

General occurrence of polar twisted minima in the ionic singlet excited surfaces of polyenes

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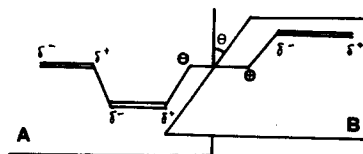
Except for a few cases, the lowest closed shell SCF solutions for the twisted geometries of polyenes involves delocalized nonpolarized MO's, and represents a meaningless mixture of radicalar ground state and ionic excited states. Higher (quasi) solutions allow a realistic approach of the polarized ionic states. Orthogonality to the radicalar ground state may be imposed without important loss of energy. Further extensive CI does not modify significantly the situation. These statements are illustrated through *ab initio* calculations of butadiene and hexatriene. This approach allows us to show that slight distortions stabilize polar minima even in "homosymmetric" molecules such as all-*trans* hexatriene twisted around the central bond. The existence of polar twisted minima in the ionic singlet excited surfaces of polyenes seems therefore a general phenomenon.

I. INTRODUCTION

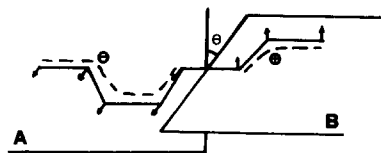
The existence of polar minima in the potential surface of the lowest ionic singlet π , π^* excited states of polyenes has been well established for the lower members of the linear polyene series. The phenomenon has been called sudden polarization of the twisted π , π^* excited states from its discovery by Bonačić-Koutecký¹; the slight disymmetry occurring in the *s-cis*, *s-trans* hexatriene rotated around the central double bond, or the twisted ethylene when one carbon atom is pyramidalized, was sufficient to break the degeneracy between the resonant A^+B^- and A^-B^+ components of the excited singlet. The extensive studies on ethylene by Brooks and Schaefer,² Bonačić-Koutecký *et al.*,³ Trinquier and Malrieu,⁴ have definitely confirmed the existence of these polar minima. Buenker *et al.*,⁵ recently explored the potential surface of ethylene as a function of both twist angle and pyramidalization of one carbon, showing that a dipole moment appears for intermediate twists when going down from the vertical transition to the potential wells of the surface; the recent works, while giving better understanding of the stability of the polar minima, progressively destroy the suddenness attributed by the early approaches to the polarity of these excited states minima.

As concern conjugated polyenes, there is a general agreement for the occurrence of such polar twisted wells for butadiene, (Bruckmann and Salem,⁶ Bruni *et al.*,⁷ Malrieu and Trinquier,⁸ Bonačić-Koutecký and Sevin⁹); the important disymmetry between the perpendicular A and B π subsystems prevents any controversy in that case. For larger polyenes the strong difference between the perpendicular fragments is kept when the rotation involves the terminal bonds, but the (near) degeneracy between A^-B^+ and A^+B^- is recovered when the rotation involves the internal bonds of a polyene and especially the central double bond of a $H(HC=CH)_{2n+1}H$ all-*trans* polyene. According to Karafiloglou and

Hiberty¹⁰ the calculated dipole moment in the twisted excited states of all-*trans* dodecahexenes is important when the rotation involves the terminal double bond, and it vanishes when the rotation concerns the most central bond. This result obtained through a rather simple procedure seems to be questionable if one remembers the local character of the electron transfer, according to the picture proposed by Bruni *et al.*⁷:



as being better than the delocalized picture:



The present paper tries to establish that polar minima occur in the potential surface *whatever the twisted double bond*; these zwitterionic minima are stabilized by proper nuclear skeleton deformations and their obtention requires a proper treatment of the σ and π polarization effects which tend to localize the positive and negative charges.

