar{m}_B| \quad S_z = -\tfrac{1}{2} \tag{7}$$

Then the ground state of the twisted molecule is given by

$$^{3,1}\Psi^{GS}{}_{A\cdot B\cdot} = |...i_A\bar{i}_A...j_B\bar{j}_B...(n_A\bar{m}_B + m_B\bar{n}_a)|/\sqrt{2} \tag{8}$$

The lowest excited state of the fragment A· will consist of excitations from doubly occupied MO's to the nonbonding n_A level or from n_A to virtual MO's $k^*{}_A$

$$^2\Psi^*{}_{A\cdot} = \lambda|...i_A\bar{n}_A...n_A| + \mu|...i_A\bar{i}_A...k^*{}_A| \tag{9}$$

Such excitations are possible on the B· fragment and the excited state of the diradicalar system may be approximated by a linear combination of the excitation on A· and the excitation on B·,

$$^{3,1}\Psi^*{}_{A\cdot B\cdot} = a\mathcal{A}(^2\Psi^*{}_{A\cdot}{}^2\Psi^0{}_{B\cdot})f(S) + b\mathcal{A}(^2\Psi^0{}_{A\cdot}{}^2\Psi^*{}_{B\cdot})f(S) \tag{10}$$

where $f(S)$ is a spin symmetrization operator. The mixing between the left and right excitations depends on the ratio of the resonance integral between the two excitations,

$$R = \langle ^2\Psi^*{}_{A\cdot}{}^2\Psi^0{}_{B\cdot}f(S)|H|^2\Psi^0{}_{A\cdot}{}^2\Psi^*{}_{B\cdot}f(S)\rangle \tag{11}$$

and the energy difference between these localized excitations. The resonance integral is rather small, as is easily seen by assuming for instance excitations from the highest doubly occupied MO ($n - 1$) to the nonbonding one (n) in both systems,

$$R = \tfrac{1}{2}\langle n_A\bar{n}_A(m_B - 1)_B(\overline{m-1})_B[(n-1)_A\bar{m}_B \pm m_B(\overline{n-1})_A] \times |H|(n-1)_A(\overline{n-1})_A m_B\bar{m}_B[n_A(\overline{m-1})_B \pm (m-1)_B\bar{n}_A]\rangle = \left\langle n(m-1)\left|\frac{1}{r_{12}}\right|(n-1)m\right\rangle \pm \left\langle n(m-1)\left|\frac{1}{r_{12}}\right|m(n-1)\right\rangle \tag{12}$$

the largest integral is at most of the dipole–dipole type. It may be smaller than the energy difference between the localized excitations if the two systems are very different, one of them being for instance much larger than the other one (for M·, no excitation is possible). Since the excitation energy of a ($2n + 1$) carbon fragment decreases with n, an upper bound of the diradical excited state may be given by considering the excitation on the largest π fragment. The excitation energies of doublet polyenes with an odd number of conjugated carbons have received less attention than those for the usual H–(CH=CH)$_n$–H polyenes. The excited states of allyl radical have been calculated at the ab initio CI level.[23,24] Using the extended basis set, Levin and Goddard obtained a neutral $^2B_1$ excited state at 3.2 eV above the ground state. Table II gives the transition energies toward the lowest neutral excited state for the first members of the odd polyene series, as obtained by a π semiempirical calculation equivalent to a full π CI,[25] assuming equal bond lengths. One may notice that for allyl the agreement of the corresponding value (3.4 eV) with the ab initio one is satisfactory.

Table II. Transition Energies[a] of the Lowest Neutral Excited State, ΔE, of Odd Polyenes (No Bond Alternation) with N Carbon Atoms

N	ΔE	N	ΔE
3	3.40	7	1.90
5	2.46	9	1.55

[a] D. Maynau, private communication.

Table III. Energies from the Planar Ground State of the Twisted Neutral Ground and Excited States of a Few Molecules (in eV) (Open Shell SCF + Extended CI)

	butadiene M^0A^0		hexatriene A^0A^0	styrene M^0B^0
	MBS	EBS	MBS	MBS
ground state				
singlet	1.94	2.49 (A″)	1.81 (^{1}A)	2.31 (A″)
triplet	2.04	2.54 (A″)	2.09 (^{3}B)	2.42 (A″)
excited state				
$^1D_1$	5.41	5.73 (A″)	5.10 (^{1}A)	4.66 (A″)
$^1D_2$			5.73 (^{1}B)	6.94 (A″)
^3T	5.35	5.62 (A″)	5.11 (^{3}A)	

The nonvertical transition energy to the diradicalar excited state of a polyene twisted on the terminal bond may be approximated by adding the ground state rotational barrier to the vertical transition energy of the H(CH)$_{2n-1}$–H radical. Assuming a 40–50 kcal/mol rotational barrier (i.e., $\simeq$2 eV), one finds the following estimate for the nonvertical transition energies to the twisted diradical excited states 5.40 eV for M·A·, 5.4 – $\mathcal{R}$ (eq 11) for A·A·, 4.46 eV for M·P·, and 3.90 eV for M·H· (H = heptatrienyl). The comparison with the previously discussed transition energies to the ionic states, which lie in the range of 6.0–7.0 eV above the GS energy (cf. Table I) when the minimal basis set is used, suggests that *the neutral twisted excited states should be lower than the ionic ones*.

