

- (11) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance", New York, N.Y., 1967, and other textbooks on electron spin resonance.
 (12) D. M. Silver and R. M. Stevens, *J. Chem. Phys.*, **59**, 3378 (1973).
 (13) W. Meyer, *J. Chem. Phys.*, **58**, 1017 (1973); *Int. J. Quantum Chem., Symp.*, **5**, 341 (1971).
 (14) R. Ahlrichs, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J. Chem. Phys.*, **62**, 1225 (1975).
 (15) M. Jungen and R. Ahlrichs, *Theor. Chim. Acta*, **17**, 339 (1970).
 (16) V. Staemmler, Habilitationsschrift, Bochum, 1975.
 (17) R. Ahlrichs, H. Lischka, B. Zurawski, and W. Kutzelnigg, *J. Chem. Phys.*, **63**, 4685 (1975).
 (18) M. J. S. Dewar and H. Kollmar, *J. Am. Chem. Soc.*, **97**, 2933 (1975).

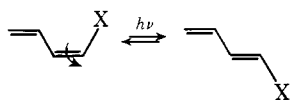
On the Extent of Charge Separation in Suddenly Polarized Twisted Excited States of Linear Polyenes

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Abstract: The lowest $^1\pi\pi^*$ singlet excited states of butadiene are stabilized when twisted to 90° around one double bond and become strongly ionic. These zwitterionic excited states, which occur in cis-trans photoisomerizations of polyenes, are rather difficult to treat in a correct manner. It is shown that an open shell SCF calculation for the diradical ground state, followed by a limited CI, overestimates the charge separation and dipole moment in the ionic excited states. By allowing a larger flexibility to the wave functions, one demonstrates that (i) the positive and negative net charges attract each other and tend to concentrate on either side of the twisted double bond and (ii) the σ polarization effect stabilizes these localized structures and diminishes the net charges. Both phenomena diminish the excited state dipole moment and charge separation. These conclusions do not hold for the protonated Schiff bases, for which the excited state bears a single charge without the counterpart of opposite sign and where an important charge migration may occur.

Several semiempirical studies have shown that in its lowest singlet $^1\pi\pi^*$ excited state, the butadiene molecule might undergo a rotation around one of its double bonds² losing its center of symmetry. The first ab-initio study of the excited state geometry^{3a} kept the center of symmetry of the molecule, and only allowed two simultaneous and equal rotations ($\theta_1 = \theta_2$) around the C₁C₂ and C₃C₄ double bonds. An analytic approach to the problem also suggests a full rotation (θ_1 or $\theta_2 = 90^\circ$) around one double bond.^{3b} This is a likely phenomenon if one remembers that in ethylene the $\theta = 90^\circ$ rotation diminishes the energy of the V¹ $\pi\pi^*$ singlet state from 7.6 to 4.9 eV according to the simplest experimental considerations (energy stabilization of 2.7 eV) and from 8.2 to 6.2 eV according to the most recent and refined quantum mechanical calculations⁴ (energy stabilization of 2.0 eV). The vertical S₀-S₁ transition of butadiene occurs at about 5.9 to 5.7 eV,⁶ i.e., 1 eV above the lowest estimate of the (0-0) transition of ethylene; one may therefore guess that a twisted butadiene, where the excitation is located on one double bond, is already more stable than the planar excited singlet state. The residual delocalization which may occur in a twisted butadiene should give a supplementary stabilization of the 90° structure and bring its energy below 4.9 eV. A recent ab-initio study⁵ actually confirms that the perpendicular structures are more stable than the planar one. Moreover the twisted conformations of the lowest excited singlets appear to be very likely intermediate in direct cis-trans photoisomerizations of C-C bonds.



These photoisomerizations are a basic photochemical reaction of conjugated chains and concern, for instance, besides ethylene and butadiene, styrene, stilbene, and retinene. (For recent theoretical studies of these molecules, see for instance ref 7-9.)

It may be important therefore to analyze the electronic structure of these twisted intermediates.

From elementary considerations of valence bond theory one may divide the four lowest excited states of ethylene into covalent and ionic states. The ground state is essentially covalent since in the π part of the wave function, described from the two $2p_\pi$ AO's a and b, the radical components $|a\bar{b}|$ and $|\bar{a}b|$ have a larger weight than the ionic structures $|a\bar{a}|$ and $|\bar{b}b|$; the



ionic component disappears for $\theta = 90^\circ$ ($\phi_0^\pi = 1/2^{1/2} |a\bar{b} + \bar{a}b|$). For all values of θ , the $\pi\pi^*$ triplet state is purely covalent, $\phi_T^\pi = 1/2^{1/2} |a\bar{b} - \bar{a}b|$. The lowest singlet V state, represented by the $\pi\pi^*$ single excitation, is purely ionic, $\phi_V^\pi = 1/2^{1/2} |a\bar{a} - \bar{b}b|$. Another singlet state may be introduced in the π minimal basis set; for the planar configuration it is essentially a doubly excited configuration $\pi^*\bar{\pi}^*$ in the MO representation, but for the perpendicular conformation this state becomes purely ionic $\phi_Z^\pi = 1/2^{1/2} |a\bar{a} + \bar{b}b|$. The two ionic states are close in energy, and if the symmetry is broken by a chemical substitution or a deformation on one CH₂ group, ϕ_V and ϕ_Z may interact and strongly mix. Bonacic-Koutecky et al.¹⁰ have shown that for $\theta = 90^\circ$, a slight perturbation on one carbon gives two very polar, excited states with a net charge of about ± 0.9 e on each carbon. The full charge displacement, $\Delta g = 1.0$ e, is represented by the limit wave functions $\phi_{Z_1}^\pi = |a\bar{a}|$ ($-e, +e$ structure) and $\phi_{Z_2}^\pi = |\bar{b}b|$ ($+e, -e$ structure). $\phi_{Z_1}^\pi$ and $\phi_{Z_2}^\pi$ are weakly mixed in the calculated wave functions. The same authors¹⁰ analyzed the charge distribution of the excited *s-cis,s-trans*-1,3,5-hexatriene when rotated around the central double bond (which is most likely to undergo a rotation^{2e}).

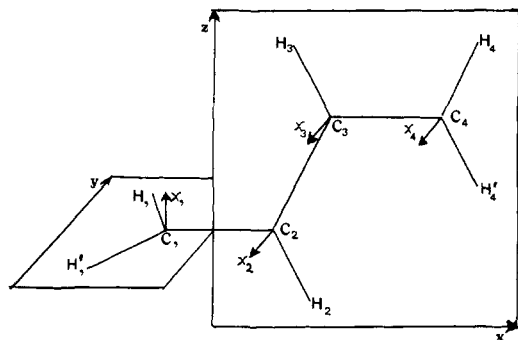
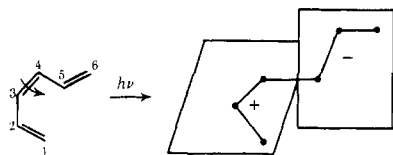


Figure 1. Geometric definition of the problem; labeling of the atoms and π atomic orbitals.



For the 90° conformation, an almost complete charge separation ($\Delta q = 0.86 e$) occurs between the two three-atom π allylic subsystems. If the net charges are centered on the 2 and 5 carbon atoms, centers of symmetry of the conjugated subsystems, the 90° conformation will present a high dipole moment. Going on to larger compounds, one may imagine the cis-trans isomerization of retinal and related molecules, which is the basic photochemical process of vision; the 90° rotation around the bond defines two delocalized π subsystems, each involving five π AO's. Bruckmann and Salem⁹ treated this problem by performing an open shell calculation of the radical ground state and a further small CI to get the ionic states. In retinal the charge separation is such that a final very high change in the dipole moment itself (33 to 40 debyes) between S_0 and S_1 was obtained. In the protonated Schiff base, an analogous charge displacement was obtained, and these electronic changes were supposed to play the role of an electric signal in the primary process of vision.