II. LOCALIZED AND DELOCALIZED APPROACHES OF THE TWISTED EXCITED SINGLET: AN APPARENT CONTRADICTION

Most of the treatments start the more or less extensive CI from a set of nonpolar MO's (see, e.g., Refs. 1-3, 10, and 11). These MO's may be obtained from the open shell RHF or Nesbet SCF calculations of the diradicalar ground state singlet or lowest triplet. No polarization is brought in the closed shell (π) and (σ) distributions and

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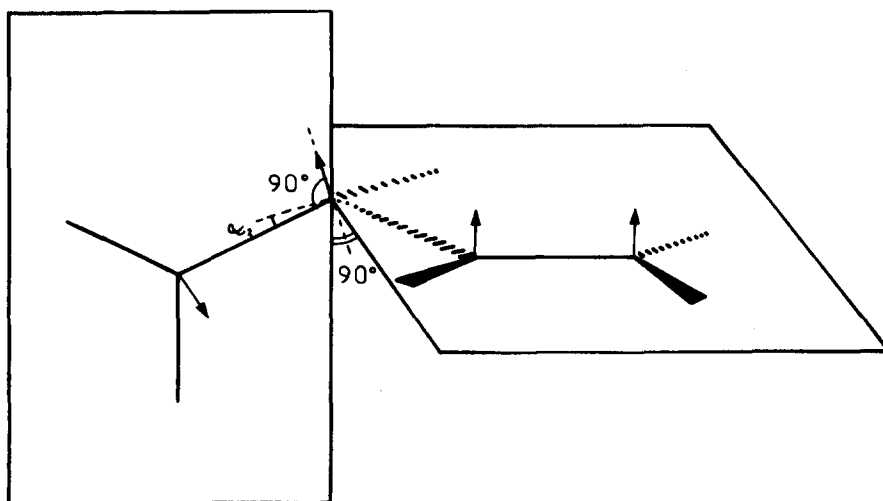


FIG. 2. Definition of the C_2 pyramidalization angle α_2 , for twisted butadiene.

closed shell solutions is not a better starting point than the open shell one. The subsequent 3×3 CI involving, besides Φ_d , the singly excited $\phi_d - \phi_d^*$ and doubly excited $(\phi_d - \phi_d^*)^2$ determinant gives the same result as the 3×3 CI from the open shell MO's, the energies of the ionic states remain far too high:

	E (kcal/mol)
ionic	175
Φ_d	115
${}^1\Phi_0$	55
${}^1\Phi_0(\text{planar})$	0

Energy differences: 60 kcal/mol between ionic and Φ_d ; 60 kcal/mol between Φ_d and ${}^1\Phi_0$.

A strange apparent contradiction seems therefore to exist between these results on one hand, and the conclusions obtained by Malrieu *et al.*⁸ for the case of molecules possessing a plane of symmetry and their general statement of the adequacy of the closed shell treatment to approach the ionic states.

The contradiction disappears when one understands that the localized and delocalized closed shell solutions belong to different SCF maps. Each of the three maps corresponds to a specific SCF calculation and it is meaningless to try to approach, for instance, the ground state A^*B^* or the A^+B^- energies from the A^-B^+ MO's; since the A^-B^+ solution introduces important specific σ polarization effects in the field of the π dipole:

$$\Phi_{A^-B^+} = |\phi_1'' \bar{\phi}_1'' \cdots \phi_i'' \bar{\phi}_i'' \cdots \bar{\phi}_{n-1}'' \phi_{n-1}'' \phi_A'' \bar{\phi}_A''|, \quad (13)$$

these closed shell A^-B^+ MO's are not relevant either for the ground state through

$${}^1\Phi_{(-)(A^-B^+)} = |\phi_1'' \cdots \phi_i'' \bar{\phi}_i'' \cdots \bar{\phi}_{n-1}'' (\phi_A'' \bar{\phi}_B'' + \phi_B'' \bar{\phi}_A'')|, \quad (14)$$

or for the A^+B^- state through

$$\Phi_{A^+B^-(-)A^-B^+} = |\phi_1'' \cdots \phi_i'' \bar{\phi}_i'' \cdots \bar{\phi}_{n-1}'' \phi_{n-1}'' \bar{\phi}_B'' \bar{\phi}_B''|, \quad (15)$$

which are much too high in energy. An important σ reaction dipole remains in ${}^1\Phi_{(-)(A^-B^+)}$ leading to an overestimated dipole moment (≈ 2 D) and adds to the π dipole in $\Phi_{(A^+B^-)(-)(A^-B^+)}$, leading to a meaningless dipole moment (≈ 7 D). These remarks rationalize the somewhat strange results presented by Baraldi *et al.*,¹³ and confirm the need for independent calculations of the various surfaces. Using the delocalized apolar MO's for the construction of the polar state is as inefficient as using polar MO's for the ground state representation.

