

GEOMETRICAL RELAXATION IN THE EXCITED SINGLET STATES OF PROPYLENE

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Abstract—The consequences of the twist around the double bond in propylene for the properties of its low lying excited singlet states have been investigated by the *ab initio* large-scale multireference configuration interaction method (MRD-CI). A substantial increase in the dipole moments of the S_1 and S_2 excited states was found for a large interval of the twist angle $\theta = 50$ – 130° . The variation of the VB covalent and VB ionic contributions to the correlated wavefunctions of these two states as a function of twisting has been analyzed. The connection with the occurrence of an avoided crossing of the two excited singlets near the twist angle $\theta = 75^\circ$, which results in no change in dipole moment directions, is pointed out. The existence of destructive or constructive interference between acceptor and donor substitution has been investigated on the example of the pyramidalization at one of the vinylic C atoms. A competition of opposing effects matrix can invert the dipole moment direction in the excited states. Preliminary investigation of the nonadiabatic coupling elements indicates that the “sudden polarization” effect will not disappear through vibronic coupling, and that the return of excited molecules to the ground electronic state will not be immediate.

1. GENERAL BACKGROUND

Variations in molecular geometry can have a strong influence on the electronic structure and properties of molecular electronic states. A theoretical understanding of these effects and the calculation of potential energy as a function of molecular geometry, which provides potential energy surfaces, is of great interest in the study of chemical reactivity. We are particularly intrigued by excited state energy surfaces, which are needed in photochemistry, in investigations of nonvertical electronic transitions, and in other fields of molecular spectroscopy. In addition to more or less trivial small alterations in bond lengths and bond angles in the excited states relative to equilibrium ground state geometries, substantial geometrical relaxation can occur as an excited molecule seeks a minimum on the excited state potential energy surface after initial light absorption and during its usually rapid thermalization by collision with neighboring molecules.

Such relaxation can induce qualitatively new electronic properties for the excited states. There are qualitative reasons for believing that such “non-vertical” minima in the lowest excited surfaces are likely to be located at biradicaloid geometries,¹ i.e. those at which the simple MO description yields nearly degenerate HOMO and LUMO orbitals for the ground state. Electronic structure calculations for singlet states at such geometries pose severe methodological problems and the commonly available standard programs of SCF type, possibly with limited configuration interaction (CI), are not adequate. In the present paper, we employ one of the possible solutions to the problem, namely large-scale configuration interaction at the *ab initio* level, and investigate the geometrical relaxation of an unsymmetrically substituted C=C double bond in its lowest singlet excited states. A twisting type of relaxation was postulated on

basis of simple MO theory as early as in 1933 by Mulliken,² who pointed out that it would account for the photochemical *cis-trans* isomerization of olefins in their excited singlet state.

It has been shown since in a number of papers³⁻¹⁵ that after a vertical excitation the twisting relaxation of an olefinic double bond leading to a biradical species with two unequal biradical centers gives rise to qualitatively new electronic distributions in the two low-lying excited singlet states. This phenomenon, named the sudden polarization effect, has been investigated predominantly employing *ab initio* procedures with very limited configuration interaction. Such a small-scale CI is capable of making qualitative predictions in the case of medium-size biradicals with two unequal radical sites^{3-5,7} which are presumed to be intermediates in *cis-trans* isomerizations and possibly in other photochemical reactions.^{16,17} The estimates of energy surface shapes and of the amount of charge separation have nevertheless left open the question to what extent the essential features of the chemical predictions depend on the level of the theoretical treatment employed.

An adequate description of close-lying energy hyper-surfaces offers a challenge for theoretical treatments because the regions of crossings and avoided crossings play a key role for the processes taking place in excited molecular states. The sudden polarization effect serves as a good example for the manifestation of new properties of excited states in the region of an avoided crossing. Extensive CI studies were carried out on the simplest prototype model of a unsymmetrical biradical, i.e. 90° twisted monopyramidalized ethylene in order to establish the amount of charge separation in the relevant pair of excited singlet states.¹¹⁻¹³ Pyramidalization which describes the main features of sp^2 to sp^3 rehybridization introduced at one of the CH_2 groups models different electronegativities of two radical centers. In addition, the development of a biradical species and of polar character in the two lowest excited singlet states due to a simultaneous twist of the double bond and the geometrical change which differentiates the two biradical centers (monopyramidalization) was investigated.¹⁵