The present paper essentially discusses the charge separation phenomenon in these ionic excited states, taking butadiene as a test case. Using the current variation procedures one meets a lot of difficulties in treating these excited states, and/or in following their changes from the planar to the twisted structure; the most convenient procedure for one configuration may be impracticable or unreliable for another one. This paper approaches the problem through a range of techniques (closed shell or open shell Hartree-Fock calculations, delocalized and localized pictures, CI of increasing dimension, . . .). All calculations confirm the charge separation phenomenon in the unsymmetrical twisted conformations of the excited state, but the amplitude of this charge separation, and therefore the dipole moment of these zwitterionic states,⁹ may be greatly overestimated when using for instance the delocalized MO's of the diradical ground state without a sufficient subsequent CI. A variational Hartree-Fock (HF) procedure or/and a large CI on these ionic states relocalize the positive and negative charges on the carbon atoms of the rotating bond, through their electrostatic interaction. The mechanism of this relocalization is analytically discussed in a perturbative scheme. Moreover the π charges polarize the σ framework, the σ reaction field diminishing the total net charges and dipole moments. Both phenomena always occur in neutral molecules, but the electronic behavior may be completely different in charged molecules, such as protonated Schiff bases, where charge transfer between the two decoupled π subsystems may neutralize the ground state ionic site; the electrostatic attraction

	σ_s	σ_a	π_1 [X ₁]	π_2 [X ₂ , X ₃ , X ₄]
σ_s		0	h	0
σ_a	0		0	h'
π_1	h	0		0
π_2	0	h'	0	

Figure 2. Structure of the Fock operator; h and h' represent small σ - π hyperconjugation interactions.

between the hole and the particle tends to disappear, and the excited state behaves as a competing ionic state, where the charge is delocalized on the other side of the molecule. Our discussions of the polarization phenomena, while it would invalidate large dipole moment predictions in neutral molecules, support Salem's analysis of the charge migration in the retinal protonated Schiff base.⁹

The whole numerical study has been performed using the CNDO Hamiltonian, for obvious financial reasons, since the qualitative phenomena discussed in this paper are essentially governed by electrostatic forces, which are correctly mimicked by the CNDO Hamiltonian. Our main conclusions, especially the decrease of the charge separation and dipole moment under a consistent variational treatment of the excited states, should not depend on the integral approximations, and their order of magnitude should not be changed by going to the ab-initio level.

(A) Delocalized Approach

(1) **Symmetry Analysis of the Butadiene Problem.** A 90° rotation around the C_1C_2 bond destroys the center of symmetry of the molecule, but the $C_1C_2C_3C_4$ plane remains a plane of symmetry for the molecule (Figure 1). The only atoms out of this plane are the H_1 and H_1' hydrogen atoms. Starting from a basis of core and valence AO's one may distinguish four kinds of subspaces, from symmetry and energy considerations: (i) The σ_s symmetrical σ subspace will be built from all s , p_x , and p_z AO's of carbons $C_2C_3C_4$, all s orbitals from the hydrogen atoms linked to C_2 , C_3 , and C_4 , the s and p_x AO's from C_1 , and the symmetrical combinations of s AO's from H_1 and H_1' . This subspace includes all σ bond MO's, except for the C_1H_1 and C_1H_1' bonds for which it only involves their symmetrical combination $\sigma_s = [C_1C_2(\sigma), C_2C_3(\sigma), C_3C_4(\sigma), C_2H_2, C_3H_3, C_4H_4, C_4H_4', (C_1H_1 + C_1H_1')]/2^{1/2}$, and their virtual counterparts]. (ii) The σ_a antisymmetric σ subspace reduces to the $C_1 p_y$ AO and the antisymmetric combination of H_1 and H_1' $1s$ AO's. In language of bonds, σ_a represents the antisymmetric combination of the C_1H_1 and C_1H_1' bonds $\sigma_a = [(C_1H_1 - C_1H_1')]/2^{1/2}$, and its virtual counterpart]. (iii) The π_1 symmetric π subspace is built from the p_z AO of C_1 . (iv) The π_2 antisymmetric π subspace is built from the p_y AO's from C_2C_3 and C_4 . Whatever its precise definition, the Fock operator may be built in such a basis and its structure appears in Figure 2. The σ and π systems of the same symmetry interact through matrix elements which physically introduce the hyperconjugation between π and σ systems. The $\pi_a\sigma_2$ block for instance (h' in Figure 2) induces a slight delocalization between the σ_2 MO's on $C_2C_3C_4$ and the C_1H_1 and C_1H_1' bonds. Due to the difference in the diagonal energies of σ and π MO's this $\sigma\pi$ mixture, as it turns out, and in accord with chemical intu-

ition, remains a weak phenomenon and one may focus first upon the diagonalization of the π blocks. In a minimal basis set, π_1 reduces to a single π AO $\chi_1(z)$ leading to a nonbonding level $a_0 = \chi_1$; π_2 will be spanned by three π AO's, $\chi_2(y)$, $\chi_3(y)$, $\chi_4(y)$, such as in the allyl radical. At the first iteration of the SCF process, the Fock diagonal matrix elements $\langle \chi_2 | F | \chi_2 \rangle$, $\langle \chi_3 | F | \chi_3 \rangle$, and $\langle \chi_4 | F | \chi_4 \rangle$ may be supposed to have similar values; it will be so if the first guess of the Fock operator is a Hückel-type Hamiltonian, as is usually done in the direct iteration technique. Its diagonalization will lead to (i) a three-center bonding MO $a_1 \simeq \chi_2/2 + \chi_3/2^{1/2} + \chi_4/2$; (ii) a nonbonding MO $a_2 \simeq (\chi_2 - \chi_4)/2^{1/2}$; (iii) a virtual MO $a_3 \simeq \chi_2/2 - \chi_3/2^{1/2} + \chi_4/2$. As concerns the Fock energies one may be sure that $\langle a_1 | F | a_1 \rangle \ll \langle a_2 | F | a_2 \rangle \simeq \langle a_0 | F | a_0 \rangle \ll \langle a_3 | F | a_3 \rangle$. To go further on in this discussion, and to perform new iterations in the SCF process, one must specify the choice of the Fock operator, i.e., the occupancy of the approximate MO's. One may either use a closed shell Fock operator or an open shell representation.

(2) Open Shell Representation. One may study a "diradical" wave function in which the lowest π MO a_1 is doubly occupied while the two competing nonbonding MO's a_0 and a_2 are singly occupied. The π part of the wave function may be singlet or triplet. One knows from valence bond considerations that such wave functions correctly describe the neutral ground state and lowest triplet state for these twisted situations.

$$\phi_0^\pi = 1/2^{1/2} [a_1 \bar{a}_1 (a_0 \bar{a}_2 \pm a_2 \bar{a}_0)] \quad (1)$$

These states represent two π orthogonal radical systems, with 1 electron per carbon atom in each subsystem. For a practical calculation, one may use either an exact Hartree-Fock open shell formalism,¹¹ or an approximate Nesbet-type Fock operator¹² where g_σ represents the field of nuclei

$$F_{os} = T + g_\sigma + 2J_1 - K_1 + J_0 - \frac{K_0}{2} + J_2 - \frac{K_2}{2} \quad (2)$$

and σ electrons. The calculations performed by Salem et al.^{9,10} used this procedure. During the iterations the MO's and their occupancy cannot change significantly. In our case a_0 and a_2 , belonging to different symmetry subspaces, cannot mix. Since the calculated states are electrostatically neutral, the MO's will not receive any significant polarization, and remain methyl- or allyl-like. Neglecting the hyperconjugation delocalization,

$$\phi_2 \simeq a_2 = 1/2^{1/2} (\chi_2 - \chi_4) \quad (3)$$

Table I reproduces the two singly occupied SCF MO's; one sees that the allylic shape of a_2 is kept, and that a_2 has a slightly lower energy than a_0 . One may use these diradical neutral MO's to build the ionic excited states; Salem et al.¹⁰ perform a 3×3 limited CI between ϕ_0 and the two lowest closed shell determinants

$$\phi_1^\pi = [a_1 \bar{a}_1 a_2 \bar{a}_2] \quad (4a)$$

$$\phi_2^\pi = [a_1 \bar{a}_1 a_0 \bar{a}_0] \quad (4b)$$

(where the σ parts of the wave function are not explicit). One may notice that in ϕ_1 the four π electrons are in the allylic system, the state is a M^+A^- ionized structure Z_1 with a localized CH_2^+ positive charge and a negative delocalized charge in the allyl π_2 system. ϕ_2 represents the reverse ionic $Z_2 M^-A^+$ structure with a CH_2^- negative localized charge and a positive delocalized charge on the π_2 system. In the butadiene case ϕ_0 being antisymmetric does not interact with the symmetric ϕ_1 and ϕ_2 determinants and the limited CI reduces to the interaction between ϕ_1 and ϕ_2 ,

$$\langle \phi_1 | H | \phi_2 \rangle = \langle a_2 a_2 | 1/r_{12} | a_0 a_0 \rangle = K_{a_2 a_0} \quad (5)$$

Table I. SCF Singly Occupied MO's for the Ground State Diradical State

(i)	$\langle a_2 F a_2 \rangle = -0.1532$ au $a_2 = 0.7354C_{2y} + 0.0291C_{3y} - 0.5375C_{4y} + 0.2894(H_1' - H_1) + 0.0415C_{1y}$
(ii)	$\langle a_0 F a_0 \rangle = -0.1466$ au $a_0 = -0.8772C_{1z} - 0.1607C_{3z} - 0.1542C_{3x} - 0.1865C_{3z} - 0.3497H_2 + (\epsilon)$

