Theoret. Chim. Acta (Berl.) 54, 59–72 (1979)

THEORETICA CHIMICA ACTA

Further Investigations about the Zwitterionic Excited States of Twisted Conjugated Molecules

Jean-Paul Malrieu and Georges Trinquier

Laboratoire de Physique Quantique, Université Paul Sabatier, 118, route de Narbonne, F-31077 Toulouse CEDEX, France

For twisted zwitterionic excited states, the single-determinant closed-shell SCF approach favours one of the two possibly resonant structures A^+B^- or A^-B^+, but gives a very low energy by allowing π reorganization and σ polarization under the π field. This effect is very difficult to include in CI developments using neutral symmetry adapted MO's. The closed-shell SCF approach is always relevant for energy, and only fails for the wavefunction in the (near) degeneracy region between A^-B^+ and A^+B^-, where the Born–Oppenheimer approximation, anyway, breaks down. The process is applied in nonempirical (minimal + diffuse AO basis set) calculations of butadiene. The role of geometry optimization and of further electron correlation is illustrated. The extent of σ polarization is shown in ethylene, suggesting a neutral two carbene limit picture of this excited state.

Key words: Zwitterionic excited states – Butadiene

1. Introduction

After its discovery [1, 2] and the discussion of its possible chemical and biological implications [2–4], the sudden polarization phenomenon in twisted singlet excited states of linear polyenes raised much interest, but encountered some scepticism, since the calculations involved a rather poor wave function. The extent of charge separation when the dimension of the conjugated system increases was actually grossly overestimated by a too crude description [6]. Recent extended CI calculations [7–9] on twisted pyramidalized ethylene have definitely assessed that the ethylene singlet excited state potential surface does present a strongly dipolar minimum. These demonstrations have been performed using non-polar basic MO's, resulting from an HF calculation of the triplet state [8] or from a constrained zeroth

0040-5744/79/0054/0059/$02.80

order wavefunction [7]. The present paper first tries to compare two possible strategies to approach the exact wavefunction and energy, one using symmetry MO's, the other allowing polarization to occur through a closed-shell SCF calculation. A parallel is made with the well-known problem of the localization of the core hole in diatomic homonuclear molecules. In a second section non-empirical calculations on butadiene excited states are presented, involving methodological comparisons, geometry optimization effects, study of the extent of σ polarizations.

2. Theoretical Considerations; the Relevance of an SCF Closed-Shell Approach of the Zwitterionic Excited State for Important Symmetry Breaking

Most of the previous calculations on the sudden polarization effect use diradicalar neutral MO's. Our previous paper [6] demonstrated the reliability of an SCF closed-shell approach in the case of butadiene. We think that the relative validity of symmetry keeping and symmetry breaking strategies must be analyzed, trying to see at what level (SCF or CI) they introduce the physical significant events, when they are reliable for energy, when they may fail for the wavefunction.

2.1. An Analogous Situation: the Core Ionization of Homonuclear Diatomics

Zwitterionic excited states are a peculiar example of a more general class of situations which may be defined as the *result of a weak interaction between nearly degenerate strongly polarized components.* The simplest example is the core ionization of a homonuclear diatom, as discussed for instance for O_2^+ [10–14]. Using delocalized MO's for the K shell,

$$ {}^1\sigma_{g,u} = (s_a \pm s_b)/\sqrt{2}, $$

one may build zeroth order symmetry adapated wavefunctions. Starting from the ground state SCF wavefunction ϕ_0

$$ \phi_0 = |{}^1\sigma_g {}^1\overline{\sigma_g} {}^1\sigma_u {}^1\overline{\sigma_u} \times \text{valence}| = |s_a \overline{s_a} s_b \overline{s_b} \times \text{valence}|, $$

the ionic single determinants are, in second quantization formalism,

$$ \phi_g^+ = a_g \phi_0 \qquad \phi_u^+ = a_u \phi_0 $$

and one may try to optimize the valence MO's in $\phi_{g,u}^+$ in order to fit the new core field created in the absence of a core electron, spread on both nuclei. As noticed first by Snyder [10], the energy lowering obtained through such a variational procedure leading to SCF $\phi'_{g,u}$ determinants, remains weak, since

1) the field modification created by the hole is symmetrical and prevents any left-right migration.

2) the valence electric clouds on each atom feel an electric field created by a half charge on each nucleus, and the spatial contraction of the valence shell remains one half of the corresponding effect in the atom (its energetic benefit also remains one half of the atomic effect).