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The results can be summarized as follows: The gap between the two energy surfaces of excited singlet states increases with increasing pyramidalization at one end of the ethylene CC bond because this geometrical change is in general favorable for the lower excited singlet state. On the other hand, the energy of the second excited singlet state increases drastically. At the same time the interval of the twisting angle for which considerable dipole moments of opposite direction arise in the two excited states becomes larger for the increased degree of pyramidalization. It is worth mentioning that simultaneous pyramidalization at both CH₂ centers, whether introduced in a symmetrical or antisymmetrical manner, is energetically unfavorable for both excited states. Therefore, pyramidalization at one center has been assumed to be an acceptable simulation of the true chemical situation. In fact, the energy and dipole moment surfaces obtained for a small and a large pyramidalization angle simulate the situation corresponding to a biradical with the two centers of fairly similar and fairly dissimilar electronegativity, respectively. All of these results are in qualitative agreement with chemical intuition when it is considered that the S₁ and S₂ states of twisted ethylene can be represented as two resonance hybrids I↔II, and when the effects of pyramidalization on the energies of these two VB structures are taken into account. In this respect, a twisted olefin is a typical example of a biradical with three relatively low-lying singlet states (a covalent ground state and two zwitterionic excited states), resulting from the three VB structures I–III, or in an equivalent description, from the three MO configurations IV–VI^{1,18} (Scheme 1).

The presence of close-lying excited states and of strong sudden charge separation in the narrow geometrical interval found for 80–85° twisted and 10° monopyramidalized ethylene can be compared with the situation found for nearly orthogonal *s-cis*, *s-trans*-hexatriene twisted around the middle double bond.^{3–7} Here, substituent effects have been extensively discussed⁷ in connection with the mechanism of its photochemical conversion to bicyclohexene.¹⁶ It has been also proposed that the formation of biradical intermediates containing the *s-cis*, *s-trans*-hexatriene chromophore may be responsible for the observed dual photochemistry of previtamin D.^{7,17} Once again, the influence of substituents placed at different C atoms of the *s-cis*, *s-trans*-hexatriene moiety, stabilizing considerably one or the other of the two excited states with opposite charge distribution, is assumed to be essential for the chemical outcome.

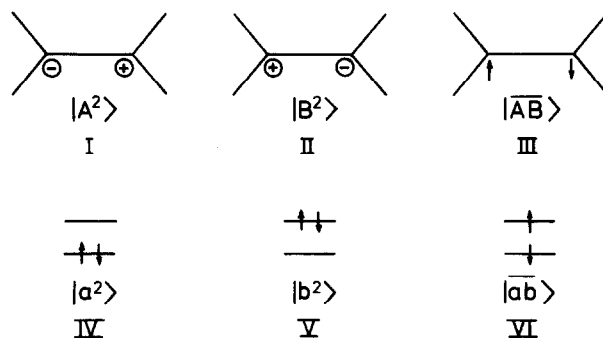
Evidently, the substitution effect splits the two closely

lying excited states of polar character apart. Development of their very pronounced polarity occurs in parallel with the development of biradical features as the result of geometrical relaxation. Therefore, it is to be expected that the effect of charge separation does not occur suddenly and in a narrow geometrical interval. Twisting of strongly monopyramidalized ethylene (40°) offers an adequate model for this situation. Investigation of this system has shown that the prediction of the excited state energies and their dipole moments are insensitive to the details of the large CI treatment employed.¹⁵

Turning now attention to the methodological aspects of the problem, it should be noted^{13,15} that the "large-scale CI methods" are likely to run into difficulties only in the case of small pyramidalization angles at large degrees of twist, for which the energy surfaces of the two singlet excited states are very close to each other. In such instances the calculated energies and dipole moments may depend critically on the choice of one-electron functions (molecular orbitals) used. However, they are little sensitive to other aspects of the calculation, such as the choice of AO basis set. If two energy surfaces come close to each other, a large charge separation occurs in a narrow geometrical region as consequence of an abrupt change in the character of the wavefunction. Therefore, special care should be taken that both excited states are simultaneously well described or, in other words, relative importance of the electronic configurations describing the biradical centers should enter the correlated wavefunctions in a balanced manner. In the case of an unbalanced or inadequate description of the biradical centers at the level of one-electron functions used for building up the CI spaces, even very large CI might not be capable to establish equally good description of both excited states. This problem is directly relevant to chemical and spectroscopical predictions relative to the proximity of the two energy surfaces and to the rapid changes in the character of the wavefunctions as a function of molecular geometry.¹⁹

Both factors might cause the breakdown of Born–Oppenheimer approximation in which case the sudden polarization effect might disappear due to vibronic coupling between the two excited states with large dipole moments of opposite direction.