III. MULTIPLICITY OF THE CLOSED SHELL SOLUTIONS EXAMPLIFIED ON BUTADIENE

Baraldi *et al.*,¹³ already succeeded to reach the delocalized Φ_d solution in the 90° twisted butadiene which possesses a plane of symmetry. In that case, the delocalized solution is symmetry-broken and its obtention requires to introduce unsymmetrical trial vectors (the eigenfunctions of the $\theta = 88^\circ$ Fock operator for instance). They thus prolonged the physically meaningless solution to the situation where the physically ionic solutions are directly obtained. We propose to travel the opposite way, and to find the ionic solutions even in the absence of symmetry and when the direct solution is the physically meaningless delocalized solution.

To do this one must start from the 90° $\Phi_{A^+B^-}$ or $\Phi_{A^-B^+}$ ionic eigenvectors as trial vectors for the nonsymmetrical situations. The SCF closed shell problem may be thought as a three maps problem, the lowest one (except for ethylene) is the delocalized mixture of radical and ionic states, the two upper surfaces bear the ionic A^+B^- or A^-B^+ situations. Special symmetry conditions may make the obtention of these later solutions straightforward, but in general careful procedures are necessary to bring them to evidence.

The existence of these three surfaces have been established through *ab initio* calculations of butadiene in nonsymmetrical geometries. For a 90° twist angle about the C_1-C_2 bond, pyramidalization of the C_2 carbon (see Fig. 2) destroys the plane of symmetry, should

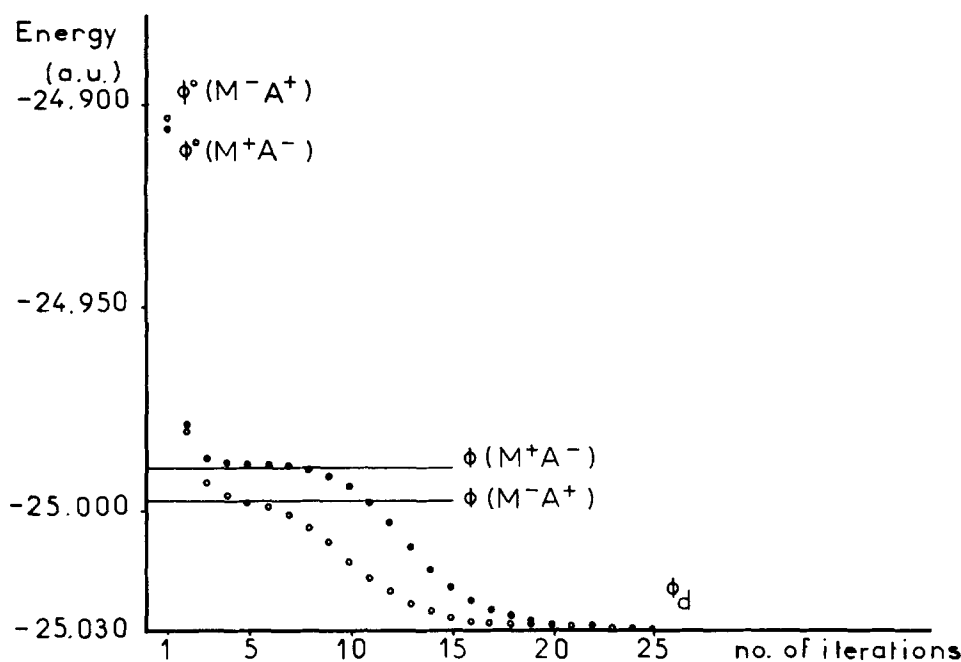


FIG. 3. Total energies of the closed shell determinants along the iterative SCF process, for twisted C_2 pyramidalized ($\alpha_2 = 10^\circ$) butadiene; the horizontal lines indicate the positions of the "quasisolutions."

stabilize the methyl⁺allyl⁻ (M^+A^-) determinant, and destabilize the lower M^-A^+ solution (as well as the ground state and the delocalized solution). The basis set was minimal plus a diffuse $p_{x,y,z}$ on each carbon atom as in

the preceding work⁸ which explored the role of pyramidalization on C_1 .