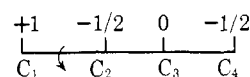
This interaction is a weak exchange integral between two orthogonal π systems located on two different regions of space. If ϕ_1 and ϕ_2 have different energies, i.e., if the two pure zwitterionic structures are not degenerate,

$$|\Delta E_{12}| = |\langle \phi_1 | H | \phi_1 \rangle - \langle \phi_2 | H | \phi_2 \rangle| \gg K_{a_2 a_0} \quad (6)$$

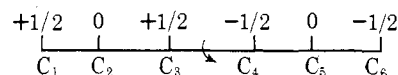
The interaction between them only introduces a weak perturbation,

$$\psi_1 = \phi_1 + \frac{K_{a_2 a_0}}{\Delta E_{12}} \phi_2, \quad \psi_2 = -\frac{K_{a_2 a_0}}{\Delta E_{12}} \phi_1 + \phi_2 \quad (7)$$

and the eigenstates keep a strongly ionic character, as shown by the calculations concerning the substituted ethylene, the *s-cis,s-trans*-hexatriene,¹⁰ and retinene.⁹ One may notice however that using the π delocalized MO's obtained for the neutral ground state one forces a strong delocalization of the net charges in the ionic states. In the ϕ_1 ionic state of butadiene, the negative charge at this level of approximation is equally spread on C_2 and C_4 (eq 3).



For the *s-cis,s-trans*-hexatriene twisted around the central bond, the two systems are allylic ($a_0 \simeq \chi_1 (\mp) \chi_3 / 2^{1/2}$, ($a_2 \simeq \chi_4 (\mp) \chi_6 / 2^{1/2}$) and the net charge distribution becomes



The center of gravity of its positive and negative net charges is located on the central atoms of the two orthogonal subsystems (for instance C_2 and C_5 in the preceding case). For a linear skeleton this means that the distance between the mean positive and negative charges is about one-half of the total length of the carbon skeleton, and the dipole moment in the ionic state increases linearly with the number of carbon atoms, i.e., the length of the conjugated system. This explains the large charge separation obtained by Salem and Bruckmann for the retinal molecule.⁹ However, the open shell SCF limited CI procedure is a crude approximation. To improve it, one may improve the quality of the excited state MO's or/and enlarge the extent of the CI.

(3) Closed Shell Representation. The σ bonding levels being doubly occupied, one must fill two π MO's with the four π electrons of the problem. Although χ_2 and χ_4 are not neighboring, one may suppose that their interaction stabilizes the a_2 level which becomes slightly bonding as it does in the allyl radical and anion, and as verified in Table I.

$$\langle a_2 | F | a_2 \rangle < \langle a_0 | F | a_0 \rangle, \text{ with } (a_0 = \chi_1) \quad (8)$$

In the most likely occupancy scheme, a_1 and a_2 are filled up, a_0 and a_3 are empty MO's, and one starts the calculation of a M^+A^- structure in which C_1 is positively charged, the negative charge being spread over the largest delocalized π system. This does not mean that the M^-A^+ structure is higher in energy; in the direct iterative procedure the occupancy is determined from the orbital SCF energy levels only and not by total energy comparisons. A possible difficulty might arise from the near

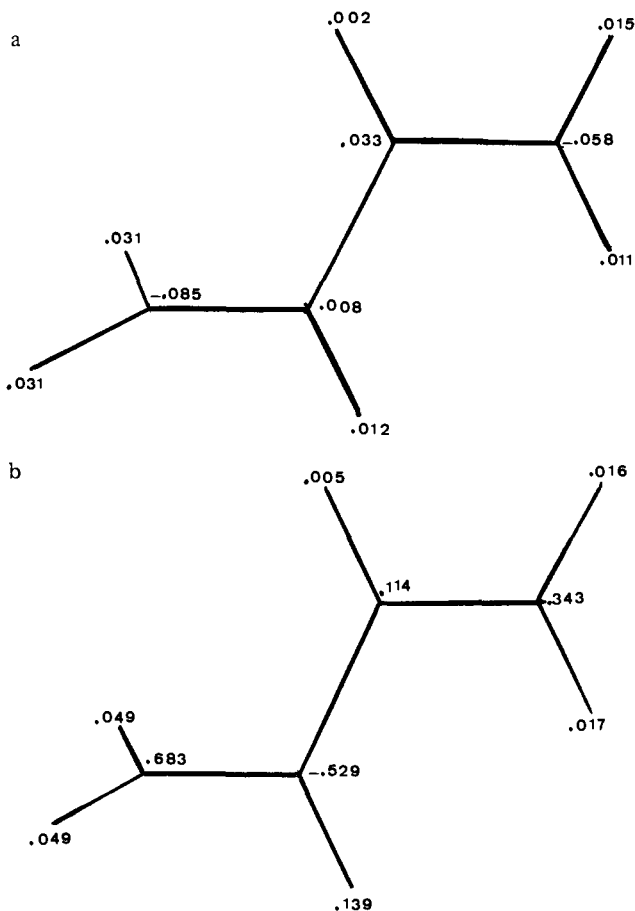


Figure 3. Net charges from an open shell SCF calculation: (a) ground state, (b) M^+A^- excited state obtained from the same MO's.

degeneracy between a_0 and a_2 ; these MO's are of different symmetry and cannot mix, but a_0 might become lower in energy than a_2 , leading to an oscillatory behavior of the iterations. The actual calculation did not present such convergence difficulties and the M^+A^- structure was kept along the iterations. This is due to the polarization phenomenon, which immediately fits the electronic distribution to the M^+A^- structure.

One may analyze the extent of these polarization phenomena by comparing the total net charges for the M^+A^- structure obtained from the open shell and closed shell SCF-MO's (see Figures 3b and 4). In the M^+A^- description obtained from the open shell SCF-MO's, the hyperconjugation already delocalizes the positive charge (0.25 e) on C_3 and H_2 and the negative charge on H_1 and H_1' (-0.1 e). But the C_4 carbon atom is significantly charged (-0.34 e). The variation closed shell procedure diminishes the C_4 charge by a factor of 2 (to -0.17 e). The net charge is essentially concentrated on C_1 and C_2 (± 0.43 e), but the polarization has diminished the net charges.

This polarization phenomenon goes through two mechanisms: (1) The polarization of the σ system diminishes the net charges; its importance is illustrated by comparing the total and π (between parentheses) net charges in Figure 4; the σ screening reduces the net charges by a factor $2/3$. (2) The delocalized negative charge will move toward the positive C_1 carbon atom concentrating itself on the C_2 carbon atom in order to maximize the electrostatic interaction between the net charges. The ratio of the atomic net charges for the two negatively charged carbon atoms C_2 and C_4 changes from 1.5 in the open shell representation to 2.5 in the closed shell one. Both mechanisms will diminish the dipole moment of the excited state.

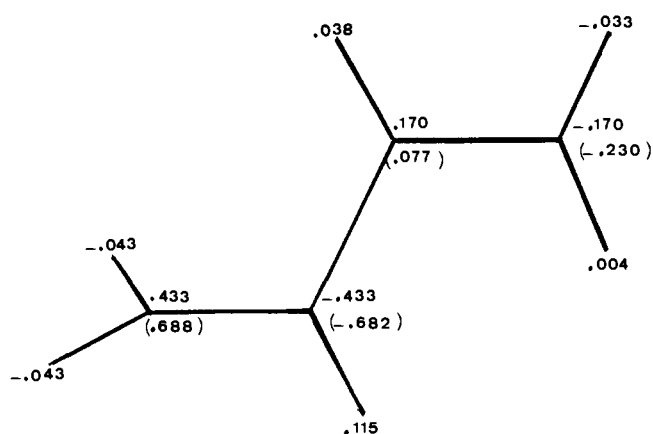


Figure 4. Net charges from an SCF closed shell calculation of the excited M^+A^- state (the numbers in parentheses are the π net charges).