The present paper contains the results of the investigation of geometrical relaxation in excited singlet states of the simplest substituted olefin, propylene, employing large-scale configuration interaction (MRD–CI).²⁰ In this case the twist around the double bond produces a biradical with two fairly different radical



Scheme 1.

centers. Moreover, the ground state, and the two excited singlet states from which the zwitterionic states develop as the twisting proceeds, possess dipole moments even in planar geometry. Therefore, emphasis is placed on the study of the increasing magnitude of dipole moments as a consequence of the substantial change in the character of the wavefunction in the two excited states as the biradical character develops due to the twisting motion. The study of the relaxation effect in the low lying excited singlet states of propylene represents the first attempt to investigate a real chemical compound rather than a model, such as strongly pyramidalized ethylene, at the *ab initio* large-scale CI level of treatment. The influence of the Me group on the properties of the singlet excited states is analyzed in order to generalize the results for application to larger polyenes.

The paper is structured as follows: after the general introduction, the twisting of the double bond in propylene is considered in Section 2. The effects of pyramidalization are described in Section 3, and vibronic coupling is discussed briefly in Section 4. Since the detailed discussion of the results is necessarily somewhat technical, a qualitative summary of the results for the non-specialist is provided in Section 5.

2. TWISTING OF THE DOUBLE BOND IN PROPYLENE

(a) Qualitative features of the wavefunctions as a function of geometry

In this work special attention has been paid to the changes in the nature of the covalent singlet state and the two zwitterionic states which are the lowest lying excited states produced by a large twist around an olefinic double bond. The corresponding energy surfaces have been calculated for the whole interval from the planar to the 90° twisted geometry. An AO basis set of double-zeta quality has been used.²¹ The previous investigation on pyramidalized ethylene has shown that for large degrees of twist the properties of interest are essentially independent of further enlargement of the AO basis set.¹³

The multireference double excited CI procedure (MRD-CI)²⁰ has been used similarly as in related studies on ethylene.^{13,15} The three roots, three reference configurations CI treatment (3M/3R) for singlet states has been employed throughout the paper. The reference configurations are

$$\begin{aligned} |a^2\rangle &= (\phi_1\alpha) \dots (\phi_{N-1}\beta)(a\alpha) \cdot (a\beta) \\ |b^2\rangle &= (\phi_1\alpha) \dots (\phi_{N-1}\beta)(b\alpha) \cdot (b\beta) \\ |\bar{ab}\rangle &= (\phi_1\alpha) \dots (\phi_{N-1}\beta) \sqrt{\left(\frac{1}{2}\right)} [(a\alpha)(b\beta) - (a\beta)(b\alpha)] \end{aligned} \quad (1)$$

which differ from each other only in occupation numbers of the frontier molecular orbitals |a⟩ and |b⟩. The configurations obtained by single and double excitations with respect to these three leading configurations have been selected according to the energy lowering threshold T criterion: at each geometry an estimate was made in a perturbative manner as to which configurations will contribute to the lowering of the energy of the particular state by an amount larger than $T = 10 \mu\text{hartree}$. These configurations were included in the variational 3M/3R CI treatment²⁰ so that secular equations of order up to 10,000 were solved. Through the extrapolation technique described elsewhere,²² the energies of the three lowest singlet states were estimated for the limit $T = 0$ corresponding to the CI treatment which includes all

configurations obtained through single and double excitations with respect to the three leading configurations.

If the geometrical relaxation gives rise to two very different biradical centers, as happens in the case of propylene due to the presence of the Me group, dipole moments and extrapolated energies of the excited states are not very sensitive to the energy selection threshold T at a sufficiently large level of CI as was previously shown on strongly pyramidalized ethylene.¹³ This can be also easily understood with the help of qualitative considerations. The frontier molecular orbitals which play an important role in the reference configurations can be written as linear combination of localized group orbitals |A⟩ and |B⟩ which describe the parts of the molecule separated by the olefinic bond (i.e. the unsubstituted and the substituted end of propylene, respectively):

$$\begin{aligned} |a\rangle &= \lambda_1|A\rangle + \lambda_2|B\rangle \\ |b\rangle &= \lambda_3|A\rangle - \lambda_4|B\rangle. \end{aligned} \quad (2)$$

It is obvious that the localized group orbitals |A⟩ and |B⟩ do not enter the SCF molecular orbitals |a⟩ and |b⟩ with the same weights even at planar geometry of propylene because of the Me substitution at one end. This implies that the two closed-shell reference configurations will not be equally represented in the correlated wavefunction of any of the three singlet states at planar and twisted geometries. As long as the weight ratio of configurations |a²⟩ and |b²⟩ deviates considerably from 1 there is no danger that the procedure with automatic selection of configurations might introduce a remarkable imbalance at different but sufficiently low selection thresholds in the determination of this ratio. In contrast, in the case of biradicals with very similar radical centers such an imbalanced description might occur due to an accidental favoring of one of the centers.