In order to test the validity of this scheme, the diradicalar twisted excited states have been calculated through an open shell

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[25] J. P. Malrieu and D. Maynau, *J. Am. Chem. Soc.*, in press.

SCF procedure followed by an extensive CI, performed according to the same procedure used for the ionic excited states (although the convergence required a larger multiconfigurational wave function). The results concerning M·A·, A·A·, and M·B· are reported in Table III.

The energy of the twisted ground state is reasonable (1.8–2.5 eV, 42–57 kcal/mol) and represents an upper bound to the thermal rotational barrier around the concerned double bond since the geometries were not optimized. One may notice that the singlet actually is lower than the associated lowest triplet by a few kilocalories per mole. The main point concerns the lowest excited diradicalar singlet; M·A*· is 3.47 eV above the twisted ground state M·A· in the minimal basis set (3.24 eV in the extended basis set), which may be related to the vertical excitation of the allyl radical (3.40 eV in the π semiempirical calculation (Table II), 3.20–3.25 eV according to Levin and Goddard[23,24]). Going to hexatriene twisted around the central bond should split the degenerate excited level A·A*·, A*·A· into symmetry eigenfunctions, according to the preceding remarks

$$\begin{aligned} \mathrm{M{\cdot}A^{*}{\cdot}} = 5.41\ \mathrm{eV} &\rightarrow (\mathrm{A{\cdot}A^{*}{\cdot}} + \mathrm{A^{*}{\cdot}A{\cdot}})/\sqrt{2} = 5.73\ \mathrm{eV} \\ &\rightarrow (\mathrm{A{\cdot}A^{*}{\cdot}} - \mathrm{A^{*}{\cdot}A{\cdot}})/\sqrt{2} = 5.10\ \mathrm{eV} \end{aligned}$$

which means that $\mathcal{R}$ (eq 11), the resonance integral between the left and right excitations, is about 0.31 eV (7 kcal/mol).

For styrene the lowest diradicalar twisted singlet excited state B*·M· is 2.35 eV (54.2 kcal/mole) above the twisted ground state, which compares favorably with the experimentally known (0–0) transition of benzyl, 2.73 eV[26] (and a calculated value of 2.87 eV[27]). The hyperconjugation of the π system with the twisted CH_2 group, which occurs in our problem, might actually induce a small decrease of the transition energy.

These numerical results confirm our previous qualitative statements, i.e., the existence of low lying diradicalar twisted excited states. With use of the minimal basis set, these states are always lower than the lowest ionic twisted excited state; in view of the rapid decrease of the excitation energy of odd polyenes (cf. Table II) when the dimension of the conjugated system increases, there is no doubt that this ordering is valid for large enough systems. The only exception might concern the butadiene molecule; the use of diffuse AO's leads to a greater stabilization of the ionic state, as expected, and after proper pyramidalization of the terminal CH group the M^-A^+ state is nearly degenerate (5.62 eV above the planar ground state) with the lowest twisted (non pyramidazlied) diradicalar excited state (5.73 eV). One must remember, however, that the carbon skeletton geometry had been optimized for the ionic state.

Our results for butadiene may be compared with recent results[28] obtained with a split-valence basis set and small CI ($\simeq$100 configurations), which also give near degeneracy between M·A*· and M^-A^+ (0.2 eV above), but at significantly larger energies (7 eV) above the planar ground state (due to restrictions in the CI).

V. Correlation with the Planar Excited States

The absorbing states are ${}^1B_u$ in symmetry and ionic in character (in the sense of the VB theory); from their physical nature, the twisted ionic excited states are correlated with the ${}^1B_u$ states. On similar grounds the diradicalar twisted excited states are correlated with the ${}^1A_g$ neutral (in the sense of the VB theory) excited states. For intermediate angles of the C=C bond torsion ($0 < \theta < 90°$), the symmetry is usually destroyed and avoided crossings may occur. Disregarding the case of ethylene and assuming that the lowest twisted diradicalar excited state always lies below the excited state induced by the vertical absorption, the actual physical process of the cis–trans isomerization will depend on two basic features: (i) the relative position of the ionic twisted minimum with respect to the vertical transition (the ionic twisted minimum cannot be reached if it lies above the vertical transition, as will occur for large enough conjugated systems, according to our discussion in Section III), and (ii) the relative position of the neutral ${}^1A_g$ and ionic ${}^1B_u$ vertical excited states.