Mechanism of the π Polarization. We demonstrate here how, starting from nonpolar allylic π bonds, the closed shell variational procedure and/or a proper CI concentrates the π negative charge. The nonpolar allylic a_2 MO has opposite coefficients on χ_2 and χ_4 . In the M^+A^- excited state the "hole" on the C_1 atom brings the negative charge from χ_4 to χ_2 . This result is obtained by mixing the a_2 and a_3 MO's, or in a CI language by mixing the ϕ_1 determinant with $a_3^+a_2\phi_1 = |a_1\bar{a}_1a_2\bar{a}_3|$ and its spin-homologous $|a_1\bar{a}_1a_3\bar{a}_2|$. In the open-shell calculations

$$\langle a_2 | F_{os} | a_3 \rangle = \left\langle a_2 \left| T + g_\sigma + 2J_1 - K_1 + J_2 - \frac{K_2}{2} + J_0 - \frac{K_0}{2} \right| a_3 \right\rangle = 0$$

For the ionic state,

$$\begin{aligned} \langle \phi_1 | H | a_3^+a_2\phi_1 \rangle &= \langle a_1\bar{a}_1a_2\bar{a}_2 | H | a_1\bar{a}_1a_3\bar{a}_2 \rangle \\ &= \langle a_2 | T + g_0 + 2J_1 - K_1 + J_2 | a_3 \rangle \\ &= \langle a_2 | F_{os} + 0.5J_2 - J_0 + 0.5K_0 | a_3 \rangle \\ &= \langle a_2 | J_{22} - J_0 + 0.5K_0 | a_3 \rangle \end{aligned} \quad (9)$$

One may notice that in the intrinsic symmetry of the allylic fragment (plane of symmetry bisecting $C_2C_3C_4$) a_2 is antisymmetric and a_3 is symmetric. Therefore $\langle a_2 | J_2 | a_3 \rangle = 0$. Since a_0 has a negligible differential overlap with a_2 and a_3 , which lie on a different part of the molecule, $\langle a_2 | K_0 | a_3 \rangle$ is negligible. Hence, the calculated matrix element,

$$\langle a_1\bar{a}_1a_2\bar{a}_2 | H | a_1\bar{a}_1a_3\bar{a}_2 \rangle = -\langle a_2 | J_0 | a_3 \rangle \quad (10)$$

represents the interaction between the positive charge a_0^2 and the transition dipole a_2a_3 . Neglecting the π differential overlap, the a_2a_3 distribution may be approximated by $-(1/2[2]^{1/2})\chi_2^2 + (1/2[2]^{1/2})\chi_4^2$; since $a_0^2 = \chi_1^2$,

$$\begin{aligned} \langle \phi_1 | H | a_3^+a_2\phi_1 \rangle &= \frac{1}{2[2]^{1/2}} \langle \chi_2\chi_1, \chi_2\chi_1 \rangle - \langle \chi_4\chi_1, \chi_4\chi_1 \rangle \\ &= \frac{1}{2[2]^{1/2}} (g_{12} - g_{14}) \end{aligned} \quad (11)$$

where g_{12} is the coulombic bielectronic integral between the χ_1 and χ_2 AO's. These integrals decrease as $1/r$ and $g_{14} \ll g_{12}$. The calculated matrix element is therefore positive and lies in a range of 4-5 eV. After this configuration interaction, the perturbed wave function may be written

$$\psi^{+-} = \phi_1 + \frac{1}{4} \frac{g_{12}}{\Delta E_{2 \rightarrow 3}} |a_1\bar{a}_1(a_2\bar{a}_3 + a_3\bar{a}_2)| + \mathcal{O}_{(2)} \quad (12)$$

where $\Delta E_{23} = \langle \phi_1 | H | \phi_1 \rangle - \langle a_3^+ a_2 \phi_1 | H | a_3^+ a_2 \phi_1 \rangle$ is the $a_2 \rightarrow a_3$ excitation energy (with changed sign) and $\mathcal{O}_{(2)}$ represents second-order corrections. Defining $\lambda = 0.25g_{12}/\Delta E_{(2\rightarrow 3)}$, which is a negative quantity, one sees that ψ may be written as a single determinant

$$\psi = |a_1 \bar{a}_1 (a_2 + \lambda a_3) (\bar{a}_2 + \lambda \bar{a}_3)| + \mathcal{O}_{(2)} \quad (13)$$

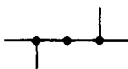
where the a_2 MO has been changed into a_2'

$$a_2' = a_2 + \lambda a_3 = (-1/2^{1/2} + \lambda/2)\chi_2 - \lambda/2^{1/2}\chi_3 + (1/2^{1/2} + \lambda/2)\chi_4 \quad (14)$$

Since λ is negative, the new π MO has a larger coefficient on χ_2 (in absolute value), a small coefficient on χ_3 , and a strongly diminished coefficient on χ_4 . The amplitude shape becomes



instead of



the modified MO, adapted to the ionic structure is concentrated on χ_2 , in the neighborhood of the positive charge. The phenomenon is important since $g_{12}/4$ and $\Delta E_{(2\rightarrow 3)}$ are of the same order of magnitude. The electronic reorganization might concern the a_1 MO as well, by mixing it with the a_3 MO. A similar analytic derivation is possible.

Mechanism of the σ Reorganization. In the neutral diradical state, the C_1C_2 bond for instance is nonpolar. In the M^+A^- excited state, this bond is submitted to a strong electrostatic field. This leads to a mixture of the σ bonding and σ^* antibonding MO's; $\langle \phi_1 | H | a_{\sigma^*} a_{\sigma} \phi_1 \rangle = \langle \sigma^* | -J_0 + J_2 | \sigma \rangle$ (neglecting the $\sigma\pi$ exchange integrals); if the $\sigma^*\sigma$ distribution is defined as $-+$ on C_1C_2 , the matrix element is positive. The modified wave function

$$\psi' = \phi_1 + \lambda' a_{\sigma^*} a_{\sigma} \phi_1 \quad (15)$$

has a negative λ' coefficient and may be approximated (to the second order) by a modified determinant in which the new σ MO

$$\sigma' = \sigma + \lambda' \sigma^* = 1/2^{1/2} (1 - \lambda') h_1 + 1/2^{1/2} (1 + \lambda') h_2 \quad (16)$$

has a larger coefficient on the C_1 sp_2 hybrid h_1 and a smaller coefficient on the C_2 sp_2 hybrid h_2 .

The π and the σ reorganization effects are taken into account in the closed shell SCF procedure. To introduce them in a treatment starting from the SCF neutral MO's (obtained from the open shell Fock operator) one must perform a sufficient CI; the single excitations at least must be introduced, but the SCF process sums up contributions from higher excitations representing *simultaneous* polarization effects on the various bonds. The *3*3 CI cannot reproduce the polarization phenomena and its estimate of the dipole moment is overestimated.*

(4) Status of the $Z_2(M^-A^+)$ State. The second ionic closed shell determinant ϕ_2^π (eq 4b) is more difficult to reach from the delocalized direct iteration procedure. One may notice however that it will remain orthogonal to ϕ_1 . Let us call $\sigma_1 \dots \sigma_n$ the σ MO's. All of them except σ_n are symmetrical. Then if the M^+A^- ϕ_1 single determinant is written as

$$\phi_1 = |\sigma_1 \bar{\sigma}_1 \dots \sigma_n \bar{\sigma}_n a_1 \bar{a}_1 a_2 \bar{a}_2| \quad (17)$$

with three doubly occupied antisymmetric MO's (σ_n, a_1, a_2), the $Z_2(M^-A^+)$ ionic state will be represented by

$$\phi_2 = |\sigma_1' \bar{\sigma}_1' \dots \sigma_n' \bar{\sigma}_n' a_1' \bar{a}_1' a_0 \bar{a}_0| \quad (18)$$

with only two doubly occupied antisymmetric MO's (σ_n', a_1'). All SCF-MO's will be different for these states, and they are not necessarily orthogonal

$$\langle \sigma_i | \sigma_j' \rangle \neq 0, \quad \langle a_i | a_j' \rangle \neq 0 \quad (19)$$

but the symmetry implies that $\langle a_1' | \sigma_i \rangle = \langle a_1 | \sigma_i' \rangle = \langle a_2 | \sigma_i' \rangle = 0$, for all $i = 1, n$. The two SCF determinants are necessarily orthogonal since in the $\langle \phi_1 | \phi_2 \rangle$ scalar product one must necessarily associate two antisymmetric with two symmetric MO's. Therefore the two closed shell (M^+A^- and M^-A^+) determinants having respectively 4 and 6 electrons in the antisymmetric subspace are orthogonal. This result no longer holds if symmetry is broken, such as in a substituted ethylene molecule, in *s-cis,s-trans*-hexatriene or tetraene, for which the closed shell SCF process will lead to two different but nonorthogonal determinants.