When the SCF iterative process was started using the nonpyramidalized polar M^+A^- ($\alpha_2 = 0^\circ$) eigenvectors as a trial vectors, self consistency was almost achieved after a few iterations for $\alpha_2 \neq 0^\circ$. If a 10^{-4} a.u. convergence threshold is required the iterative process will stop on a polar solution for which the wave function is very close to polar symmetry-adapted ($\theta = 90^\circ$) wave functions. For smaller convergence thresholds the iterations may go on and the previous solution will appear as a "quasisolution," an inflexion point on the curve plotting the total energy as a function of iteration numbers (see Fig. 3).

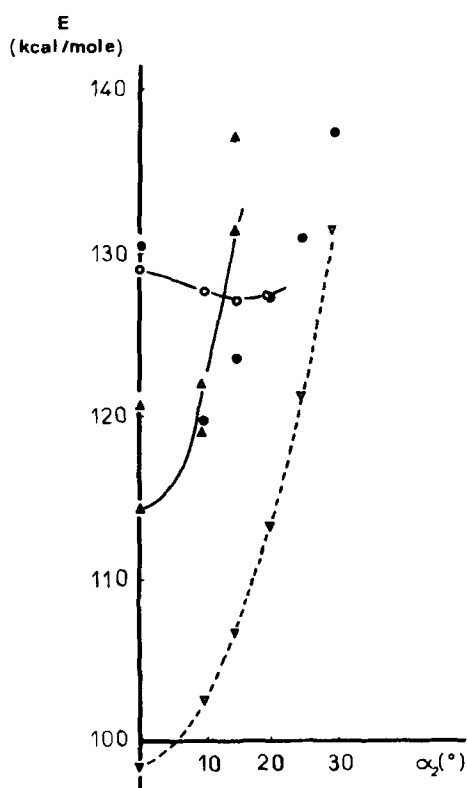


FIG. 4. Closed shell SCF energies for twisted butadiene as function of the C_2 pyramidalization angle. (The planar ground state SCF energy is taken as zero.) ∇ ----- delocalized neutral SCF solution; Δ — M^-A^+ ionic (quasisolution); \circ — M^+A^- ionic (quasisolution); \blacktriangle M^+A^- ionic solutions with orthogonality constraint; \bullet M^+A^- ionic solutions with orthogonality constraint.

After a certain number of iterations the energy begins to decrease, then falls down and the delocalized meaningless solution Φ_d is obtained. Starting from the eigenvectors of the opposite M^-A^+ ($\alpha = 0^\circ, \theta = 90^\circ$) solution gives an other $\Phi_{M^-A^+}$ ionic "quasi-solution" before converging down to the same delocalized Φ_d solution. The energies of the delocalized solutions as a function of the pyramidalization angle α_2 are shown in Fig. 4.

The reliability of these ghost self consistent wave functions may be inferred from the following remarks: (i) the "quasisolutions" do not depend either on the choice of the trial vectors [one may start for instance from $\Phi_{A^+B^+}$, Eq. (3), defined from the open shell solutions, provided that the singly occupied MO's are well localized], or on the SCF iterative procedure (direct iterations, mixing of the density matrices, perturbative iterations^{14,15}), as has been verified. (ii) the energies obtained from these solutions varies as expected from physical grounds (cf. Fig. 4) along well shaped curves, and lie of course in the correct energy range (≈ 120 kcal per mol above the ground state minimum). (iii) the dipole moment variation is regular (see Table I).