As a result the ΔSCF ionization potential obtained by the optimization of $\phi_{g,u}^{+}$ remains much higher than in the atom, in contradiction with experiment [14]

$$\langle \phi_g'^{+} | H | \phi_g'^{+} \rangle - \langle \phi_0 | H | \phi_0 \rangle \simeq \langle \phi_u'^{+} | H | \phi_u'^{+} \rangle - \langle \phi_0 | H | \phi_0 \rangle$$
$$\gg \text{Exptl. ionization potential.}$$

By loosing the symmetry of the wave function, one may consider locally ionized determinants

$$\phi_a^{+} = a_{s_a} \phi_0 ; \qquad \phi_b^{+} = a_{s_b} \phi_0 .$$

A variational SCF procedure applied to $\phi_{a,b}^{+}$ leads to symmetry broken degenerate SCF determinants $(\phi_{a,b}'^{+})$. The process brings in a lot of energy since

1) the σ and π bond MO's polarize their distribution to bring electrons to the ionized atom (this effect is obtained in a minimal basis set),

2) the valence cloud of the ionized atom is contracted to the same extent as in the isolated atom (if non-minimal basis sets are used), and the calculated *IP*'s are now of the right order of magnitude

$$\langle \phi_a'^{+} | H | \phi_a'^{+} \rangle - \langle \phi_0 | H | \phi_0 \rangle = \langle \phi_b'^{+} | H | \phi_b'^{+} \rangle - \langle \phi_0 | H | \phi_0 \rangle \simeq \text{exptl } IP.$$

The optimized symmetry breaking determinants have not the correct symmetry properties, but the correct energy. They are degenerate and the small splitting between the exact nearly degenerate levels is neglected. A better approximation would be given by combining $\phi_a'^{+}$ and $\phi_b'^{+}$, which are no longer orthogonal,

$$\psi_{g,u} = \mathcal{N} (\phi_a'^{+} \pm \phi_b'^{+}).$$

Such a wavefunction introduces the most important physical effects, since at each moment the hole is *either* on the left *or* the right atom (the frequency of migration being small since $\langle s_a | F | s_b \rangle$ is small) and the valence distribution follows the strong electric field. The final interaction between the locally ionized determinants is small with respect to the local polarization of the valence shell

$$|\langle \psi_g | H | \psi_g \rangle - \langle \psi_u | H | \psi_u \rangle (\simeq 2 \langle s_a | F | s_b \rangle)| \ll |\langle \phi_{a,b}'^{+} | H | \phi_{a,b}'^{+} \rangle - \langle \phi_{g,u}'^{+} | H | \phi_{g,u}'^{+} \rangle|$$

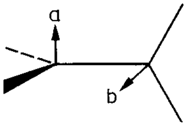
The resonance in the ionized (excited) shell is smaller than the polarization of the other shells, and the later effect is immediately obtained through a symmetry breaking description.

Of course one may reach the exact solution without leaving symmetry; then what was called "polarization energy" becomes "correlation corrections" obtained besides the SCF level, through double substitutions, as shown by us [12] and re-demonstrated a few years after by Cederbaum [13]. As in many cases of Hartree–Fock instability, symmetry breaking introduces at the single determinant level a large amount of the canonical correlation energy [20]. Among all the relevant Hartree–Fock instabilities, the present type concerns the departure from the *spatial* symmetry [21]. It is frequent that the symmetry non-adapted solutions are more localized [22] than the symmetrical one.

2.2. Zwitterionic Excited States; Performance of the SCF *Closed-Shell Approach for Exact Degeneracy between* A^-B^+ *and* A^+B^-

The situation in zwitterionic excited states is rather similar, except that the hole is now replaced by a strong dipole. The two basic local events are A^+B^- and A^-B^+

$$\phi^{+-} = |b\bar{b} \times \Sigma|, \qquad \phi^{-+} = |a\bar{a} \times \Sigma|.$$



If symmetry is maintained ϕ^{+-} and ϕ^{-+} are degenerate and the two determinant symmetry adapted zeroth-order descriptions are

$$\phi_{Z,V} = |(a\bar{a} \pm b\bar{b}) \times \Sigma|/\sqrt{2} = (\phi^{+-} \pm \phi^{-+})/\sqrt{2}.$$

At this level, the splitting between the Z and V states is a weak exchange integral,

$$\langle\phi_Z|H|\phi_Z\rangle - \langle\phi_V|H|\phi_V\rangle = 2K_{ab}.$$

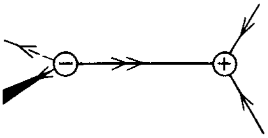
Since the π distribution is symmetrical, the Σ distribution cannot be improved much by a variational 2 configurations procedure, leading from ϕ_Z and ϕ'_Z,

$$\langle\phi'_Z|H|\phi'_Z\rangle - \langle\phi_Z|H|\phi_Z\rangle$$

is small and the main corrections will be given by CI.