For a quantitative description of the two unequal biradical centers in propylene, the choice of the one-electron basis for constructing determinantal functions which are needed for the CI procedure requires great care. The molecular orbitals obtained from the closed shell SCF procedure based on the |a²⟩ Slater determinant will clearly be most convenient for the description of the singlet states which contain large contribution from this configuration in the correlated wave-function. On the other hand, it is not an easy task to correct sufficiently the description of other states characterized by large contributions of |b²⟩ and |ab⟩ configurations even with a large but not complete CI treatment. Triplet state SCF MO's offer another possibility although it is to be expected that this procedure which utilizes a determinant with HOMO and LUMO both singly occupied will try to equalize description of both biradical sites giving rise to equally bad description of the states containing significant contributions from both closed-shell configurations. Yet other possible choices are the use of the MCSCF method and the use of the natural orbitals of a state of interest obtained by the diagonalization of the density matrix obtained from a CI calculation based on either triplet or closed-shell singlet SCF molecular orbitals.²⁰ Clearly, for the proper description of a given state it is necessary to employ its own natural orbitals. Therefore, the use of the natural orbitals of a given singlet state as the basis for new CI calculations excludes simultaneous adequate description of other singlet states in a single 3M/3R calculation. This was already discussed in previous work on twisted pyramidalized ethylene.¹⁵

In order to discuss the change in character of the wavefunctions of all three singlet states during the geometrical relaxation it is easy to analyze the results of different CI treatments in terms of the contributions of the three main configurations. The correlated wavefunction for the k th state can be written approximately as:

$$\Psi_K \approx C_{a,K}|a^2\rangle + C_{b,K}|b^2\rangle + C_{\overline{a\overline{b}},K}|\overline{a\overline{b}}\rangle \quad (3)$$

where $|a^2\rangle$, $|b^2\rangle$ and $|\overline{a\overline{b}}\rangle$ are given in eqn (1) and the coefficients are determined by large-scale CI. An equivalent possibility is to express the wavefunctions in terms of the ionic and covalent configurations I-III based on localized group orbitals through eqns (1)-(3):

$$\Psi_K \approx \eta_{A,K}|A^2\rangle + \eta_{B,K}|B^2\rangle + \eta_{\overline{A\overline{B}},K}|\overline{A\overline{B}}\rangle + \dots \quad (4)$$

with

$$\begin{aligned} |A^2\rangle &= |\dots\rangle|A\alpha\rangle|A\beta\rangle \\ |B^2\rangle &= |\dots\rangle|B\alpha\rangle|B\beta\rangle \\ |\overline{A\overline{B}}\rangle &= |\dots\rangle\frac{1}{\sqrt{2}}[|A\alpha\rangle|B\beta\rangle - |B\alpha\rangle|A\beta\rangle]. \end{aligned} \quad (5)$$

The coefficients in the wavefunction expansions (3) and (4) are related through group orbital coefficients λ_i (see eqn (2)) which are taken from the calculated molecular or natural orbitals:

$$\begin{aligned} \eta_{A,K} &= C_{a,K}\lambda_1^2 + C_{b,K}\lambda_3^2 + \sqrt{2}C_{\overline{a\overline{b}},K}\lambda_1\lambda_3 \\ \eta_{B,K} &= C_{a,K}\lambda_2^2 + C_{b,K}\lambda_4^2 - \sqrt{2}C_{\overline{a\overline{b}},K}\lambda_2\lambda_4 \\ \eta_{\overline{A\overline{B}},K} &= \sqrt{2}C_{a,K}\lambda_1\lambda_2 - \sqrt{2}C_{b,K}\lambda_3\lambda_4 \\ &\quad + C_{\overline{a\overline{b}},K}(\lambda_2\lambda_3 - \lambda_1\lambda_4). \end{aligned} \quad (6)$$

The weights of group orbital configurations are particularly convenient for characterizing the covalent

$$W_C = \eta_{\overline{A\overline{B}},K}^2 / \sum_I \eta_{iK}^2 \quad (7a)$$

and ionic

$$W_I = (\eta_{A,K}^2 + \eta_{B,K}^2) / \sum_I \eta_{iK}^2 = W_{IA} + W_{IB} \quad (7b)$$

nature of the wavefunction, respectively.