Of course these localized solutions have no reason to

TABLE I. Dipole moment (D) of the ionic states of butadiene for various pyramidalization angles.

$\alpha_2(^{\circ})$		0	10	15	20
M ⁺ A ⁻	CS ^a	7.0596	6.7252	6.4295	6.1344
	OC ^b	7.5384	5.2175	6.2114	6.6046
M ⁻ A ⁺	CS ^a	6.9434	6.4212	5.2669	...
	OC ^b	9.4018	7.0314	7.8346	...

^aQuasi SCF solutions.^bOrthogonality constraint.

be strictly orthogonal but they differ not only through the location of the highest occupied MO on two nearly orthogonal fragments but through the opposite polarization of the σ and π closed shells:

$$\langle (\sigma')(\pi'_A)(\pi'_B)\phi_B^2 | (\sigma'')(\pi''_A)(\pi''_B)\phi_A^2 \rangle \approx 0. \quad (16)$$

They are no longer orthogonal to the ground state radical determinant ${}^1\Phi_0$, although the overlap should not be important. One may at least say that these "quasisolutions" including most of polarization effects seem to be a good starting point for further CI.

IV. A SIMPLE PROCEDURE TO CALCULATE POLAR CLOSED SHELL DETERMINANTS ORTHOGONAL TO THE DIRADICALAR GROUND STATE

In order to solve this orthogonality problem

$$\langle {}^1\Phi_0 | \Phi_{A^+B^-} \rangle \neq 0, \quad (17)$$

one might use the SCF constrained processes; we decided to follow a simpler approximate procedure. One starts from the open shell MO's relative to ${}^1\Phi_0$; the singly occupied MO's ϕ_A and ϕ_B are supposed to be properly localized on the fragments A and B. One builds the trial vector $\Phi_{A^+B^-}^0$ [Eq. (2)] and starts the iterative perturbative SCF procedure proposed by Lefebvre¹⁴ and Daudey¹⁵:

$$|\phi'_i\rangle = |\phi_i\rangle + \sum_{j^*}^{\text{virtual}} \frac{\langle \phi_{j^*} | F | \phi_i \rangle}{\epsilon_i - \epsilon_{j^*}} |\phi_{j^*}\rangle, \quad (18)$$

followed by $S^{-1/2}$ orthogonalization. If, all along the process, the occupied orbital ϕ_B in $\Phi_{A^+B^-}$ is kept unchanged, the closed shell determinant contains one orbital which is strictly orthogonal to all the MO's of the diradicalar singlet and is therefore orthogonal to the best ground state determinant:

$$\langle \Phi_{A^+B^-}^1 | {}^1\Phi_0 \rangle = \langle \cdots \phi'_i \bar{\phi}'_i \cdots \phi'_{n-1} \bar{\phi}'_{n-1} \phi_B \bar{\phi}_B | \cdots \phi_i \bar{\phi}_i \cdots \phi_{n-1} \bar{\phi}_{n-1} (\phi_A \bar{\phi}_B + \phi_B \bar{\phi}_A) \rangle = 0 \quad (19)$$

(where the ϕ'_i are the polarized MO's resulting from this constrained SCF process). This procedure fixes the shape of the π MO on fragment B bearing the excess π charge; one may kept as well the "virtual" orbital ϕ_A unchanged, which fixes the shape of the "hole" on fragment A; the result will be slightly different.

The same process may be repeated for A^-B^+ . There is of course no guarantee for the $\Phi_{A^+B^-}^1$ and $\Phi_{A^-B^+}^1$ thus obtained to be orthogonal.

The energies obtained according to this procedure also appear in Fig. 4. They exhibit a somewhat irregu-

lar variation along the C_2 pyramidalization, due to a local mixing of the singly occupied MO's of the diradicalar solution (they become degenerate and therefore delocalized for $\alpha_2 = 13^{\circ}$).

The process has been applied to the unpyramidalized ($\theta = 90^{\circ}$, $\alpha_2 = 0^{\circ}$) geometry where orthogonality is insured by symmetry; the previously proposed orthogonality constraint leads to minor energy loss (3 kcal/mol). The dipole moment is overestimated by 0.5 to 2.5 D, due to an excessive delocalization of the constrained π charge.

