Non-orthonormal CI for molecular excited states. II. The zwitterionic states of terminally twisted butadiene

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The proper and accurate description of excited states is often very sensitive to the function space which is used to describe them. This suggests the application of a theoretical approach which is state specific. In cases of valence-Rydberg mixings, of charge localization, or of various transition processes, such an application results in nonorthonormal basis sets describing different parts of the system. The present molecular NONCI method has been applied to the determination of the interaction in the low-lying zwitterionic states of terminally twisted butadiene, as a function of pyramidalization at the twisted-bond carbon atom. The results of the NONCI calculations give negligible mixing between the two states and as a result, they are in agreement with large, orthogonal basis MRD-CI calculations, for the relative ordering of these states and their dipole moment.

I. INTRODUCTION

The existence of polar minima in the singlet excited states of twisted linear polyenes has been well established.[1–6] These minima occur as a consequence of the sudden rise in the polarity of the zwitterionic states with a geometrical change in the molecule, an effect which is often confined to a small region of the space of nuclear geometries and for this reason it has been named "the sudden polarization effect".[2] In paper I,[7] a recently developed nonorthonormal configuration interaction (NONCI) method was applied successfully to the sudden polarization in the zwitterionic states of twisted ethylene, accompanying a bending of one of the CH_2 groups. The two zwitterionic states, Z and V in ethylene,[8] are given mainly by the plus and the minus combination of two configurations of type a^2 and b^2, corresponding to the two oppositely polarized structures I and II below (with R = H for ethylene), where in each structure the two electrons of the broken π bond are localized on one (C_1 for I C_2 for II) of the two carbon atoms involved.[8] Use of

(1)

$$\text{I} \qquad\qquad \text{II}$$
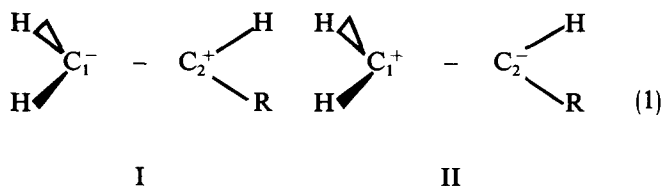
a single set of one-electron function a^2 or b^2 for these states leads to problems for the D_{2d} geometry (i.e., 0° bending angle) with large dipole moments calculated though none can exist by symmetry.[5,7,8] Nonpolar basis sets, such as the MO of the triplet (ab) configuration[4,9] or sets otherwise constrained to give equal weights to the two configurations,[8] may lead to reasonable results for the D_{2d} geometry but are less adequate for the bent geometries, with a tendency to underestimate the existing polarization.[5,7]

In the full CI limit, the above problems do not exist. However, such a solution is not feasible for systems of rea-

sonable size. Furthermore, the real understanding of excited atomic and molecular states is probably more dependent upon notions which are based on a physically motivated and tractable computational approach.

The description of excited states and related phenomena is improved drastically if $state$-$specific$ wave functions are obtained at the zeroth order as well as at the correlation level.[10–12] In the present case of polyenes, this implies that the wave functions described by the configurations a^2 and b^2 should be built from two basis sets which are not orthonormal between them. The correct mixing of these two wave functions then requires the application of NONCI.

NONCI calculations on ethylene gave the correct symmetry for the D_{2d} structure, i.e., zero dipole moment, while predicting the rapid increase in the dipole moment upon pyramidalization of one of the CH_2 units.[7]

In this work, NONCI calculations are carried out on the zwitterionic states of terminally twisted butadiene. In this case there is dissymmetry between the two carbon atoms C_1 and C_2 and, consequently, the two states Z_1 abnd Z_2 already possess a large dipole moment in the 90° twisted conformation.[3,5,13] Although this polarization occurred gradually, as a function of the twist angle, it is still of interest to calculate the interaction of these two states correctly, as we shall see in the next section.