(b) Energy surfaces

The singlet energy surfaces for twisting around the double bond in propylene are given in Fig. 1. The bond length of the C=C bond around which twisting has been carried out is assumed to be 1.416 Å, corresponding to the optimized bond length value in the singlet excited states for large twisting angles (see Ref. 11). Of course, the ground state energy of the planar geometry with such a long C=C bond is higher than that obtained for the experimental value of the double bond length in the ground state of propylene, but as already mentioned a good description of the states of planar propylene was not attempted in this work. The twisting of the propylenic double bond gives rise to a rotation barrier in the ground state, while the energies of both excited states decrease substantially, approaching each other in a similar manner as for twist and one-end (40°) pyramidalization of ethylene (see Refs. 15 and 23).

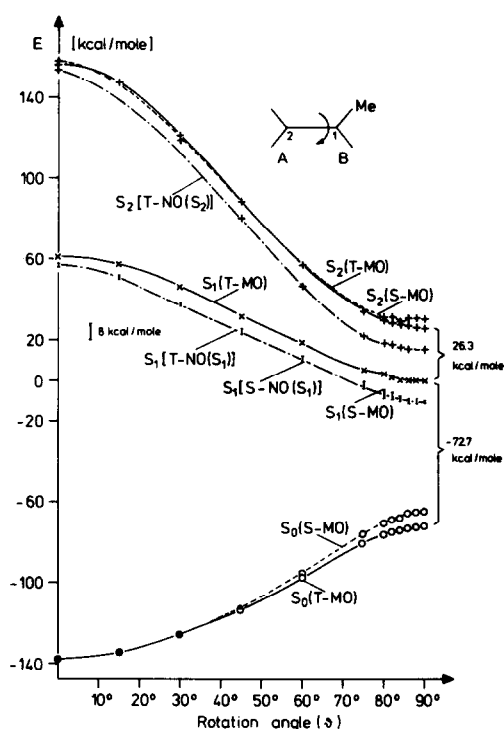


Fig. 1. Pure torsion potential curves for the lowest three singlet states of propylene obtained in CI 3M/3R with configuration selection threshold $T = 10 \mu\text{h}$ employing different one-electron functions: triplet SCF MO's (T-MO, —), closed-shell singlet SCF MO's (S-MO, ---), and natural orbitals of the states in question as obtained from triplet MO-CI (T-NO(S_1), T-NO(S_2), - - - -) and singlet MO-CI calculations (S-NO(S_1)). The potential curves for the S_1 state obtained from three of the treatments; S-MO-CI, S-NO(S_1)-CI and T-NO(S_1)-CI, nearly coincide and are given by one line (- - -).

Let us first compare the energy surfaces obtained by the 3M/3R ($T = 10 \mu\text{hartree}$) CI procedures employing triplet SCF MO's (T-MO-CI) with those obtained using closed shell singlet MO's (S-MO-CI) (Fig. 1). The first five lowest energy SCF MO's which are composed primarily of s AO's on carbon atoms have been taken as core orbitals which are excluded from the CI treatment. As expected, the qualitative considerations from previous section are reflected in the results of the large-scale CI procedure.

The analysis of the correlated wavefunctions (3 and 4) for all three singlet states in terms of coefficients of the reference configurations (eqns (1)-(3)) as well as in terms of weights of covalent W_C vs ionic W_I contributions (eqn (7)) obtained from T-MO-CI and S-MO-CI is given in Tables 1 and 2 and in Fig. 2. Both treatments yield a ground state of predominantly covalent character which further increases with the rotation angle θ . The contribution from the covalent configuration $|\overline{A\overline{B}}\rangle$ in the first excited state S_1 is relatively small and reaches a maximum near $\theta = 75^\circ$. In contrast, the second excited state S_2 exhibits some covalent character at planar geometry which gradually decreases with the twist. In both states the covalent contributions vanish by symmetry at $\theta = 90^\circ$. The wavefunction of the first excited state S_1 has a large contribution of the group orbital configuration $|A^2\rangle$, which grows further with increasing twist angle θ . The contribution of $|B^2\rangle$ is small throughout the twisting