V. CI RESULTS

The closed shell determinants $\Phi_{A^+B^-}^1$ and $\Phi_{A^-B^+}^1$ are somewhat arbitrary, but they lie in the correct range of energy and their polarity is likely; they may be taken as starting point for a further CI. The CIPSI procedure¹⁶ was applied, perturbing to the second order a variational multireference wave function; for the A^+B^- solution this wave function involved besides the corresponding variational determinant $\Phi_{A^+B^-}^1$, the doubly excited determinant of opposite polarity $\Phi_{A^-B^+}^1$ (built with the same MO's), the ground state like open shell determinant, and a few other singly and doubly excited determinants which essentially introduce the polarization of the previously constrained π charge. Several 10^5 determinants are included in the perturbation. The only root considered as rapidly convergent has its main component on the variational closed shell determinant. Similar process were repeated independently on $\Phi_{A^-B^+}^1$. The resulting energies are reported in Fig. 5 which show the existence of crossing between the two ionic surfaces near $\alpha_2 = 13^{\circ}$ and a great similarity with the SCF "quasisolutions" behavior. The upper surface exhibits a small well, resulting from the avoided crossing; due to the deep differences between the polar determinants (two electron jump between disjoint fragments and opposite polarizations) the crossing should be weakly avoided:

$$\langle \Phi_{A^-B^+}^1 | H | \Phi_{A^+B^-}^1 \rangle \text{ small.}$$

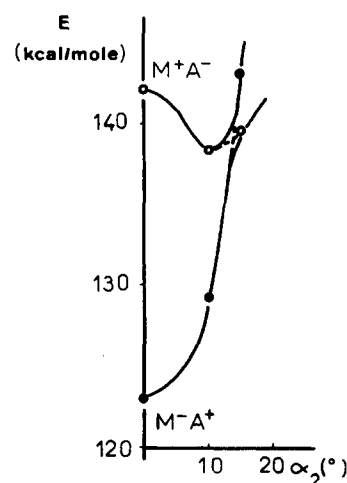


FIG. 5. CI energies of the two lowest ionic excited states of twisted butadiene as function of the C_2 pyramidalization angle (the zero of energy is taken for the CI ground state planar energy).

Our procedure is not able to treat correctly the interaction between nonorthogonal determinants. However, an upper bound may be given by neglecting scalar products between orbitals of opposite polarities:

$$\begin{aligned} & |\langle \Phi_{A^-B^+}^{\pm} | H | \Phi_{A^+B^-}^{\pm} \rangle| \\ & < |\langle \Phi_{A^-B^+}^{\pm} | H | \Phi_{A^+B^-}^{\pm} (\sim \pi_{B^+}) \rangle| = K_{\psi_A^{\pm} \psi_B^{\pm}} \end{aligned} \quad (20)$$

The exchange integral between the π distributions has been calculated to be about 0.5 kcal/mol for butadiene, which means that the distance between the surfaces in the regions of avoided crossing or touching is less than 1 kcal/mol, i. e., significantly smaller than the well depths obtained by specific geometry distortions of a given polar form. Moreover, as noticed previously,⁸ the Born–Oppenheimer approximation breaks down in such nearly degenerate situations, and the exact knowledge of the surfaces in these regions is of moderate interest.

Figure 5 shows that the lowest ionic surface [which presents a deep (12 kcal/mol, methylallyl*) minimum for an important pyramidalization of the terminal carbon ($\alpha_1 = 24^\circ$)⁸] does not exhibit a second M^*A^- minimum; the delocalization of the negative charge in the allylic fragment makes the pyramidalization of C_2 less efficient. The resulting picture is quite different from the one suggested by the first (more approximated) treatment.⁶