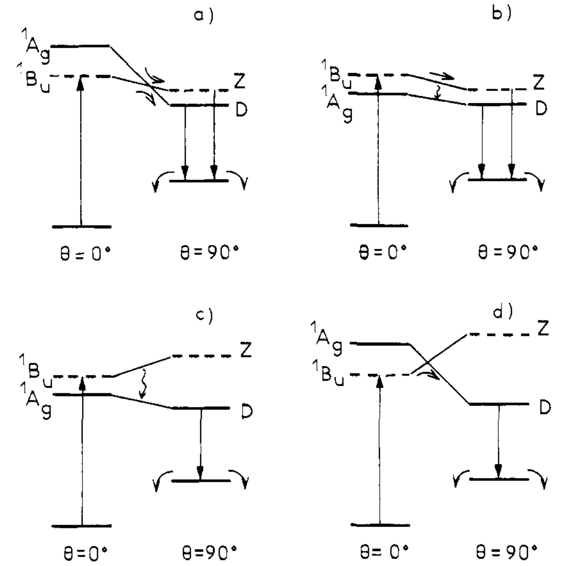

Figure 2. Four possible situations of vertical and twisted excited states and their possible implications concerning the mechanism of the cis–trans isomerization (---, ionic states, —, neutral states).

One may therefore conceive four possible situations which are qualitatively pictured in Figure 2.

In case a ($Z < {}^1B_u < {}^1A_g$) an avoided crossing takes place between the neutral and ionic surfaces and two photoisomerization mechanisms remain possible, either through the Z or D funnels, depending on the probability of surface hopping in the surface crossing region.

In case b ($Z < {}^1B_u$, ${}^1A_g < {}^1B_1$) the ionic funnel Z may be reached along the ionic surfaces, but the photoreaction also may proceed through the neutral funnel D after a decay from the ionic to the neutral surface.

In case c ($Z > {}^1B_u > {}^1A_g$) the (ionic)* → (neutral)* decay must necessarily take place to bring the system to the neutral funnel D.

In case d ($Z > {}^1B_u$, ${}^1A_g > {}^1B_u$) an avoided crossing between the ionic and neutral surfaces will allow D to be reached (possibly through a thermal barrier).

The relative position of the ${}^1A_g$ and ${}^1B_u$ vertical states is only assessed for octatetraene[6a] and larger polyenes,[6b,28] for which ${}^1A_g < {}^1B_u$. For butadiene, most calculations predict the same ordering[4,9,29–31] but experiment[7] only succeeded to put in evidence for a forbidden valence state 1.3 eV above the allowed ${}^1B_u$ structure. For hexatriene electron impact[8] as well as two-photon absorption[32] spectroscopic measurements failed to exhibit a ${}^1A_g$ excited state below the ${}^1B_u$ state. Our own calculations[33] support the hypothesis recently formulated by Karplus et al.,[9] who suggested that the ${}^1B_u$ and ${}^1A_g$ lowest excited states are nearly degenerate for butadiene and hexatriene.

The N dependance of the ${}^1B_u$ transition is well-known from experiment to follow an empirical law (cf. Figure 3 and ref 2 and 3)

$$\Delta E = A + B(N^{-1})$$

where the asymptotic value of the most intense vibrational peak is 2.0 eV. The N dependance of the ${}^1A_g \rightarrow {}^1A_g$ transition energy

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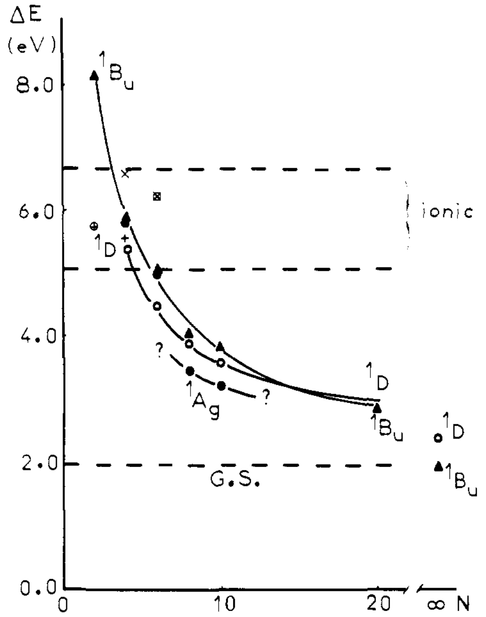