One may derive immediately a further result; any linear combination of "4 antisymmetric-electron" determinants is orthogonal to any linear combination of "6 antisymmetric-electron" determinants. Therefore if one performs a CI process from ϕ_1 and from ϕ_2 without changing the number of electrons in the antisymmetric subspace, the two resulting multiconfigurational wave functions remain orthogonal. If μ and ν represent respectively symmetric and antisymmetric MO's,

$$\left. \begin{aligned} \psi_1 &= \sum_I C_I \mathcal{A} \left(\prod_{k=1}^{n-6} \mu_{kI} \right) \left(\prod_{i=1}^6 \nu_{iI} \right) \\ \psi_2 &= \sum_J C_J \mathcal{A} \left(\prod_{k=1}^{n-4} \mu'_{kJ} \right) \left(\prod_{i=1}^4 \nu'_{iJ} \right) \end{aligned} \right\} \rightarrow \langle \psi_1 | \psi_2 \rangle = 0 \quad (20)$$

The same polarization phenomena occur, with opposite directions, in the ϕ_- closed shell SCF determinants. The σ bonds receive opposite polarizations. The delocalized charge is now the positive π charge but it will concentrate on the C_2 carbon atom. The π reorganization phenomenon occurs through the interaction between $\phi_2 = |a_1 \bar{a}_1 a_0 \bar{a}_0|$ and $|a_1 \bar{a}_2 a_0 \bar{a}_0|$. One shows that $\langle \phi_2 | H | a_1 \bar{a}_2 a_0 \bar{a}_0 \rangle = \langle a_1 | J_0 - J_1/2 | a_2 \rangle$ (neglecting intersystem exchange integrals), $= \langle a_1 | J_0 | a_2 \rangle$ (due to local symmetry considerations in the allylic fragment), and $= -(1/2[2]^{1/2})(g_{12} - g_{14})$. The SCF a' MO on the π_2 system of the M^-A^+ ionic structure may be approximated by $a_1' = a_1 + \lambda a_2$, where $\lambda = (-1/2[2]^{1/2})(g_{12} - g_{14})/\Delta E_{(1\rightarrow 2)}$ is positive. The new coefficients of a' ($1/2 - \lambda/[2]^{1/2}$ on χ_2 , $1/[2]^{1/2}$ on χ_3 , $1/2 + \lambda/[2]^{1/2}$ on χ_4) concentrate this MO upon the C_4 carbon atom, bringing therefore the positive charge on the C_2 carbon atom, in front of the C_1 negative charge.

We have not been able to reach the $Z_2(M^-A^+)$ state from a direct delocalized procedure, but its SCF determinant was obtained through a localized approach.

(B) The Localized Approach

It is well known that if sufficient CI is performed, the choice of reference MO's is not important. For the ground state, equivalent localized MO's are obtainable, which keep the SCF determinant invariant.¹³ For excited states, the excitonic methods write the wave functions as linear combinations of locally excited determinants.¹⁴ In our case the delocalized analysis shows that the excitation tends to concentrate in the twisted C_1C_2 bond. One may try to analyze the problem in terms of localized MO's. As a first step, we show that one may introduce a single determinantal approximation of ϕ_1 and ϕ_2 using fully localized bond MO's.

(1) Fully Localized Single Determinant Representation of ϕ_1 and ϕ_2 . Let us build for each σ bond and for the C_3-C_4 π bond a fully localized bonding MO φ_i from two directional hybrids h_{i1} and h_{i2} ,

$$\varphi_i = c_i h_{i1} + d_i h_{i2}$$

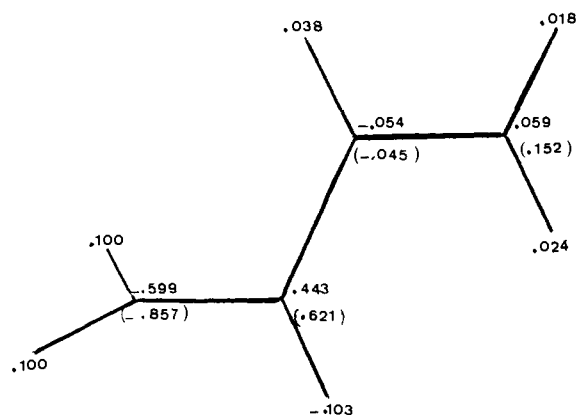


Figure 5. Net charges from an SCF closed shell calculation of the excited M^+A^+ state (the numbers in parentheses are the π net charges).

as done in the PCILO scheme.¹⁵ For the C_1 and C_2 carbon atoms one may introduce the symmetric and antisymmetric π_1 MO

$$\pi_1 = (\chi_1 + \chi_2)/2^{1/2}, \quad \pi_1^* = (-\chi_1 + \chi_2)/2^{1/2}$$

which are degenerate. The ground state wave function is a linear combination of two degenerate closed shell determinants,

$$\phi_0 = |\sigma_1 \dots \bar{\sigma}_n \pi_1 \bar{\pi}_1 \pi_2 \bar{\pi}_2| \quad (21)$$

$$\phi_{(\pi\pi \rightarrow \pi^*\pi^*)} = |\sigma_1 \dots \bar{\sigma}_n \pi_1^* \bar{\pi}_1^* \pi_2 \bar{\pi}_2| \quad (22)$$

$$\psi_0 = [\phi_0 - \phi_{(\pi\pi \rightarrow \pi^*\pi^*)}]/2^{1/2} \quad (23)$$

while the triplet state is $\phi_T = |\sigma_1 \dots \bar{\sigma}_n (\pi_1 \bar{\pi}_1^* - \pi_1^* \bar{\pi}_1) \pi_2 \bar{\pi}_2|/2^{1/2}$. The ionic states may be described from this set of MO's as linear combinations of determinants but it is simpler to write them in a single determinantal form

$$\phi_1^{M^+A^-} = |\sigma_1 \dots \bar{\sigma}_n \chi_2 \bar{\chi}_2 \pi_2 \bar{\pi}_2|$$

$$\phi_2^{M^-A^+} = |\sigma_1 \dots \bar{\sigma}_n \chi_1 \bar{\chi}_1 \pi_2 \bar{\pi}_2| \quad (24)$$

Without authorizing any delocalization between bonds, one may optimize independently these various determinants by optimizing the bond polarities, (i.e., the coefficients c_i and d_i of the bond MO's) in a self-consistent way. One obtains in this manner the best fully localized single determinant descriptions (for a given choice of hybrids). The $\sigma_1 \dots \sigma_n, \pi_2$ MO's are polarized in order to minimize the energy of the considered determinant. One may find in Table II the corresponding optimal bond polarities; π_2 and all σ bonds are polarized to fit the M^+A^- and M^-A^+ C_1C_2 distributions of ϕ_1 and ϕ_2 ; one notices that the polarizations have opposite directions, as expected. The final charge diagrams already qualitatively resemble the SCF closed shell picture: in the M^+A^- state for instance the carbon atoms bear respectively +0.569, -0.661, +0.045, and -0.110, compared to +0.433, -0.433, +0.170, and -0.170 in the SCF calculation. For the M^-A^+ state the fully localized net charges are -0.714, +0.604, -0.096, and -0.036 in the C_1, C_2, C_3, C_4 carbon atoms, respectively. The charges are more important and more concentrated than after the delocalization but the σ polarization already reduces them to the right order of magnitude.

From these locally optimized bond MO's one may improve the wave function in two directions: (i) improve the localized MO's to obtain SCF localized MO's using the iterative perturbative approach recently proposed by Daudey;¹⁶ (ii) go to a multiconfigurational wave function through CI techniques.

(2) **SCF Localized Wave Function.** Starting from the PCILO localized wave functions one allows the fully localized

Table II. Optimized Polarities (d) of Fully Localized Bonds in the $+ -$ and $- +$ States^a

	M^+A^- state	M^-A^+ state	
π	C_1C_2	-1.	+1.
	C_3C_4	-0.063	+0.058
	C_1C_2	+0.287	-0.284
	C_1H_1	+0.072	-0.001
σ	C_2C_3	-0.062	+0.062
	C_2H_2	+0.010	+0.050
	C_3C_4	-0.014	+0.010
	C_3H_3	-0.030	+0.090
	C_4H_4	+0.025	+0.044
	C_3H_4'	+0.008	+0.060

^a The coefficients of the XY bond MO's are $[(1+d)/2]^{1/2}$ and $[(1-d)/2]^{1/2}$ on the X and Y atom hybrids).

bond MO's to have tails on the other bonds through a perturbative process

$$|i'\rangle = |i\rangle + \frac{\langle j^*|F|i^*\rangle}{\langle i|F|i\rangle - \langle j^*|F|j^*\rangle} |j^*\rangle \quad (25)$$

The new i' MO's are orthonormalized and the process is repeated until Brillouin's theorem is satisfied ($\langle i'|F|j^*\rangle = 0$). These SCF localized MO's closely resemble the fully localized bond MO's. For the ϕ_1 state, the final determinant is identical with the delocalized SCF determinant. The ϕ_2 M^-A^+ state was very difficult to obtain in a direct iteration technique; Daudey's procedure¹⁶ starting from the fully localized picture ϕ_2 gives immediately a second orthogonal closed shell determinant of the same overall symmetry. This second SCF closed shell solution lies at -884.25 eV, i.e., slightly higher than the M^+A^- SCF closed shell determinant (-884.67 eV) and 2.1 eV above the SCF open shell ground state determinant (-886.11 eV).