II. THE BUTADIENE ZWITTERIONIC STATES

Bruckmann and Salem[3] have studied the 90° twisted butadiene molecule using a 3 × 3 CI and the singlet diradical $(a\,b)$ type MO, with the object of determining the polarity of the lowest ionic state (Z_1) and whether it is altered by geometry optimization. They found that the favored polarization depended on the choice of AO basis set used, with the results of a minimal basis calculation being reversed by calculations using larger basis sets.[3] Their geometry optimization gave the result that while structure I was favored for pyramidal

C_1 (with a minimum at 26° pyramidalization), structure II was more stable than I when C_2 was allowed to pyramidalize, with the "halfway" structure with both C_1 and C_2 planar being at a maximum between the two minima I and II, but also favoring structure I. The photochemical implications of such a double-well potential are important and the findings of Ref. 3 have stimulated further work involving such geometry optimizations, on other systems[6] as well as on butadiene.[5] Malrieu and Trinquier,[5] using the closed shell polar MO for each state, found a large energy difference between I and II at the halfway geometry, and concluded that the energetic ordering of the structures could not be reversed by geometry optimization. It should be noted that, while the ethylene molecule is within the capabilities of conventional computational chemistry even with modest computer facilities, the butadiene molecule poses to theorists the additional problem of large size and the consequent dependence of the conclusions on the extent of computation.[3,5,13,14] Large scale, state of the art MRD-CI calculations were found necessary in order to obtain reliable qualitative information on the low-lying excited states of butadiene in the recent work by Bonacic-Koutecky *et al.*,[13] where the MO of the triplet were used as the one electron basis. It should also be noted that in the above work,[13] at 90° twist the lowest excited state was found to be ionic, with the negative end of the dipole at the methylenic carbon (cf. structure I), in agreement with previous work.[3,5] In contrast with the earlier work, the reported results of Ref. 13 for pyramidalization at C_1, following a 90° twist, show no minimum for the Z_1 state with the lowest energy computed at 60° pyramidalization, the largest such angle used (see Table II in Ref. 13). In this work, we did not carry out geometry optimizations. Instead, we dealt with the interaction of the two zwitterionic states, each expressed in the MO optimum for that state using the NONCI method. In particular, it is interesting to check whether the mixing of the two states supports the result of Bruckman and Salem[3] that the geometry with planar both C_1 and C_2, is at the avoided crossing of the curves for the two zwitterionic states.

III. REVIEW OF THE PRESENT NONORTHONORMAL CONFIGURATION–INTERACTION (NONCI) METHOD

Nonorthonormal CI methods for molecules have been applied before for ground states (valence-bond[15] or MOCI[16] methods) or for symmetry breaking problems.[17]

As discussed in Ref. 7, the present molecular NONCI method has been developed as a necessary tool for the theoretical treatment of molecular excited states in the context of a state-specific theory. The emphasis of this approach is on the appropriate choice and optimization of the occupied and virtual function space for each state of interest. A large numer of atomic excited state properties have been treated successfully,[10–12,18] as well as molecular electron correlation in the ground state.[19] The overall computation is physically transparent and economical—provided that, when necessary in cases of off-diagonal matrix elements of the Hamiltonian or other perturbing operators, nonorthonormality effects are explicitly accounted for.

For closely lying states as the ones examined here,

NONCI can be implemented at the two-state level, where each state specific wave function is expressed in terms of its own small CI expansion. This method requires the previous determination of the (orthonormal) CI vectors for each state, so that the contribution of each configuration within each state be fixed by these predetermined coefficients.

It was found in ethylene[7] that relaxation of this constraint, i.e., carrying out $n \times n$ NONCI, with n being the total number of configuration functions, or symmetry adapted functions, while giving lower energies, did not alter the results of 2×2 NONCI concerning the magnitude of the dipole moment and its sudden rise with the bending of the CH_2 group.

In a NONCI calculation, the secular equation to be solved is

$$|H - E S| = 0, \tag{1}$$

where the overlap matrix S is not the unit matrix because of the nonorthonormality of the N-electron determinants. Two determinants, Δ_A and Δ_B constructed from two basis sets **a** and **b** which are not orthonormal, have overlap

$$S_{AB} = \langle \Delta_A | \Delta_B \rangle = \det(D), \tag{2}$$

where

$$D_{ij} = \langle b_i | a_j \rangle. \tag{3}$$

Similarly, in the construction of the H matrix, the Slater–Condon rules do not apply. Instead, one obtains N-electron integrals.