A large part of the CI correction may be obtained easily by a symmetry breaking SCF procedure, since in ϕ^{+-} for instance, the Σ distribution feels the strong field of the π dipole. The minimization of $\langle\phi'^{+-}|H|\phi'^{+-}\rangle$ through a closed-shell SCF variation will polarize the Σ MO's of the adjacent bonds, especially the C^+—C^- bond. The polarization energy is large

$$\langle\phi'^{+-}|H|\phi'^{+-}\rangle - \langle\phi'_Z|H|\phi'_Z\rangle \ll \langle\phi'_Z|H|\phi'_Z\rangle - \langle\phi_Z|H|\phi_Z\rangle$$



A further CI treatment is possible from ϕ'^{+-} to introduce correlation effects and approach the final exact energy. Of course an SCF treatment is also possible for ϕ^{-+}, giving a degenerate determinant ϕ'^{-+}, but its SCF MO's have polarities opposite to those of ϕ'^{+-} and the two sets are not orthogonal. An excellent two-determinant symmetry adapted wavefunction would be given by

$$\Phi'_{Z,V} = \mathcal{N}_{Z,V}(\phi'^{+-} \pm \phi'^{-+})$$

but the non-orthogonality problem makes the calculation of its energy complex. It is not easy to determine to which of the two exact solutions ψ_Z or ψ_V, the CI development from ϕ'^{+-} in its own basis set of MO's would lead, if treated for instance in a Møller–Plesset Rayleigh–Schrödinger perturbation [15]. There is no reason that such a development would not converge, at least for the energy, since in the MO basis of ϕ'^{+-} no (near) degeneracy occurs. But the convergence of the wavefunction is dubious; since ϕ'^{-+} is only a linear combination of doubly, triply, ... excited determinants in the ϕ'^{+-} MO basis set, the symmetry of the wavefunction can only be restored by inclusion of highly excited (i.e. high order) corrections.

The symmetry breaking SCF wavefunction, if decomposed in the basis of determinants built from the set of non-polar MO's, necessarily includes n times excited determinants with respect to the reference determinants, if n is the number of σ bonds (5 in the present work), since it allows simultaneous consistent polarizations of the various bonds. On the contrary the doubly excited determinants from non-polar MO's allow simultaneous polarizations of two bonds only.

Therefore, one finds two possible strategies:

1) if one keeps symmetry all along the treatment, the two-determinant approximation $\phi'_{Z,V}$ is very poor and the CI effort to reach a reasonable energy is very expensive, since one has to go to very high levels of excitation to introduce in a consistent way the simultaneous polarizations of the different σ bonds required to fit the σ cloud to the instantaneous π dipole. It is therefore unlikely that double excitations CI from a two-determinant wavefunction may bring a "definitive" answer to the excited state problem of the twisted double bond [7]. This approximation must be regarded as of intermediate quality.

2) if one leaves symmetry from the very beginning in an SCF closed shell treatment, the exact solution for the energy is rapidly approached with much less effort; a further doubly excited CI may be considered as sufficient. But it seems quite impossible to restore the symmetry of the wavefunction and perhaps to reach the splitting between the Z and V nearly degenerate levels.

The situation is summarized in Fig. 1. As in the case of the core hole ionization, it results from the smallness of the resonance between the elementary components of the excited (π) shell with respect to the polarization energy of the other (σ) shell.

2.3. Departure from Symmetry

These conclusions are valid when the total Hamiltonian remains symmetrical. One may notice that in such a case the Z and V states remain nearly degenerate. In the potential energy surfaces these near-degeneracy regions must be considered with some criticism since the Born–Oppenheimer approximation is certainly no longer valid there.

As soon as a significant perturbation breaks symmetry, ϕ^{+-} and ϕ^{-+} are no longer equivalent, they are not degenerate, and if

$$|\langle\phi^{-+}|H|\phi^{-+}\rangle - \langle\phi^{+-}|H|\phi^{+-}\rangle| \gg 2|\langle\phi^{-+}|H|\phi^{+-}\rangle|$$

the ϕ^{-+} single determinant is a good starting point for a closed-shell SCF procedure and a standard CI development. In such a case the previously noticed difficulty

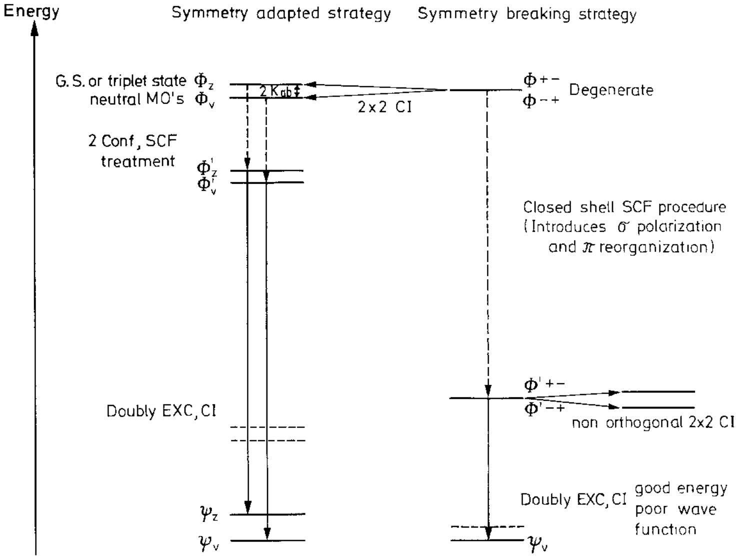


Fig. 1. Comparison of the two possible strategies, with respect to the energy, for a case of degeneracy between ϕ^{+-} and ϕ^{-+}. The dotted arrows are SCF procedures, the full ones represent CI processes