Figure 5 gives the charge diagram for this new state (the charges for ϕ_1 M^+A^- were already given in Figure 4). The σ system does not change very much and its polarization diminishes the π net charges (between parentheses in Figures 4 and 5). The main change is a π delocalization; the "hole" or "particle" which was kept on the C_2 atom in the fully localized description is delocalized on the C_3C_4 π_2 bond through single excitations from or toward this bond.

(3) **Localized CI. (a) Method.** If the CI is large enough to approach the exact solution of the N -electron problem, the result should not depend on the choice of MO's. Starting from "a priori" or SCF, delocalized or localized MO's one should find the same result. We therefore tried various sets of MO's and performed the CI according to the CIPSI technique;¹⁷ the m most important determinants are chosen through an iterative technique, the CI matrix restricted to these determinants is diagonalized, giving m configuration wave functions, and the interaction of these wave functions with the other determinants is treated as a perturbation, to the second order in energy. The most important determinants in this perturbation may be selected to build an enlarged CI matrix and an improved multiconfigurational zeroth order wave function, which again may be perturbed in the next step of the iterative process.

Each iteration gives two energies: the zeroth order variational energy is an upper bound, corresponding to a limited CI, the second order corrected energy is no longer an upper bound, but it lies closer to the exact eigenvalue of the problem. The zeroth order wave functions involved up to quadruply excited determinants. In practice the zeroth order wave function included up to 209 determinants, and for this calculation 2×10^5 determinants were taken into account in the perturbation.

(b) **Starting from Ground State (Nonpolar) Bond MO's.** We performed a first set of calculations using the fully localized

Table III. The Four Lowest States Zeroth and Second Order Energies (eV) and Carbon Net Charges Obtained from Several CI Calculations Using Nonpolar Localized Bond MO's, Respectively Involving 11, 100, 138, and 209 Determinants

		S_0	T_1	$S M^-A^+$	$S M^+A^-$
11	E_0	-878.72	-878.46	-873.39	-872.62
	E_2	-890.73	-892.17	-888.63	-886.97
	q_1	-0.10	-0.08	-0.75	+0.65
	q_2	-0.03	-0.04	+0.56	-0.66
	q_3	-0.01	-0.02	0	-0.02
	q_4	-0.06	-0.06	+0.01	-0.16
100	E_0	-882.98	-882.98	-881.05	-880.46
	E_2	-890.38	-890.38	-889.10	-889.18
	q_1	-0.09	-0.09	-0.73	+0.51
	q_2	-0.05	-0.05	+0.45	-0.61
	q_3	0	0	-0.03	+0.05
	q_4	-0.07	-0.08	+0.04	-0.16
138	E_0	-883.93	-883.01	-881.73	-881.17
	E_2	-890.11	-890.39	-889.18	-889.34
	q_1	-0.10	-0.09	-0.54	+0.31
	q_2	-0.04	+0.05	+0.27	-0.55
	q_3	0	0	-0.02	+0.04
	q_4	-0.07	-0.08	0	-0.14
209	E_0	-884.28	-883.10	-882.07	-881.58
	E_2	-890.12	-890.42	-889.35	-889.49
	q_1	-0.10	-0.09	-0.51	+0.29
	q_2	-0.04	-0.05	+0.26	-0.44
	q_3	0	0	-0.02	+0.05
	q_4	-0.07	-0.08	0	-0.14

bond MO's determined for the ground state. These bond MO's are practically nonpolar and they are rather poor for the polar excited states. A lot of determinants must be included in the zeroth order wave functions for the polar singlets. This procedure (CIPSI-PCILO) has already been applied on styrene,⁷ propiophenone,¹⁸ benzaldehyde,¹⁹ and stilbene²⁰ excited state calculations.

Table III gives the energies of the four lowest states of four iterations involving 11, 100, 138, and 209 determinants. The zeroth and second order energies tend to stabilize, suggesting a good behavior of the perturbation. One must notice however that while the zeroth order energy always predicts the M^+A^- state to be higher in energy than the M^-A^+ state, the second order energies fall in the reverse order. This means that in such a near degeneracy situation, the search for the exact eigenvalues is a very difficult task and would require a still larger CI which was impossible for financial reasons.

Despite this inversion in the second order corrected energies the eigenvectors were very stable. Table III also gives the net charges on the four carbons for the successive zeroth order wave functions. These charges clearly identify the M^+A^- and M^-A^+ states, but they tend to decrease with iteration. Their values are rather similar to that of the SCF calculation but slightly less contrasted. As a matter of fact, starting from nonpolarized MO's, the CI process must include a lot of (multiple) excitations to introduce a good polarization of the electronic clouds in the two polar states, and the zeroth order functions are not better than the closed shell SCF single determinants. However, this procedure has a significant advantage since it simultaneously gives the four lowest states.

(c) **Starting from the polarized fully localized bond MO's**, one may calculate independently the M^+A^- and M^-A^+ excited states. Since the bond polarities are adjusted, a 32 or 36 determinant variational wave function is sufficient to reach the variation energy of the 138 determinant zeroth order wave functions obtained from nonpolar MO's. The M^+A^- singlet state zeroth order energy, -881.40 eV, was decreased to -890.34 eV by the second order perturbation, while the zeroth

and second order energies were -881.49 and -890.39 eV for the M^-A^+ singlet state. The net charges (and π net charges) of the carbon atoms were respectively

+0.350 -0.449 +0.061 -0.135 for the + - state,
(+0.813) (0.880) (+0.036) (-0.086)

C_1 C_2 C_3 C_4
-0.580 +0.319 -0.56 +0.000 for the - + state,
(-0.960) (+0.732) (-0.018) (+0.094)

in qualitative agreement with the SCF closed shell representation (Figures 4 and 5).

(d) **Starting from SCF localized MO's** one can only reach the corresponding polar state; the M^+A^- and M^-A^+ states require separate series of calculations, keeping in mind the orthogonality constraints developed in section A4. The perturbation of the SCF closed shell determinants leads to -889.41 and -888.82 eV second order corrected energies for the M^+A^- and M^-A^+ states. The most important correction arises from the $(\pi_2 \rightarrow \pi_2^*)^2$ double excitation; when it is included in a two configuration zeroth order wave function, the second order corrected energies become -889.28 and -888.68 eV. From this calculation 13 intrapair and $\sigma\pi$ interpair doubly excited determinants were selected and the new zeroth order wave function was perturbed; 2.9×10^5 determinants were involved in the perturbation leading to -889.27 eV for the M^+A^- state and -888.64 eV for the M^-A^+ excited state. One may notice the stability of the second order energies, and of the energy difference (0.6 eV) between the two polar states, which is increased by the correlation energy. The energy levels no longer cross and one may consider this last calculation, using the best zeroth order variational wave function, to be the most reliable. The charges are not significantly changed under the perturbation.

We do not perform the CI from SCF delocalized MO's. Our experience in CI techniques always showed that the delocalized CI's are less sensitive and less rapidly convergent (with respect to the number of determinants) than localized CI's.²³

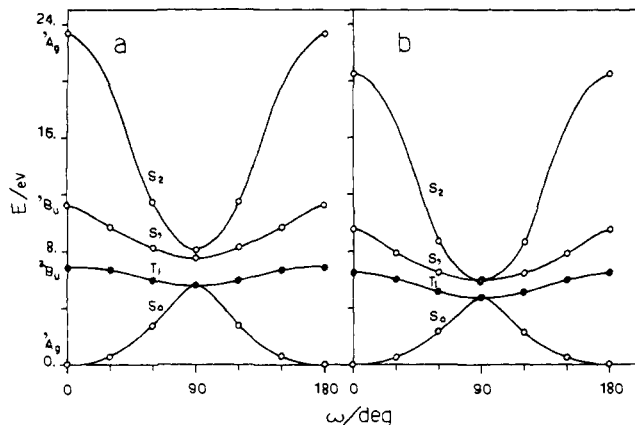


Figure 6. CIPSI-PCILO evolution of the four lowest states of butadiene under a rotation around a double bond: (a) zeroth order energy for a 100×100 CI; (b) second order corrected energy, from the preceding wave functions.

(4) Adequacy of the Localized CI from Nonpolar Bonds for Intermediate Deformations. The preceding developments only concerned the 90° twisted structure, and took benefit of symmetry considerations. For intermediate values of the torsion angle or for pyramidal carbon atoms, the symmetry is destroyed, resulting in orthogonality problems and collapses of the iterative procedures upon the same levels. A real problem appears to follow the whole potential energy curve from $\theta = 0$ to 90° . For the planar structure, an SCF closed shell procedure is required for the ground state, while the excited states involve *several* singly and doubly excited states. On the other side of the surface, the single determinantal description of the ground state results from an open shell SCF calculation while the ionic states are well described by closed shell SCF determinants. The classical methods cannot connect in a smooth manner these extreme descriptions. If one starts from the closed shell SCF-MO's for the small values of θ and from the open shell SCF-MO's for large values of θ , a large CI will be necessary to join the potential surfaces of the ground state itself and a still larger CI will be necessary to represent reasonable descriptions of the excited states.