Table 1. Characteristics of the wavefunctions for S_0 , S_1 , S_2 states obtained from 3M/3R, $T = 10 \mu\text{h}$ procedure employing triplet SCF MO basis for CI

a)	λ_2/λ_1 b)	ELECTRONIC STATE	$c_{a,K}$ c)	$c_{b,K}$ c)	$c_{aB,K}$ c)	w_{A1}^2 d)	w_{B1}^2 d)	w_C^2 d)
						$n_{A,K}^2 / \sum_i n_{iK}^2$	$n_{B,K}^2 / \sum_i n_{iK}^2$	$n_{AB,K}^2 / \sum_i n_{iK}^2$
90°	0.00	S_0	0.	0.	-1.000	0.	0.	1.000
		S_1	0.999	0.052	0.	0.997	0.003	0.
		S_2	-0.056	0.999	0.	0.003	0.997	0.
88°	0.17	S_0	0.311	-0.229	-0.922	0.004	0.000	0.996
		S_1	0.948	0.108	0.301	0.989	0.004	0.008
		S_2	-0.035	0.967	-0.253	0.004	0.995	0.000
86°	0.30	S_0	0.526	-0.365	-0.768	0.015	0.000	0.985
		S_1	0.842	0.232	0.486	0.961	0.009	0.030
		S_2	-0.004	0.901	-0.433	0.010	0.990	0.000
80°	0.54	S_0	0.782	-0.464	-0.417	0.035	0.002	0.962
		S_1	0.595	0.462	0.658	0.900	0.011	0.089
		S_2	0.107	0.763	-0.637	0.013	0.975	0.012
75°	0.64	S_0	0.862	-0.426	-0.275	0.054	0.009	0.937
		S_1	0.445	0.473	0.760	0.873	0.000	0.127
		S_2	0.183	0.783	-0.594	0.000	0.949	0.051
60°	0.76	S_0	0.944	-0.311	-0.113	0.094	0.026	0.880
		S_1	0.180	0.279	0.943	0.764	0.125	0.110
		S_2	0.231	0.922	-0.312	0.092	0.664	0.244
45°	0.79	S_0	0.966	-0.250	-0.065	0.110	0.032	0.858
		S_1	0.090	0.156	0.984	0.682	0.246	0.071
		S_2	0.196	0.966	-0.167	0.165	0.487	0.348
30°	0.80	S_0	0.975	-0.219	-0.047	0.117	0.031	0.852
		S_1	0.057	0.103	0.993	0.644	0.301	0.055
		S_2	0.173	0.979	-0.106	0.194	0.416	0.390
15°	0.80	S_0	0.978	-0.206	-0.037	0.119	0.028	0.853
		S_1	0.043	0.087	0.995	0.632	0.316	0.052
		S_2	0.171	0.982	-0.077	0.209	0.386	0.405
0°	0.80	S_0	0.979	-0.203	-0.035	0.119	0.026	0.855
		S_1	0.040	0.081	0.996	0.629	0.321	0.050
		S_2	0.170	0.981	-0.093	0.202	0.392	0.406

a) Twisting angle;

b) Localization parameters of HOMO (compare Eq. (2)). Localization parameters of LUMO $|\lambda_3/\lambda_4|$ have similar values to λ_2/λ_1 .c) Coefficients of reference configurations Eqs(1) in expansion of correlated wave functions obtained from large scale CI treatment (3M/3R, $T=10\mu\text{h}$)d) Weights of ionic $|A^2\rangle$, $|B^2\rangle$ and covalent $|\overline{AB}\rangle$ group orbital configurations (cf. Eqs. 6 and 7).

interval and reaches a minimum value equal to zero at $\theta = 75^\circ$. The role of $|A^2\rangle$ and $|B^2\rangle$ contributions is exchanged in the second excited state S_2 (Fig. 2). This is qualitatively understandable when it is considered that the Me group is a π donor and therefore prefers to have the nearest p orbital at the unsaturated C atom empty. In our notation this orbital represents a predominant part of the group orbital |B). For this reason electronic charge flows towards the group orbital |A) and consequently Me substitution stabilizes the group orbital configuration $|A^2\rangle$.

Both excited states are very polar, because of the prevailing contribution of one of the ionic group orbital configurations. Moreover, zero contributions of one of these ionic group orbital configurations in each of two excited states S_1 and S_2 at $\theta = 75^\circ$ show an avoided crossing of these states. This is indicated by the

exchange of signs between $\eta_{B,1}$ and $\eta_{A,2}$ (Fig. 3), which are the coefficients of $|B^2\rangle$ in S_1 and of $|A^2\rangle$ in S_2 , respectively (see eqn (6)): the avoided crossing between the two excited states in relaxed propylene is characterized by the sign change of the smaller ionic contribution to the wavefunction. Therefore, the polarity of these states given by the larger ionic contribution does not change even when the features of the wavefunctions undergo a qualitative change. The avoided crossing between two singlet excited states of twisted ethylene pyramidalized at one end is similar to and goes over into the allowed crossing for the non-pyramidalized ethylene geometry (see Ref. 15).