concerning the wavefunction no longer holds, since the exact solutions actually are non-symmetrical. If the symmetry breaking perturbation is large enough, the SCF single determinants ϕ'^{+-} or ϕ'^{-+} may be regarded as good approximations of the final wavefunctions, and the dipole moment calculated from this single-determinant approximation may be reliable. The standard procedure for ground states (closed-shell SCF + (double) CI) may therefore give excellent results for both the energy and the monoelectronic observables as soon as the departure from symmetry is sufficient. It fails for the wavefunction and dipole moment when symmetry is restored, i.e. in a region where the Born–Oppenheimer approximation fails. In that region, the research of the exact solutions of the electronic Hamiltonian is a somewhat academic exercise, anyway.

The symmetry adapted strategy using non-polar MO's is very expensive, as noticed previously, but it allows to go continuously from perfect symmetry to important symmetry breaking. If high degrees of excitation are not introduced, the final polarization for unsymmetrical situations should be *underestimated.* This remark should be verified through further calculations, but if it is true, it makes even more convincing the conclusions of Refs. [7] and [8] concerning the occurrence of an important dipole in pyramidalized twisted excited ethylene, since their calculated pyramidalization angle and dipole should be underestimated, due to the constraints of their wave functions (Double CI). On the contrary, if the Hamiltonian departs enough from symmetry, the classical closed-shell SCF + (D) CI procedure, which is much less expensive, will give a good approach for the potential surface. One must simply remember that the calculated dipole moment would not tend to zero

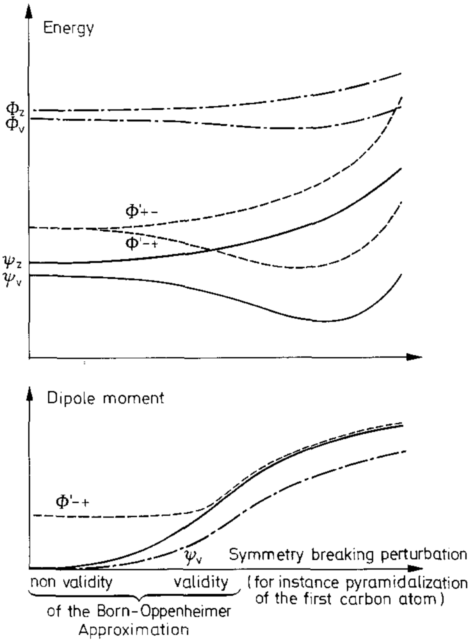


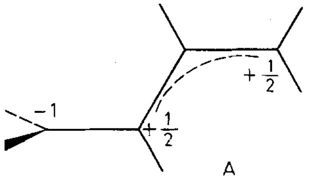
Fig. 2. Qualitative situation of various approximations for the perturbed twisted excited state of ethylene: ——— exact solution; —·—·— two determinants symmetry adapted SCF description; - - - - - SCF closed shell symmetry breaking description

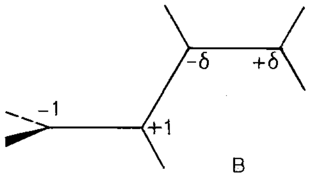
when the symmetry breaking perturbation decreases and is likely to be overestimated (see Fig. 2).

The whole discussion was implicitly centred on the case of ethylene (the π system reduces to one double bond). It has been shown elsewhere [6] that in larger π systems the SCF closed-shell procedure also allows an important π reorganization to take place. This π reorganization, which essentially brings the two + and − π charges on the atoms of the rotated bond, acts as the σ polarization to favour the SCF closed-shell approach. The adjacent π bonds behave, like the σ bonds, as a polarizable environment.

3. Butadiene Zwitterionic Excited States Revisited

Twisted butadiene excited states have been explored by Bruckmann and Salem [2] in a minimal basis set, performing a 3 × 3 CI using the open-shell non-polar MO's. Bruni *et al.* [6] showed from analytic considerations that such a wavefunction is poor since it 1) delocalizes too much the π charges exaggerating the charge separation and therefore their contribution to the dipole moment, 2) does not introduce the σ polarization which follows the π polar distribution to screen it, diminishing the dipole moment. This demonstration was numerically illustrated through various CNDO calculations. The relevance of a closed-shell description (even for the wave function) is easy to demonstrate, taking benefit of the plane of symmetry which keeps the orthogonality between the diradicalar (A'') and ionic (A') states. This relevance is due to the non-degeneracy between the methylene$^+$ allyl$^-$ ($M^+ A^-$) and methylene$^-$ allyl$^+$ ($M^- A^+$) states. This energy difference is already important for non-pyramidal structures (planar carbon atoms) but it is increased by geometry optimizations, which follow opposite directions for each states. The π charge distribution A induced by the openshell non-polar MO's without sufficient CI is much less correct than description B in which the + and − charges are localized on the rotated bond,





polarizing the π vicinal bond and the σ cores.