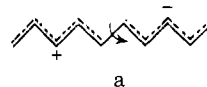
A smooth surface can only result from the use of a consistent set of MO's, valid for all θ values. The a-priori localized bond MO's, although arbitrary in principle, may be used for any geometry. The σ bond MO's were determined from a maximum overlap criterion hybridization procedure²¹ (as done in PCILO¹⁵) and it is very simple to perform the whole π CI. Then the energy curve is uniquely defined. Figure 6 gives the evolution of the zeroth and second order energies for the four lowest states using a 100-determinants zeroth order wave function. The rotation increases the ground state energy and stabilizes the three lowest excited states. The use of CNDO parameters overestimates the ground state barrier and the vertical and adiabatic transition energies by a factor 1.5, despite the high degree of π and $\sigma\pi$ correlation introduced in the calculation.

The near degeneracy between the Z_1 and Z_2 states for $\theta = 90^\circ$ immediately suggests that a further geometrical deformation might split the two levels. In these highly polar states, the negatively charged carbon atoms should be pyramidal, since CH_3^- , as the isoelectronic NH_3 molecule, is pyramidal.²² Such deformation of the C_1 and C_2 sites have been explored by Bruckmann and Salem⁵ in a successful manner; these deformations respectively stabilize the M^-A^+ and M^+A^- states. Such pyramidalizations concentrate the negative net charges on a particular carbon atom and locate it on the rotating bond. They therefore diminish the charge separation in the excited states and this phenomenon contributes to concentrating the electrostatic interaction in the region of the rotating bond.

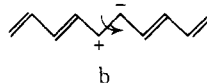
(C) General Discussion. Charge Separation and Charge Displacements in Zwitterionic Excited States. The Case of Retinal and Its Protonated Schiff Base

(1) Neutral Conjugated Chains. The present paper has shown that the charge separation, which definitely appears in unsymmetrical twisted zwitterionic excited states, is overestimated when one only performs an open shell HF calculation, reliable for the neutral diradical ground state or triplet state, followed by a very limited CI. This simple algorithm leads to two nearly orthogonal positively and negatively charged π subsystems, the + and - centers of charge are located around the central carbon atoms of the two subsystems and the excited state dipole moment linearly increases with the length of the conjugated system. Excited twisted retinal would therefore exhibit a fantastic dipole moment (≈ 30 – 40 debyes). Three mechanisms tend to diminish these high dipole moments.

The π polarization effect is the leading one; the positive and negative net charges tend to attract each other, and to concentrate on the edges of the rupture of conjugation, i.e., on the carbon atoms of the twisted bond. Let us schematically compare two limit descriptions of the ionic states of a (substituted) decapentene twisted around its central bond. A delocalized approach will lead to two pentadienyl moieties where the net charges are delocalized on each subsystem and centered on the



C_3 and C_8 atoms. The other limit picture is a fully localized picture where the hole and the excess electron are on two



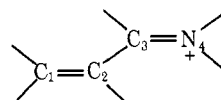
neighboring atoms. Going from a to b one loses of course the energetic benefit of delocalization of the net charges which diminishes the probability of a simultaneous presence of two electrons on the same carbon atom. (An estimate of this delocalization energy gain would be possible from the comparison of electron affinities and ionization potentials of CH_3 and C_5H_7 systems.) But one gains about 10 eV by concentrating the net charges on the rotating bonds since the $1/r$ variation of their attraction is very rapid. This electrostatic interaction of the "hole" and "particle" will be the main factor diminishing the dipole moment of these zwitterionic states.

The σ polarization effect, by a proper adjustment of the σ bonds electronic distribution to the π field, diminishes the total dipole moment and electric fields through a σ reaction field.

The electron-hole picture b is also stabilized by a proper deformation of the (C_6) negatively charged atom. The final picture, although intermediate between the a and b is certainly closer to b.

The first phenomenon will always occur in neutral conjugated molecules, even heteropolar molecules such as retinal. The only exception would concern charged molecules, if an electronic charge, already present in the ground state, may trap the supplementary charge created in the ionic excited state, and cancel out with it. In such a case the excited state is no longer zwitterionic, it represents *another charged structure*.

(2) Charge Migration in a Small Protonated Schiff Base. Let us consider the simplest conjugated protonated Schiff base, $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{N}^+\text{H}_2$, which is isoelectronic to the butadiene molecule. The fully localized picture of the ground state



implies two (polarized) π bonds $C_1=\bar{C}_2$ and $C_3=\text{N}_4$, the net charge being essentially located in the $C_3\text{N}_4$ region. An SCF

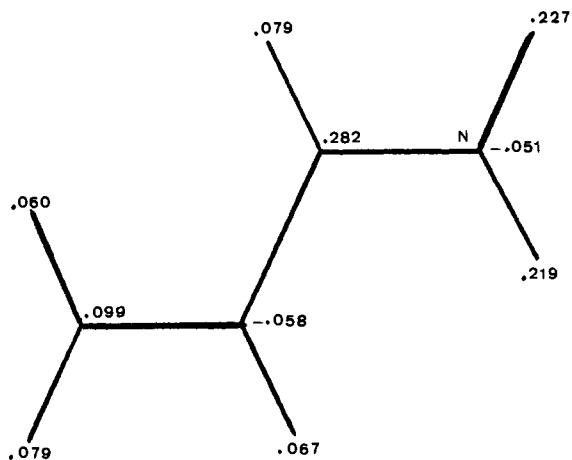
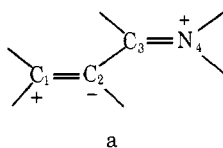


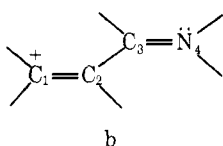
Figure 7. SCF ground state net charges of the $C_3NH_6^+$ protonated Schiff base.

calculation actually leads to the charge distribution pictured in Figure 7, where, despite an important delocalization of the positive charge, the C_3N_4 region bears $+0.75 e$.

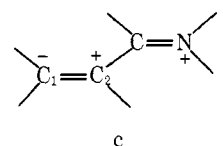
Two fully localized pictures may be invoked for the $+ -$ singlet excited state after rotation around the C_1C_2 bond. Starting from our previous conclusions, one may imagine a polarization of the C_1C_2 bond, leading to some sort of a "charged zwitterion" (a). But in the conjugated $C_2C_3N_4$ sys-



tem, the negative and positive charges may cancel and lead to a singly charged structure b. Structure b should be more likely



than structure a since it gains electrostatic energy; a $C=N$ π bond is destroyed but a $C=C$ π bond is formed and the electron pair moves from the carbon to the nitrogen atom. A reverse polarization, of the C_1C_2 bond, corresponding to the Z_2 singlet



state should be unlikely since it would concentrate two positive charges in the same region of space and the corresponding excited state should be high in energy; *the positive charge on the N^+ side removes the degeneracy between the two excited singlet states*. These qualitative statements have been confirmed through numerical calculations. Starting from the fully localized determinants built from structures a and b the SCF procedure converges toward the *same* excited state lying 4.08 eV above the ground state. The heavy atoms ($C_1 \dots N_4$) bear respectively $+0.46$, -0.36 , $+0.32$, and $-0.14 e$; this picture is intermediate between structures a and b. But the geometry relaxation favors structure b. Shortening the C_2-C_3 bond from 1.47 to 1.35 Å and lengthening the C_3-N_4 bond from 1.25 to 1.40 Å, the excited state is stabilized by 1.4 eV (leading to a very low (2.67 eV) nonvertical transition energy) and the

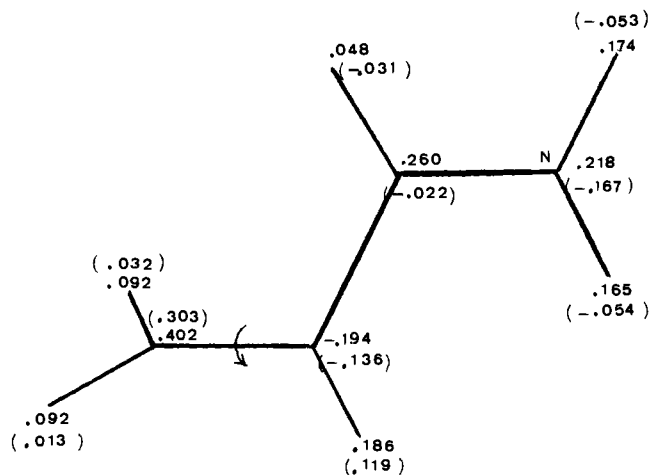
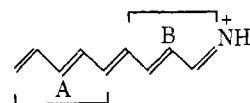


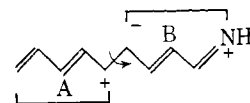
Figure 8. Twisted singlet excited state net charges of $C_3NH_6^+$ protonated Schiff base. The numbers between parentheses represent the changes in atomic populations from the ground state distribution.

positive charge (see Figure 8) tends to concentrate on the C_1H_2 group (0.6 e). The charge variations (between parentheses in Figure 8), clearly demonstrate that an overall electron transfer occurs (of about 0.47 e) from the C_1 , H_1 , H_1' , and H_2 atoms toward the previously positively charged right part of the molecule: *the singlet excited state appears as resulting from a right-left migration of the positive charge*. Moreover the twisted $- +Z_2$ excited state has been calculated, starting from c; the SCF solution was obtained lying 8.08 eV above the ground state, therefore confirming the nondegeneracy of the Z_1 and Z_2 states, and the peculiar nature of the protonated Schiff bases.