A solution to the NON problem is provided by the method of corresponding orbitals[21] introduced by King *et al.*[22] This method has proven efficient in the calculation of atomic[12] and molecular[20] transition probabilities. Given **a** and **b**, there exist two unitary tranformations **V** and **U** with

$$\hat{\mathbf{a}} = \mathbf{V}\mathbf{a}, \tag{4}$$

$$\hat{\mathbf{b}} = \mathbf{U}\mathbf{b}, \tag{5}$$

and

$$\mathbf{U}^\dagger \mathbf{D} \mathbf{V} = \mathbf{d}, \tag{6}$$

where **d** is diagonal, so that

$$\langle \hat{b}_i | \hat{a}_j \rangle = \delta_{ij} d_i. \tag{7}$$

Thus, in terms of the corresponding orbitals $\hat{a}$ and $\hat{b}$, the required matrix elements take simple forms.[22] In the present implementation of the method,[7] the one electron functions are expanded in terms of AO basis functions

$$a_k = \sum_{p=1}^{m} \chi_p f_{pk}, \tag{8}$$

$$b_l = \sum_{q=1}^{m} \chi_q c_{ql}, \tag{9}$$

consequently

$$\hat{a}_i = \sum_{p}^{m} \sum_{k}^{N} f_{pk} V_{ki} \chi_p = \sum_{p=1}^{m} d'_{pi} \chi_p \tag{10}$$

and

$$\hat{b}_i = \sum_{q=1}^{m} \sum_{l=1}^{N} c_{ql} U_{li} \chi_q = \sum_{q=1}^{m} c'_{qi} \chi_q. \tag{11}$$

We proceed with the definition of the density matrices

$$\text{Den}(q,p) = \sum_{i=1}^{N} c'_{qi} d'_{pi}/d_i, \quad \text{if all } d_i > 0, \tag{12}$$

$$\text{Den}_k(q,p) = \sum_{i \neq k}^{N} c'_{qi} d'_{pi}/d_i \begin{cases} d_i > 0 \text{ for } i = k \\ d_k = 0 \end{cases}, \tag{13}$$

$$E_k(q,p) = c'_{qk} d'_{pk}, d_k = 0. \tag{14}$$

The required matrix elements, in terms of the density matrices are:

(i) zero singularities in D (all $d_i > 0$):

$$S_{BA} = \det(U)\det(V^\dagger) \prod_{j=1}^{N} d_j, \tag{15}$$

$$O^1_{BA} = \det(U)\det(V^\dagger) \prod_{j=1}^{N} d_j \sum_{q=1}^{m} \sum_{p=1}^{m} \text{Den}(q,p)$$

$$\times \langle \chi_q | O(1) | \chi_p \rangle, \tag{16}$$

$$O^2_{BA} = \det(U)\det(V^\dagger) \prod_{i=1}^{N} d_i \left[\frac{1}{2} \sum_p^m \sum_q^m \sum_r^m \sum_s^m \right.$$

$$\times \left. \{ \text{Den}(p,q)\text{Den}(r,s) - \text{Den}(p,s)\text{Den}(r,q) \} [pqrs] \right], \tag{17}$$

where $[pqrs]$ stands for $\langle \chi_p^{(1)} \chi_r^{(2)} | O^{(1,2)} | \chi_q^{(1)} \chi_s^{(2)} \rangle$.

(ii) One singularity ($d_k = 0$):

$$S_{BA} = 0,$$

$$O^1_{BA} = \det(U)\det(V^\dagger) \prod_{j \neq k}^{N} d_j \sum_q^m \sum_p^m E_k(q,p) \langle \chi_q | O(1) | \chi_p \rangle, \tag{18}$$

$$O^2_{BA} = \det(U)\det(V^\dagger) \prod_{j \neq k}^{N} d_j \left[\sum_p^m \sum_q^m \sum_r^m \sum_s^m \right.$$

$$\times \left. \{ \text{Den}_k(p,q)E_k(r,s) - \text{Den}_k(p,s)E_k(r,q) \} [pqrs] \right]. \tag{19}$$