The present section reports new non-empirical calculations. The basis set is a minimal basis set augmented by a set of rather diffuse ($\zeta = 0.08$) p functions on each carbon atom. These diffuse AO's are known to be important in the representation of ionic states, especially for the two-electrons cloud of the negative centre, as demonstrated by all the recent works on the ethylene $\pi\pi^*$ singlet excited state [16].

Bond lengths have been optimized at the SCF closed-shell level for the lowest energy (M^-A^+) state; the pyramidalization of the negative carbon atom was included in the geometry optimization. Additional CI calculations have been performed with the CIPSI algorithm [17].

3.1. Methodological Comparison for Energy

The energetic superiority of a closed-shell calculation over a 3 × 3 CI from delocalized non-polar open-shell MO's [2] is evident when comparing their respective predictions for the same geometry. The planar equilibrium geometry ground state energy being taken as reference zero energy, the SCF closed-shell procedure lowers the M^-A^+ energy from 150.5 kcal/mole in the 3 × 3 CI value to 106.8 kcal/mole; the π and σ polarizations diminish the energy by 44 kcal/mole. For ethylene similar calculations led to a similar but somewhat smaller effect, 159.2 kcal/mole at the 3 × 3 CI level, 121.8 kcal/mole after the SCF closed-shell procedure i.e. a 37 kcal/mole lowering. In butadiene the polarizable environment involves more bonds, especially a π bond, and it is normal that the variation of the MO's leads to a larger energy lowering.

3.2. M^+A^- with Respect to M^-A^+

For the same G.S. twisted geometry (before geometry relaxation in the excited state), the M^-A^+ state is lower than M^+A^- by 14.8 kcal/mole (118.9 for M^-A^+, 133.7 kcal/mole for M^+A^-). This is a sufficient energy difference to assume that geometry relaxations cannot reverse this ordering and the geometry optimization has been performed on M^-A^+ only. Our result is in agreement with Salem's conclusions [2] while CNDO calculations give unstable (and more often opposite) results [6].

3.2. Geometry Optimization

The best pyramidalization angle[1] is $\varphi = 23.7°$ (i.e. $\widehat{HCH} = 104.9°$) which is close to Berthier's value ($\varphi = 24°$) for ethylene but much larger than Brooks and Schaefer's value. Our angle is larger than for sp^3 hybridization ($\widehat{HCH} = 109.47°$, $\varphi = 19.47°$). Pyramidalization is preferably "*trans*" with respect to the allylic system (by 2 kcal/mole) as in Bruckmann and Salem's calculations [2].

As concern bond lengths variations, our conclusions are quite different from those of Ref. [2] (see Fig. 3). Our C_1^-—C_2^+ bond lengthens by 0.13 Å, despite the strong electrostatic attraction between the positive and negative charges. This is larger than the 0.075 Å CC bond lengthening obtained by Brooks and Schaefer [7] on ethylene. To interpret this difference one may remember that 1) our wavefunction certainly introduces more σ screening as demonstrated earlier, 2) our basis set involving diffuse orbitals repels the centroïd of gravity of the negative charge "lone pair"; both effects diminish the electrostatic interaction. On the contrary the central bond shortens (by 0.022 Å) and the non-rotated double bond slightly lengthens by being polarized (through participation of the π^* MO and weakening of the π bond order).

In Bruckmann and Salem's calculation [2], the twisted bond was only slightly lengthened ($l(C_1^-$—$C_2^+) = 1.39$ Å) while the non-rotated double bond was extremely short ($l(C_3$=$C_4) = 1.31$ Å!). One may think that these effects were due to the constraints in the wavefunction which does not allow the positive charge to concentrate on the C_2 carbon atom in front of its negative C_1 partner and the only way to increase electrostatic energy is to shorten bonds (the twisted C_1—C_2 bond

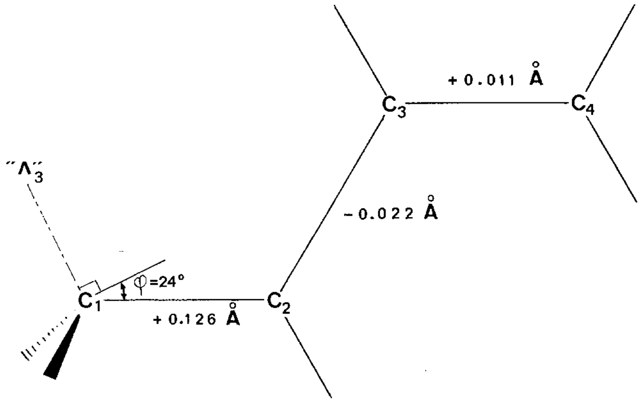


Fig. 3. C—C bond length changes from the ground state conformation. In Ref. [2] the C_1C_2 bond lengthens ($l = 1.39$ Å; $\Delta \simeq +0.05$ Å), the C_3—C_4 bond shortens ($l = 1.31$ Å; $\Delta \simeq -0.03$ Å)

---

[1] As in Ref. [9], φ is defined by $\cos \widehat{HCH} = (3 \sin^2 \varphi - 1)/2$; hence $\varphi = 19.47°$ for a tetrahedral carbon. See Fig. 3.