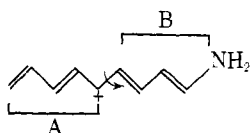
(3) **The Possibility of Charge Migration in Long Conjugated Protonated Schiff Bases.** Similar considerations hold for long conjugated Schiff bases. If the N^+ net charge is located in part B of the molecule,



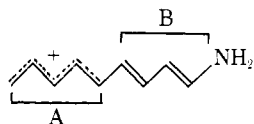
- (i) the $B \rightarrow A$ charge transfer excitation is very high in energy since it brings two positive charges in the same region of space;
- (ii) on the contrary the $A \rightarrow B$ charge transfer leads to a stable structure since the electron arrives in the positively charged B region;
- (iii) the previously proposed (section C1) picture b



is no longer likely since the negative charge may attack (and cancel) the nitrogen positive charge, leading to a neutral part B with a change in bond alternation.



Moreover since the negative net charge cancels in part B the positive charge is no longer compelled to stand on the rotating bond, and may be delocalized on the conjugated A part, leading to the very stable valence picture proposed by Salem;⁹ the A part "hole" being no longer attracted by a "particle" may



spread over its conjugated fragment without losing any electrostatic energy.

The electrostatic attraction of the "hole-particle pair" disappears if and only if one of the two subsystems already bears an electric charge, which may be canceled through the excited state charge transfer. Of course an environmental negative charge certainly exists in the N^+ region, which might prevent a neutralization of N^+ site, but the rotation around the central bond certainly moves the B part of the molecule, and the N^+ site no longer faces its negative environmental counterpart.

From these simple arguments one might understand the very specific role of the retinal protonated Schiff base. Neither the retinal nor its nonprotonated Schiff base would present such a charge displacement; in such molecules the $+ -$ couple would remain in the rotating bond region. The stability of Salem's structure also possibly explains the very low excitation energy of the molecule and the bathochromic effect of the Schiff base.

Of course the charge migration is overestimated if one imagines it as a jump of a 1.0 e charge from the nitrogen atom to the central carbon atom of the A part. Our calculations on the smallest protonated Schiff base suggest a shorter transfer of a smaller charge ($<0.5 e$). Further calculations on these large systems, allowing correct repolarization phenomena, are necessary, in order to assess the exact extent of the charge migration.

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References and Notes

- (1) (a) Università di Modena; (b) Institut de Biologie Physico-chimique; (c) Université Paul Sabatier.
- (2) (a) R. Hoffmann, *Tetrahedron*, **22**, 521 (1966); (b) N. C. Baird and R. M. West, *J. Am. Chem. Soc.*, **93**, 4427 (1971); (c) J. Langlet and J. P. Malrieu, *Theor. Chim. Acta*, **33**, 307 (1974).
- (3) (a) S. Shih, R. J. Buenker, and S. D. Peyerimhoff, *Chem. Phys. Lett.*, **16**, 244 (1972); (b) J. P. Malrieu, to be published.
- (4) R. J. Buenker and J. D. Peyerimhoff, *Chem. Phys.*, **9**, 75 (1976), and experimental references herein.
- (5) P. Bruckmann and L. Salem, *J. Am. Chem. Soc.*, **98**, 5037 (1976).
- (6) D. F. Evans, *J. Chem. Soc.*, **2**, 1735 (1960).
- (7) M. C. Bruni, F. Momicchioli, I. Baraldi, and J. Langlet, *Chem. Phys. Lett.*, **36**, 484 (1975), and references herein.
- (8) D. A. Luippold, *Chem. Phys. Lett.*, **35**, 131 (1975).
- (9) L. Salem and P. Bruckmann, *Nature (London)*, **258**, 526 (1975).
- (10) V. Bonacic-Koutecky, P. Bruckmann, P. Hliberty, J. Koutecky, C. Leforestier, and L. Salem, *Angew. Chem., Int. Ed. Engl.*, **14**, 575 (1975).
- (11) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).
- (12) R. K. Nesbet, *Rev. Mod. Phys.*, **35**, 552 (1963).
- (13) J. E. Lennard-Jones, *Proc. R. Soc. London, Ser. A.*, **198**, 1 (1949); G. G. Hall and J. E. Lennard-Jones, *ibid.*, **202**, 155 (1950); J. E. Lennard-Jones and J. A. Pople, *ibid.*, **202**, 166 (1950); for a review see P. Millie, B. Levy, and G. Berthier, "Localization and Delocalization in Quantum Chemistry", Vol. 1, O. Chalvet, R. Daudel, S. Diner, and J. P. Malrieu, Ed., D. Reidel, Dordrecht, 1975, p 59.
- (14) See, for instance, W. T. Simpson, *J. Am. Chem. Soc.*, **73**, 5363 (1951); **77**, 6164 (1955); J. N. Murrell, *J. Chem. Phys.*, **37**, 1162 (1962); H. C. Longuet-Higgins and J. N. Murrell, *Proc. R. Soc. London, Ser. A.*, **68**, 601 (1955). For a review, see J. Langlet and J. P. Malrieu, "Localization and Delocalization in Quantum Chemistry", Vol. II, O. Chalvet, R. Daudel, S. Diner, and J. P. Malrieu, Ed., D. Reidel, Dordrecht, 1976.
- (15) S. Diner, J. P. Malrieu, and P. Claverie, *Theor. Chim. Acta*, **13**, 1 (1969); J. P. Malrieu, P. Claverie, and S. Diner, *ibid.*, **13**, 18 (1969); S. Diner, J. P. Malrieu, F. Jordan, and M. Gilbert, *ibid.*, **15**, 100 (1969).
- (16) J. P. Daudey, *Chem. Phys. Lett.*, **24**, 574 (1974).
- (17) B. Huron, J. P. Malrieu, and P. Rancurel, *J. Chem. Phys.*, **58**, 5745 (1973).
- (18) J. Langlet and P. Gacouin, *Theor. Chim. Acta*, **42**, 293 (1976).
- (19) J. Langlet and P. Gacouin, *Theor. Chim. Acta*, in press.
- (20) M. C. Bruni, F. Momicchioli, and J. Langlet, to be published.
- (21) G. Del Re, *J. Chem. Soc.*, 4031 (1958).
- (22) Ph. Millie and G. Berthier, *Int. J. Quantum Chem.*, **25**, 67 (1968).
- (23) J. Langlet, J. P. Daudey, and J. P. Malrieu, *Chem. Phys. Lett.*, **45**, 481 (1977).

Nuclear Magnetic Resonance Conformational Analysis of 1,4-Dihydronaphthalenes

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Abstract: The question concerning the extent of cyclohexadiene ring puckering in 1-substituted 1,4-dihydronaphthalenes is attended to by NMR analysis of several structures including some rigid, boat-shaped model compounds. A large 1-substituent results in a highly puckered geometry (similar to 9,10-dihydroanthracene), whereas small substituents are accommodated by a less puckered (but not planar) cyclohexadiene ring. Attention is also given to the nature of the homoallylic coupling constants.

Considerable attention has been brought to bear on the conformational analysis of the cyclohexadiene ring systems 1,4-dihydrobenzene (1), 1,4-dihydronaphthalene (2), and 9,10-dihydroanthracene (3). However, despite numerous studies over several years, each of these systems became a center of controversy over some aspect of its stereochemistry.² For example, it had generally been accepted that 3 exists as

rapidly equilibrating boat conformations, but conflicting reports appeared concerning the preferred conformation of substituted derivatives (3a) with regard to pseudoaxial or pseudoaxial (shown) preference of substituents.^{3a} It was later shown by use of nuclear Overhauser enhancements and homoallylic coupling constants ($J_{9,10}$) that pseudoaxial conformations are indeed the preferred geometry.^{3b}