The behavior of the correlated wavefunctions in terms of covalent vs ionic contributions is independent of the choice of the one electron basis used for the configurations in the CI treatments demonstrating that the large

Table 2. Characteristics of the wavefunctions for S_0 , S_1 , S_2 states obtained from 3M/3R, $T = 10 \mu\text{h}$ procedure employing singlet SCF MO basis for CI

$\theta^a)$	$\lambda_2/\lambda_1^b)$	ELECTRONIC STATE	$c_{a,K}^c)$	$c_{b,K}^c)$	$c_{ab,K}^c)$	$\frac{w_{AI}^2}{n_{A,K}^2/n_{i,K}^2}^d)$	$\frac{w_{BI}^2}{n_{B,K}^2/n_{i,K}^2}^d)$	$\frac{w_C^2}{n_{AB,K}^2/n_{i,K}^2}^d)$
90° ^{a)}	0.75 ^{b)}	S_0	0.709	-0.662	-0.244	0.003	0.000	0.997
		S_1	0.654	0.473	0.591	0.979	0.019	0.002
		S_2	0.275	0.567	-0.777	0.022	0.978	0.000
88°	0.76	S_0	0.754	-0.623	-0.211	0.008	0.000	0.991
		S_1	0.605	0.518	0.604	0.968	0.019	0.012
		S_2	0.266	0.571	-0.776	0.023	0.977	0.000
86°	0.78	S_0	0.795	-0.581	-0.176	0.017	0.002	0.981
		S_1	0.552	0.559	0.618	0.951	0.018	0.031
		S_2	0.260	0.577	-0.774	0.022	0.975	0.002
80°	0.80	S_0	0.875	-0.471	-0.109	0.048	0.009	0.943
		S_1	0.416	0.610	0.674	0.894	0.006	0.100
		S_2	0.251	0.626	-0.738	0.010	0.965	0.025
75°	0.81	S_0	0.914	-0.399	-0.076	0.072	0.016	0.912
		S_1	0.321	0.587	0.744	0.858	0.000	0.141
		S_2	0.253	0.695	-0.673	0.000	0.934	0.065
60°	0.83	S_0	0.962	-0.270	-0.030	0.116	0.030	0.854
		S_1	0.133	0.368	0.920	0.773	0.091	0.136
		S_2	0.239	0.886	-0.396	0.072	0.679	0.248
45°	0.82	S_0	0.977	-0.210	-0.017	0.134	0.032	0.833
		S_1	0.060	0.201	0.978	0.696	0.215	0.089
		S_2	0.205	0.956	-0.211	0.157	0.486	0.356
30°	0.80	S_0	0.983	-0.183	-0.011	0.143	0.026	0.831
		S_1	0.037	0.135	0.990	0.663	0.263	0.076 ⁴
		S_2	0.184	0.974	-0.133	0.189	0.412	0.398
15°	0.78	S_0	0.985	-0.173	-0.009	0.146	0.019	0.835
		S_1	0.029	0.108	0.994	0.653	0.275	0.072
		S_2	0.179	0.980	-0.089	0.206	0.379	0.415
0°	0.77	S_0	0.985	-0.172	-0.008	0.146	0.016	0.839
		S_1	0.027	0.101	0.995	0.650	0.277	0.073
		S_2	0.176	0.978	-0.111	0.196	0.389	0.416

For a), b), c) and d) compare Table I.

scale CI has overcome qualitatively the arbitrary features of the one-electron functions T-MO's or S-MO's (see the last three columns of Table 1 and the corresponding ones in Table 2).

The MO's obtained from different SCF procedures are characterized by localization parameters of HOMO, λ_2/λ_1 and of LUMO, λ_4/λ_3 (see Tables 1 and 2). The ratio λ_2/λ_1 of the triplet SCF HOMO decreases properly from the value 0.8 for planar geometry to the value 0.0 for the 90° twisted conformation. For the latter case the group orbitals |A) and |B), consisting predominantly of 2p orbitals on the olefinic carbons, belong to two different irreducible representations of the C_2 point group. Therefore they cannot simultaneously enter the frontier orbital |a) or |b). In contrast, the closed shell SCF procedure yields unphysical features of HOMO and LUMO for large twist angles demonstrating the expected "strange properties" of the closed-shell single determinant SCF solutions. In the interval of the twisting angles $\theta = 75-88^\circ$ two such solutions exist as a consequence of the

nonuniqueness²⁴ of the SCF procedure. The two solutions yield different MO's and different energy expectation values. For $\theta = 90^\circ$ the nonuniqueness of the SCF procedure manifests itself in a broken-symmetry solution (called singlet instability) which has a lower energy than the symmetry adapted solution²⁵ (compare Fig. 4).