Table 1. SCF and CI energies (in kcal/mole) of the ground (N), first triplet (T) and zwitterionic excited singlet (V) states; the planar ground state energy (E_0) is taken as reference energy

	Twisted ground state geometry			Optimized V state geometry		
	N	T	V	N	T	V
SCF	63.0	61.6	118.9	65.2	63.4	106.8
IC[a]	63.3	66.2		65.4	66.3	118.4

[a] E_0 (CI) lies 220.7 kcal/mole below E_0 (SCF).

is much longer for the neutral diradical N and T states than Salem's 1.39 Å value (cf. Brooks and Schaefer: 1.49 Å)). The absence of screening makes this bond-shortening phenomenon even more pronounced. This is a good example of the possible qualitative influence of the poorness of the wavefunction on the calculated properties.

Geometry optimization lowers the energy by 12 kcal/mole in butadiene from its value in the twisted ground state geometry (118.9 kcal/mole) at the same closed-shell SCF level (see Table 1). (For ethylene the energy lowering was −10.4 kcal/mole.)

3.4. Correlation Effects

Correlation effects have been calculated for the SCF closed-shell optimized geometry. All doubly excited determinants have been generated from Φ^{-+} and treated through a 2nd order Epstein–Nesbet [18] Rayleigh–Schrödinger perturbation. The relevance of perturbation appears from the size of the first-order perturbed wavefunction coefficients, the largest of which is about 0.05. One may notice that when perturbation is started from the 3 × 3 CI eigenvector using non-polar MO's, the largest coefficient is 0.30 (corresponding to a $\pi\pi^*$ excitation, relocalizing the hole on the C_2 atom); in such a case the CI development could not be treated as a perturbation due to the bad quality of the zeroth-order approximation.

Correlation effects increase the energy difference with respect to the planar ground state in its equilibrium geometry when it is treated in a consistent manner (see Table 1). Correlation energy is 14 kcal/mole less in the zwitterionic excited state (this number may be overestimated by the smallness of our basis set, which does not allow a good correlation of the two electrons of the C^- "lone pair"; to correlate them, concentrated $3d$ AO's are necessary). The potential hole of butadiene singlet excited state surface is now 118 kcal/mole above the ground state potential hole. In ethylene the corresponding quantity (adiabatic transition energy) is found to be 136.3 kcal/mole in good agreement with Brooks and Schaefer's values (133.7 kcal/mole).

Our methodological qualitative analysis pleads in favour of the localized $\overset{-}{\bullet}—\overset{+}{\bullet}—\bullet=\bullet$ structure, but one sees from the preceding energy values that the polarization of the adjacent bond (and therefore a slight delocalization of the hole) lowers the adiabatic transition energy from ethylene to butadiene by 18 kcal/mole. The dipole is strongly localized in the twisted singlet excited state but the adiabatic transition energy is lowered when going from ethylene to butadiene, and certainly from butadiene to hexatriene for its central bond rotation. For larger molecules the adiabatic transition energies should rapidly stabilize.

3.5. Validity of the Born–Oppenheimer Approximation in the Region of the Excited State Potential Hole

It was noticed that for the non-relaxed geometry a 15 kcal/mole energy gap splits the M^+A^- and M^-A^+ levels. This difference necessarily increases when one goes to the best geometry for the M^-A^+ state, which is of course unfavourable for the M^+A^- state. But these deformations also increase the ground state N or lowest $\pi\pi^*$ triplet state T of A'' symmetry and one must be sure that they remain below and sufficiently far from the M^-A^+ potential hole in order to warrant the validity of the Born–Oppenheimer approximation in this region. A variational SCF open-shell calculation was performed for ${}^1\phi_0(A'')$ and ${}^3\phi(A'')$, they remain respectively at 65.2 and 63.4 kcal/mole above the ground state, i.e. about 43 kcal/mole below the SCF closed-shell M^-A^+ level (see Table 1). A CI was further performed at the second-order perturbation level from these two-determinant wavefunctions. Correlation only raises their energy with respect to the zwitterionic excited state by a few kcal/mol (the singlet is 65.4 kcal/mole and the triplet 66.3 kcal/mole above the correlated ground state) and the potential surface of M^-A^+ is therefore far enough from the other surfaces in the region of its minimum to consider the Born–Oppenheimer approximation as valid.