Figure 3. Energy from the planar ground state (Δ*E*) of the different vertical (^1A_g and ^1B_u) and twisted (ionic and diradicalar) excited states as a function of the number of carbons (*N*). (▲) ^1B_u vertical excited states, values for $n = 4, 6, 8$ from Table I,[9] and $n = 10, 20, \infty$ from Figure 1 of ref 3b. (●) ^1A_g vertical excited states, values for $n = 4, 6$ assuming near degeneracy with the ^1B_u state, for $n = 8$ from ref 6a, $n = 10$ from ref 34. (○) Twisted diradicalar excited states calculated adding a 2 eV ground state rotational barrier to the excitation energies reported in Table II. $n = \infty$ value extrapolated from the $n = 4$–10 ones by using a $A + B/n$ least-squares fitting with $r^2 = 0.997$. (⊕) M^+M^- ionic state for twisted and pyramidalized ethylene; (×) M^+A^- ionic state for twisted and C_2-pyramidalized butadiene; (+) M^-A^+ ionic state for twisted and C_1-pyramidalized butadiene; (⊗) A^+A^- ionic state for central bond twisted and C_3-pyramidalized hexatriene.

has not been established. Figure 3 shows the value reported for octatetraene[6a] and 2,10-dimethylundecapentaene.[34] In this figure the energies of the terminally twisted neutral excited states have been estimated by adding the lowest transition energy of a $(2n - 1)$ polyene (Table II) to a 2 eV ground state rotational barrier. Figure 3 also exhibits the approximate position of the ionic funnels, which, according to Section III, should lie at an almost constant level between 5.1 and 6.7 eV.

VI. Conclusion Concerning the Linear Polyenes

The qualitative conclusions of the preceding discussion result directly from Figure 3.

The photoisomerization of isolated ethylenic bonds is likely to proceed through the ionic funnel, which is much below the vertical $\pi\pi^*$ excited state. For butadiene our extended basis set calculation exhibits a twisted pyramidalized ionic level at 129 kcal/mol (i.e., 5.62 eV) above the planar ground state. The quantitative description of these ionic states requires the use of diffuse AO's and 3d AO's (the best calculations of the vertical transition to the ^1B_u state of butadiene exagerate this transition by 1 eV[4b,25]) and our value must be considered as an upper bound; the vertical excitation brings 6 eV to the molecule, and the photoisomerization of this molecule may proceed through the ionic funnel, although a neutral funnel is close in energy.

For hexatriene the 6.21 eV vertical ^1B_u absorbing state and the ionic twisted minimum should be close in energy, while a neutral twisted funnel should be somewhat below: our minimal basis set calculations (5.1 eV) without appropriate geometry optimization should represent an upper bound for this funnel concerning the torsion around the central bond, and our schematic model reported in Figure 3 suggests a 4.5 eV funnel for the torsion around the terminal bond. For this molecule the diradicalar funnel begins to appear as the main candidate for the isomerization process.

For larger polyenes the rapid decrease of the (G–S → ^1B_u) vertical transition energy makes impossible the travel through the ionic twisted minima while the twisted diradicalar funnels are low enough to be reached. One is always in case c of Figure 2 and the photoisomerization requires a decay to the lowest neutral diradicalar excited state (one may also conceive nonradiative decay to the vibrational levels of the ground state).

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Registry No. Ethylene, 74-85-1; butadiene, 106-99-0; hexatriene, 2235-12-3; styrene, 100-42-5.

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Semiconductor Interface Characterization in Photoelectrochemical Solar Cells: The p-InP (111)A Face

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Abstract: Spectroscopic ellipsometry and low-energy (helium) ion scattering spectroscopy show the formation of hydrated indium oxide on the (111)A (indium) face of p-InP when the crystal is etched in either air-saturated acid or methanol–bromine, or when used as photocathode in the p-semiconductor liquid junction solar cell. The stability and efficiency of the cell depend on the presence of a thin, large band gap layer of indium oxide. The relatively better performance of p-InP over p-GaAs in such a cell is attributed to the different oxide surface chemistry of the latter, which leads to contamination by elemental arsenic. The favorable performance of p-InP in the V(II)–V(III)–HCl cell is ascribed to the reduction of recombination sites in the forbidden gap by termination of the lattice by the oxide.

1. Introduction

Various strategies have been employed to overcome instabilities encountered in photoelectrochemical regenerative solar cells. Cells based on p-type semiconductors[1] have the intrinsic advantage of cathodic protection of the illuminated semiconductors.[2,3] We have

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