(iii) Two singularities ($d_k = d_l = 0$):

In this case only a two-electron matrix element exists:

$$O^2_{BA} = \det(U)\det(V^\dagger) \prod_{i \neq k,l}^{N} d_i \sum_{p=1}^{m} \sum_{q=1}^{m} \sum_{r=1}^{m} \sum_{s=1}^{m} \{ E_k(q,p)E_l(r,s)$$
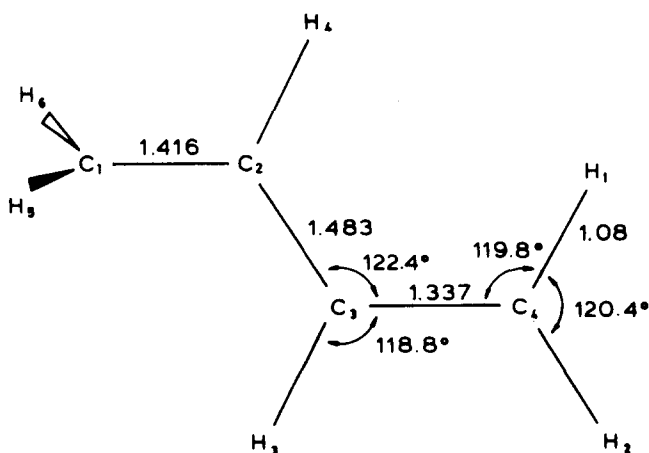
$$- E_k(p,s)E_l(r,q) \} [pqrs]. \tag{20}$$

FIG. 1. Molecular dimensions (in degrees and Å) used for the calculations on the molecule of butadiene.

TABLE I. The sets of configurations[a] used in the NONCI calculations.

Main	$8a'^2 9a'^2 1a''^2 2a''^2$	(a^2)
	$8a'^2 1a''^2 2a''^2 3a''^2$	(b^2)
Additional		
MO1(a^2)	$8a'^2 2 2a'^2 1a''^2 2a''^2$	
	$8a'^2 9a'^2 1a''^2 3a''^2$	
	$8a'^2 9a'^2 1a''^2 4a''^2$	
	$8a'^2 9a'^2 1a''^2 4a'' 5a''$	
MO2(b^2)	$8a'^2 1a''^2 2a''^2 4a''^2$	
	$8a'^2 1a''^2 3a''^2 4a''^2$	
	$8a'^2 1a''^2 3a''^2 4a'' 9a''$	
	$8a'^2 1a''^2 4a''^2 2a'' 3a''$	

[a]The eight core electrons and the first seven valence a' orbitals, doubly occupied in all the above configurations, are not shown here.

IV. DETAILS OF CALCULATIONS

The nuclear geometries used here are for 90° twist angle about the terminal C–C bond and bending angles ϕ of 0° and 26°, after Bruckman and Salem.[3] The other bond lengths and angles (given in Fig. 1) are as in planar butadiene[23] with the twisted C–C bond elongated as in Ref. 13. Calculations were also carried out using the optimum geometry for the Z_1 state as reported by Malrieu and Trinquier.[5] As it is mentioned in the discussion, this geometry was not found to be energetically favorable over the others used here. As in Ref. 7, the AO basis set consists of contracted Gaussian functions $9s5p/5s3p$ for carbon and $5s/3s$ for hydrogen.[24–26] The MRD-CI method[27,28] was used for the orthonormal CI calculations. In all cases, the C_s symmetry was used, the carbon core electrons (a total of eight) were kept frozen while the highest eight (in terms of orbital energies) virtual functions were omitted in the CI calculations. The following CI calculations were performed:

(1) Two orthonormal-basis MRD-CI calculations using $2M/1R$ (see Table I for the main configurations), $T = 10$ μhartree and the MO corresponding to the two main configurations, respectively. The size of the secular equations solved here were 8500.

(2) 2×2 NONCI calculations using two and six-configuration functions for each state (see Table I). The additional configurations were selected on the basis of their contribution to the energy of the states as obtained in the large MRD-CI calculations.