3.6. Charge Repartition and Dipole Moment

After pyramidalization it is difficult to separate "σ" and "π" distributions of the C_1 atom. Figure 4 therefore only reproduces the overall net charges given by Mulliken's analysis at the SCF level together with the dipole moments for the M^-A^+ excited state in the twisted G.S. geometry and in its optimized geometry. Bruckmann and Salem's values [2] are given for comparison as well as SCF CNDO distribution [6]. One sees that the 3×3 CI from open shell MO's actually overestimates the positive charge delocalization and therefore the overall $+-$ charge separation; this approximation also greatly overestimates the total atomic charges by lack of the σ polarization effects. In contrast, the CNDO values calculated with the same technique [6] have a correct order of magnitude. Geometry optimization increases the dipole moment by the $C_1—C_2$ lengthening and by authorizing the negative charge to take a longitudinal component along the $C_1—C_2$ axis. The validity of the SCF closed-shell approximation has been demonstrated by Berthier *et al.* [9] for the pyramidalized geometry of twisted ethylene. For that molecule in the relaxed geometry we find a 5.35 Debye dipole moment. Our value is larger than

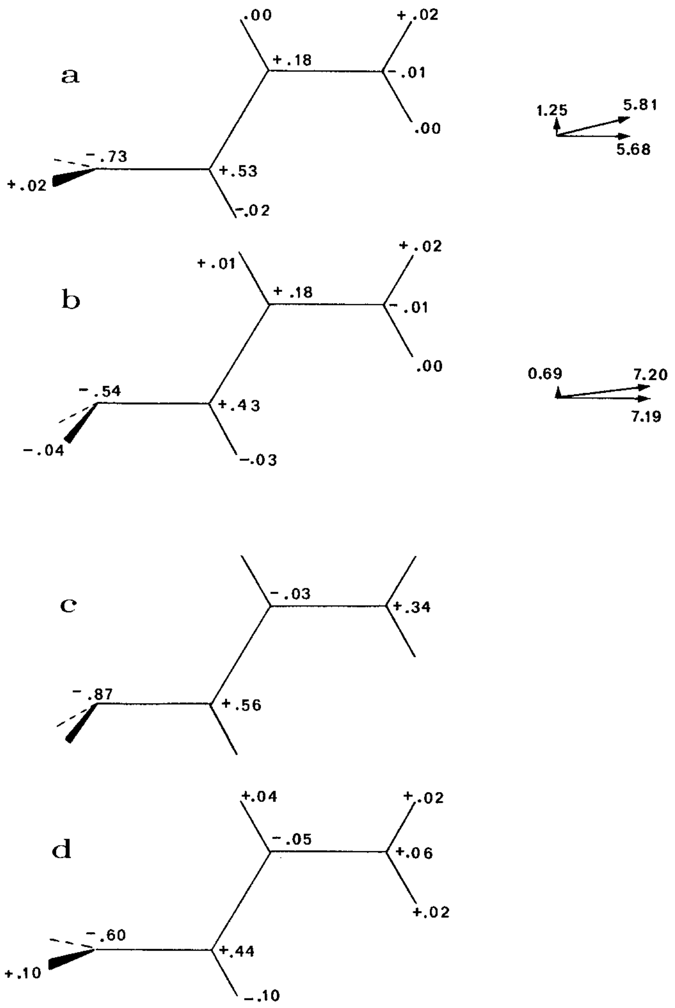


Fig. 4. Net atomic charges of the zwitterionic singlet excited state: (a) twisted ground state geometry; (b) after geometry optimization; (c) Ref. [2] (ponderated charges); (d) Ref. [6] (CNDO). Dipole moments in Debyes

values calculated by Berthier *et al.* or Brooks *et al.* (3.9 and 4.09 Debyes). This may be due to our larger C—C bond length (Ref. [9] keeps the ground state C—C distance) and to the use of diffuse AO's which puts further the centre of the carbanion lone pair.

As an illustration of the extent of σ bond polarization a detailed population analysis is given (Fig. 5) for twisted pyramidalized ethylene closed-shell SCF wavefunction. The comparison of the s and p_x population shows the extent of the C—C σ polarization. By the way, one may notice that if the C—C σ bond was fully polarized on the planar "positive" carbon atom, the molecule would no longer be polar. After a strong pyramidalization of the "negative" centre, the twisted excited

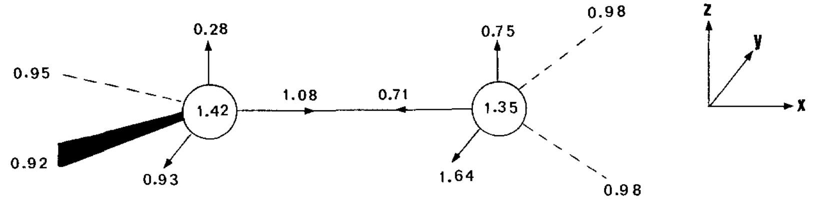
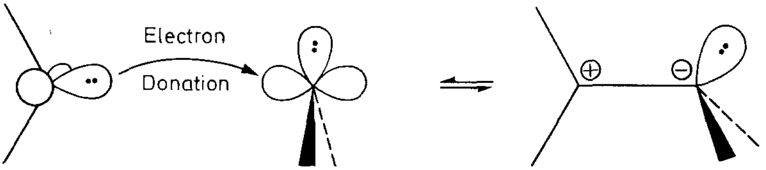