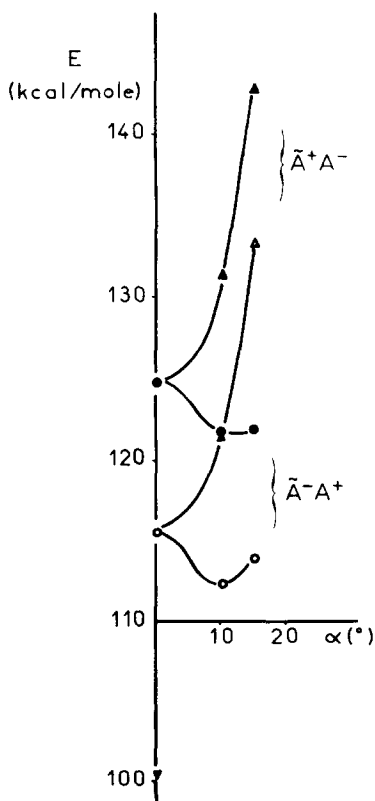


FIG. 6. Closed shell SCF energies of hexatriene twisted around the central bond as function of the pyramidalization angle of C_3 . Quasisolutions are indicated through open signs (\circ and Δ); full signs indicate SCF solutions with orthogonality constraint. (The planar ground state energy is taken as reference.)

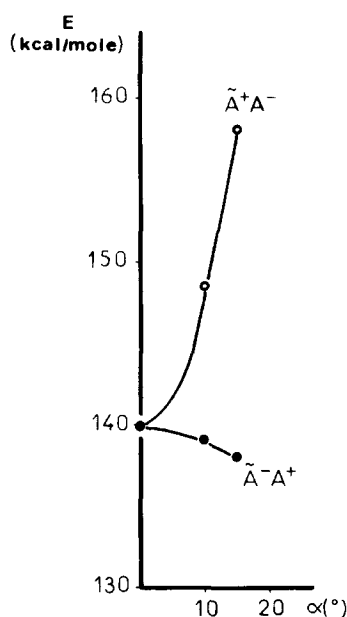


FIG. 7. CI energies of the two lowest ionic states of hexatriene twisted around the central bond (the planar ground state CI energy is taken as reference).

VI. TORSION OF THE INTERNAL DOUBLE BOND OF AN HOMOSYMMETRICAL SYSTEM

“Sudden” polarization of the singlet excited state was obtained for the rotation of internal bonds in heterosymmetrical systems such as the *cis*, *trans*-hexatriene.^{1,11} The open shell $+3 \times 3$ CI procedure failed to exhibit polar excited states minima for the rotations of internal bonds of some dodecahexenes¹⁰ even if no symmetry is possible in the twisted geometries of such molecules. The general opinion to now¹¹ is that the twisted conformations of ethylene and medium size olefines are minima on the ionic excited state surfaces, and that these minima are polar in both heterosymmetric and non symmetric polyenes, but not polar in homosymmetric ones. Our point of view is that appropriate symmetry breaking deformations of the nuclear skeleton allow the appearance of polar twisted minima in *all* cases; we believe that such a strong statement is sufficiently demonstrated if one may exhibit this occurrence in homosymmetric systems such as the all-*trans* hexatriene rotated around the internal double bond.

For this study the basis set was kept minimal, and a fixed geometry was assumed ($d_{C_1-C_2} = d_{C_5-C_6} = 1.40 \text{ \AA}$, $d_{C_2-C_3} = d_{C_4-C_5} = 1.51 \text{ \AA}$, $d_{C_3-C_4} = 1.50 \text{ \AA}$) with a lengthened central bond length. Again we would like to point out that polar closed shell determinants may be found in the correct range of energy ($\approx 120 \text{ kcal mol}^{-1}$ above the ground state planar energy), even if one compels the excited determinant to be orthogonal to the open shell ground state SCF solution.

Of course, a small disymmetry must be introduced in the geometry to break the degeneracy between A^+A^- and A^-A^+ . Pyramidalization of the C_4 carbon atom should be sufficient to stabilize significantly the A^+A^- form. Polar solutions may be obtained from the $\Phi_{A^+A^-}^0$.

TABLE II. Role of symmetry factors in various SCF solutions behavior.