V. RESULTS AND DISCUSSION

A. Large MRD-CI

The results of the orthogonal basis MRD-CI calculations are given in Table II. As mentioned earlier, these are fairly large calculations involving about 8500 selected configurations. They do not reflect the limit of the MRD-CI method, since a more accurate calculation could be carried out involving a more expanded set of reference configurations. Nevertheless, the total energies calculated here for the Z_1 and Z_2 states, are lower than the literature values.[5,13] This is partly due to our use of a larger AO basis set than in Ref. 13 and partly due to the use of the polar or "localized" MO

TABLE II. Results of the orthonormal MRD-CI calculations.

Basis set	ϕ^a	$E_T{}^b$ (hartree)	C_1^2, C_2^{2c}	D_T^d(D)
MO1	0°	− 155.052 31	0.8929, 0.0000	5.728
$(Z_1)^e$	26°	− 155.054 73	0.8932, 0.0000	5.737
MO2	0°	− 155.025 02	0.0000, 0.8926	6.114
$(Z_2)^e$	26°	− 155.012 04	0.0000, 0.8926	6.270

[a] Bending angle.
[b] Total energy.
[c] Squares of coefficients of the two main configurations.
[d] Total dipole moment.
[e] The lowest state (Z_1) was calculated using the MO of the configuration
$...8a'^2 9a'^2 1a''^2 2a''^2$, while Z_2 was calculated with the MO of $8a'^2 1a''^2 2a''^2$ $3a''^2$. In both cases $2M/1R$, $T = 1$ μhartree was used.

TABLE III. Results of the 2×2 NONCI calculations on butadiene.

n^a	State	ϕ^b	E_T(hartree)^c	C_1^2, C_2^{2d}	D_{tot}(D)^e
2	Z_1	0°	− 154.704 41	0.9970, 0.0021	5.773
		26°	− 154.706 34	0.9983, 0.0010	5.804
	Z_2	0°	− 154.678 78	0.0031, 0.9988	6.155
		26°	− 154.665 39	0.0018, 0.9991	6.329
6	Z_1	0°	− 154.720 41	0.9988, 0.0008	5.658
		26°	− 154.720 75	0.9989, 0.0006	5.704
	Z_2	0°	− 154.963 06	0.0013, 0.9992	6.116
		26°	− 154.678 88	0.0011, 0.9994	6.276

[a] Number of configurations in the basis vectors for NONCI.
[b] Bending angle of the CH_2 group.
[c] Total energy.
[d] Squares of coefficients of the two main configurations.
[e] Total dipole moment.

basis, which tends to give lower energy solutions in systems involving symmetry breaking.[5,29] As was the case in twisted ethylene,[7] the orthogonal CI calculations with the two different sets of MO results in different states as the lowest root (as shown by the direction of the dipole moment) each characterized by the main configuration whose MO are used as the one-electron basis. Of the two solutions, the lowest energy corresponds to the state with the negative charge on the CH_2 carbon, in agreement with the other work on this system.[3,5,13] The difference in energy between Z_1 and Z_2 is calculated here as 17.12 kcal/mol which is even larger than the value previously reported in Ref. 5, 14.8 kcal/mol. Bending the CH_2 group by 26° is slightly stabilizing for Z_1 (by about 1.52 kcal/mol) and destabilizing for Z_2 by 8.14 kcal/mol. As may be deduced from the coefficients of the main configuration in the final CI vectors, the contribution of one structure only (I for Z_1 and II for Z_2) is important for each state, the other structure having negligible contribution (see Table II). This is not an unexpected result since the use of polar basis set leads to unsymmetrical results, favoring the configuration for which the MO are optimum, as was also found (erroneously) for D_{2d} twisted ethylene (Ref. 7 and Table IV). However here, this result is supported by the NONCI calculations, as will be shown directly.

B. 2×2 NONCI

As mentioned earlier, these calculations involve 2×2 NONCI using two types of wave functions for basis vectors. First, two-configuration functions for each state, involving the two main configurations (cf. Table I), are used. Next, slightly larger expansions (six configurations, see Table I) are used. The results of these calculations are presented in Table III. As shown in Table III, the NONCI calculations, in agreement with large MRD-CI calculations for both calculated geometries, give negligible mixing of the two main configurations for both the Z_1 and the Z_2 states. The situation here may be contrasted with that for the Z and V states in twisted ethylene, where the NONCI results are completely different from those of the orthogonal basis MRD-CI calculations for the D_{2d} geometry, i.e., with 0° bending angle (see Table IV).