Fig. 5. Population analysis for twisted pyramidalized ethylene (SCF closed shell)

state of ethylene might be viewed as the interaction of two singlet carbenes; one of them – the "positive" planar carbon – delocalizing axially its σ lone pair into the $2p_z$ vacant MO of its partner, while the second "negative" pyramidal carbene cannot delocalize its lone pair, except through hyperconjugation with the CH bonds of its partner.



The possible barrierless addition of two singlet methylenes to give excited twisted zwitterionic ethylene is under study [19]. Anyway this extrapolation of the equilibrium geometry charge distribution shows that σ polarization may dramatically change the picture obtained from π only considerations and introduce qualitatively different views of the excited state. The whole study illustrates the high plasticity of these "ionic" excited states.

References

1. Bonacic-Koutecky, V., Bruckmann, P., Hiberty, P., Koutecký, J., Leforestier, C., Salem, L.: Angew. Chem. **87**, 599 (1975); Angew. Chem. Intern. Ed. Engl. **14**, 575 (1975)
2. Bruckmann, P., Salem, L.: J. Am. Chem. Soc. **98**, 5037 (1976)
3. Salem, L., Bruckmann, P.: Nature (London) **258**, 526 (1975)
4. Bonacic-Koutecky, V.: J. Am. Chem. Soc. **100**, 396 (1978)
5. Trinquier, G., Paillous, N., Lattes, A., Malrieu, J. P.: Nouv. J. Chimie **1**, 403 (1977)
6. Bruni, M. C., Daudey, J. P., Langlet, J., Malrieu, J. P., Momicchioli, F.: J. Am. Chem. Soc. **99**, 3587 (1977)
7. Brooks, B. R., Schaefer III, H. F.: J. Am. Chem. Soc. **101**, 307 (1979)
8. Bonačić-Koutecký, V., Buenker, R., Peyerimhoff, S.: J. Am. Chem. Soc., in press
9. Berthier, G., Levy, B., Praud, L.: Gazzetta Chim. Ital. **108**, 377 (1978), and further unpublished calculations
10. Snyder, L. C.: J. Chem. Phys. **55**, 95 (1971)
11. Bagus, P. S., Schaeffer III, H. F.: J. Chem. Phys. **56**, 224 (1972)
12. Denis, A., Langlet, J. Malrieu, J. P.: Theoret. Chim. Acta (Berl.) **38**, 49 (1975)
13. Cederbaum, L. S., Domcke, W.: J. Chem. Phys. **66**, 5084 (1977)
14. Dixon, R. N., Hull, S. E.: Chem. Phys. Letters **3**, 367 (1969)
15. Moller, C., Plesset, M. S.: Phys. Rev. **46**, 618 (1934)

16. Murchie, L. E., Davidson, E. R.: J. Chem. Phys. **66**, 2959 (1977); Buenker, R. J., Shih, S. K., Peyerimhoff, S. D.: Chem. Phys. **36**, 97 (1979) and Refs. herein
17. Huron, B., Malrieu, J. P., Rancurel, P.: J. Chem. Phys. **58**, 5745 (1973)
18. Claverie, P., Diner, S., Malrieu, J. P.: Intern. J. Quantum Chem. **1**, 151 (1967)
19. Trinquier, G., Malrieu, J. P.: to be published
20. Adams, W. H.: Phys. Rev. **127**, 1650 (1962); Hibbert, A., Coulson, C. A.: J. Phys. B **2**, 458 (1969); Löwdin, P. O.: Rev. Mod. Phys. **35**, 496 (1963), Advan. Chem. Phys. **14**, 283 (1969)
21. Čížek, J., Paldus, J.: J. Chem. Phys. **47**, 3976 (1967), **53**, 821 (1970); Paldus, J., Čížek, J.: J. Chem. Phys. **52**, 2919 (1970); Fukutome, H.: Progr. Theoret. Phys. (Kyoto) **90**, 998, 1227 (1968); Harris, R. A., Falicov, L. M.: J. Chem. Phys. **50**, 4590 (1969), **51**, 5034 (1969); Paldus, J., Čížek, J.: J. Chem. Phys. **53**, 1619 (1970); Prat, R. F.: Phys. Rev. A **6**, 1735 (1972); Toyota, A., Tanaka, I., Nakajima, T.: Intern. J. Quantum Chem. **10**, 917 (1976)
22. Prat, R. F., in: Localization and delocalization in quantum chemistry, Vol. I, p. 131. Chalvet, O., Daudel, R., Diner, S., Malrieu, J. P., Eds. Dordrecht, Holland: Reidel 1975

Received July 5, 1979