	Open shell procedure	Closed shell delocalized procedure	Closed shell localized procedure
Plane of symmetry $\theta = 90^\circ$ twist of a terminal double bond of polyenes	φ_n, φ_{n+1} singly occ. MO's localized on A and B 3×3 CI $\rightarrow \mu^{\text{exc}} \neq 0$	difficult to reach, symmetry breaking necessary	A^+B^- and A^-B^+ are normal solutions of the CS procedure
Axis of symmetry $\theta = 90^\circ$ of the cen- tral bond of $H(CH=CH)_{2m+1}H$ all- <i>trans</i> polyenes	φ_n, φ_{n+1} , singly occ. MO's delocalized 3×3 CI $\rightarrow \mu^{\text{exc}} = 0$	$\varphi_n, \varphi_{n+1}^*$ delocalized	two degenerate symmetry broken solutions (difficult to reach) artificial dipole moment
No symmetry $\theta \neq 90^\circ$, pyramidal- ization of an internal carbon, <i>cis-trans</i> polyenes	φ_n, φ_{n+1} more or less localized 3×3 CI \rightarrow variable μ	natural lowest SCF closed shell solution φ_n, φ_{n+1} more or less delocalized	2nd and 3rd SCF closed shell "quasisolutions" or solutions with orthogonality constraint
In any case	adequate MO's for the radicalar states, no repolarization included except for very large CI \rightarrow bad energy	no physical meaning of the CS determi- nant \rightarrow idem	include σ and π repolarizations of the concerned excited state good energy, exaggerate the dipole moments near the surface crossing or touching.

trial vectors built from the open shell MO's either through the inflexion point procedure or by using the perturbation process with orthogonality constraint (see Fig. 6). Starting from these MO's for a symmetry broken geometry one may even reach the degenerate associated solutions for the symmetric twisted non pyramidalized geometry. The energy curves thus obtained for A^+A^- and A^-A^+ before and after a large scale CI (cf. Fig. 7) are in qualitative agreement and they all show that in the homosymmetric all-*trans* hexatriene, a symmetry breaking deformation allows an energy gain of at least 3 kcal mol⁻¹, and stabilizes a polar form (see Fig. 7). An opposite pyramidalization angle might perhaps give a lesser interfragment repulsion.

VII. CONCLUSION

The methodology developed in the present paper stresses on the need to include most of the polarization effects of a given ionic state at the SCF step, since CI starting from non polar ground state MO's have to reach N times excited configurations to introduce this polarization in a satisfactory manner, a task which will rapidly become impossible when the number N of electron pairs increases. The obtention of the polar SCF solutions, which is easy when the carbon skeleton remains in the symmetry plane (rotation around the terminal bonds of polyenes), becomes difficult in the absence of this localizing symmetry, but approximate procedures have been proposed to overcome this difficulty, through the analysis of "quasisolutions" or with orthogonality constrained SCF closed shell solutions. The role of symmetry in making clearer or obscure the various solutions has been summarized in Table II.

A refined study of the polar minima of the excited singlet surface of linear polyenes is made difficult by the large number of geometric parameters involved when the dimension of the molecule increases. The present

paper does not pretend to give such an exploration, even for the hexatriene. But the energy stabilization obtained from one degree of freedom only, namely the pyramidalization of carbon atom on the twisted bond, is significant enough to suggest that even in "homosymmetric" situations, slight symmetry breaking deformations of the skeleton stabilize one of the two weakly resonant forms A^+A^- or A^-A^+ and destroy this degeneracy, thus leading to a polar minimum. Simultaneous specific optimizations of bond lengths would certainly increase the depths of such small wells. It was clear already that each double bond rotation induces a funnel in the ionic singlet excited surface; the present work confirms that several small specific wells are present in the bottom of these funnels, corresponding to specific polar electronic distributions and to specific stabilizing deformations of the fragments. One must remember, however, that these polar minima are not necessarily involved in the *cis-trans* isomerization mechanism, if a diradicalar excited surfaces exist below the ionic state and if they are accessible from the vertical transition through avoided crossings or (non)radiative transitions. This problem will be analyzed in a forth coming paper.

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