In Table V are collected relevant energy differences obtained with different methods. As shown, all methods give

the same value within 1 kcal/mol. This is expected since NON effects are not important for this particular system. Furthermore, it is found that electron correlation effects are not important for these states in the geometries studied, once the optimum MO are used for each state. This can be seen from the similarity of the values obtained using one-configuration Hartree–Fock energies and those obtained by the 8500 term MRD-CI calculations,

The energy difference between Z_1 and Z_2 at 0° bending (cf. Table V) is quite large and thus, as it was also pointed out in Ref. 5, it is not likely that mere geometry optimization will reverse the energetic ordering of structures I and II. The lack of any significant interaction at the supposedly "halfway" geometry[3] is further evidence towards the above conclusion.

Pyramidalization at C_1 by 26°, while leaving all other molecular dimensions fixed, is only slightly stabilizing the Z_1 state, by about 1.52 kcal/mol whereas Bruckman and Salem[3] report this stabilization as 6.6 kcal/mol and Malrieu and Trinquier as 12 kcal/mol for optimized pyramidal C_1

TABLE IV. Results of MRD-CI and 2×2 NONCI calculations on twisted ethylene.[a]

Method	State	ϕ^b	C_1^2, C_2^{2c}	D_T(D)^d
MRD-CI (MO1)	Z	0°	0.9114, 0.0072	3.341
		10°	0.9135, 0.0059	3.408
MRD-CI (MO2)	V	0°	0.0072, 0.9114	3.341
		10°	0.00.84, 0.9102	3.333
NONCI Two configurations	Z	0°	0.4904, 0.4904	0.000
		10°	0.7839, 0.2005	2.255
	V	0°	0.5099, 0.5099	0.000
		10°	0.2207, 0.7941	2.303
NONCI Six configurations	Z	0°	0.4977, 0.4992	0.006
		10°	0.9865, 0.0128	3.606
	V	0°	0.5023, 0.5008	0.005
		10°	0.0135, 0.9872	3.558

[a] From our earlier work, partly presented in Ref. 7.
[b] Bending angle of the CH_2 group.
[c] Squares of coefficients of the two main configurations.
[d] Total dipole moment.

TABLE V. Energy differences in kcal/mol, ΔE $(Z_1 - Z_2)$ and ΔE $(26° - 0°)$, obtained with different methods.

Method	$\Delta E (26° - 0°)$		$\Delta E (Z_2 - Z_1)$	
	Z_1	Z_2	$0°$	$26°$
SCF–HF	− 1.22	8.40	15.99	25.61
MRD-CI	− 1.52	8.15	17.12	26.79
NONCI Two configurations	− 1.21	8.40	16.08	25.70
NONCI Six configurations	− 0.21	8.90	17.16	26.27

geometries. These values might be too large because in both Refs. 3 and 5 the bond lengths were not optimized for the planar twisted geometry which gives the reference energy. In other work[13] where the molecular geometry is not varied except for bending at C_1, the energy of the Z_1 state is lowered by about 2.5 kcal/mol for 20° (see Table II of Ref. 13) and 5.7 kcal/mol for 40° bending. It should also be pointed out that the AO basis set used here is much larger than the earlier work[3,5] and this may lead to the different results obtained here. For example, calculations using the optimum geometry of Ref. 5 for Z_1 placed it at higher energy than the planar C_1 and C_2, twisted structure, in all levels of treatment used here. This might be due to the differences in the geometries of the reference structure (not reported in Ref. 5), but it might also show that minimal basis calculations are not very reliable for geometry optimization of excited states. From the above, it may be concluded that pyramidalization at C_1 lowers the energy of the Z_1 state. However, the accurate determination of the difference in the energy of the Z_1 state between the planar and the pyramidal structure requires geometry optimization of both structures, carried out with large basis set calculations.

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