Therefore, it is not surprising that the coefficients $c_{a,K}$, $c_{b,K}$, $c_{ab,K}$ of the reference configurations (see eqns (1)-(3)) differ strongly if the CI treatment employs S-MO or T-MO orbitals (see Tables 1 and 2). As already mentioned, large-scale CI corrects overall for these discrepancies so that the characteristics of the wavefunctions described in more physical manner in terms of group orbital configurations are the same for S-MO-CI and T-MO-CI. Nevertheless, some quantitative differences between these two treatments remain which are easily seen on the shapes of the energy surfaces in Fig. 1 [compare S_i (S-MO) with S_i (T-MO), $i = 0, 1, 2$]. The singlet ground state S_0 is better described by T-MO-CI for large twist angles because this state is of pre-

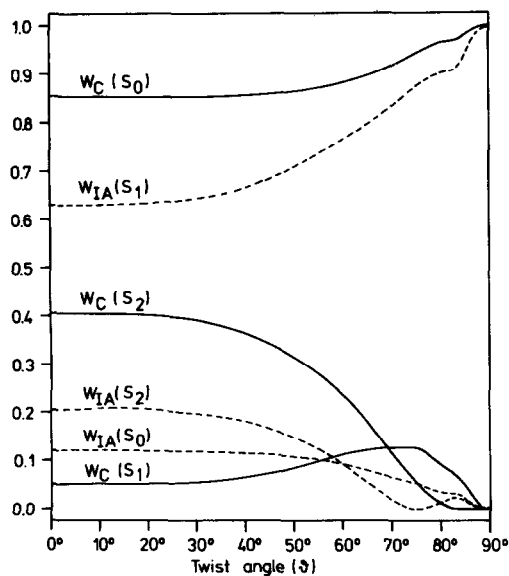


Fig. 2. Weights W_C (—) of covalent (III) and W_{IA} (---) of ionic (I) configurations (see eqn (7)) in the singlet states S_0 , S_1 and S_2 of propylene as a function of the twist angle θ . Wavefunctions from a 3M/3R, $T = 10 \mu h$, T-MO-CI treatment:

dominantly covalent nature in this geometry interval. This is apparent from the coincidence of ground state energies for 90° twist obtained from T-MO-CI and from the corresponding ground state natural orbitals—CI calculations (NO-S₀-CI) ($E = -117.0783$ a.u.). The S-MO-CI emphasizes the ionic features of the first excited state S_1 , yielding lower energies in the whole twist interval than obtained from T-MO-CI.

If the natural orbitals of the first excited state NO-S₁ obtained from T-MO-CI or S-MO-CI are employed as the basis for building up the CI spaces in the new CI calculations the energies of the first excited state S_1 lie very close to those obtained by the S-MO-CI treatment (Fig. 5). The energies of the second excited state S_2 are equally badly determined with both T-MO-CI and S-MO-CI procedures, as can be recognized from the fairly large lowering of the whole energy curve if the NO's of the S_2 state are employed in the CI treatment.

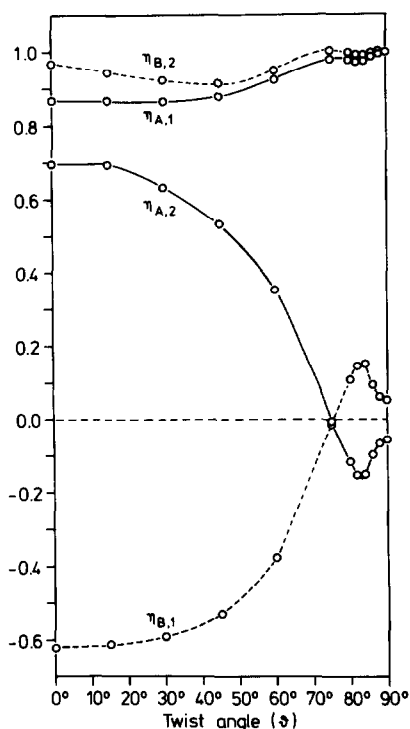


Fig. 3. Coefficients $\eta_{A,K}$ and $\eta_{B,K}$ with $K=1,2$ for S_1 and S_2 in the expansion of wavefunctions Ψ_K in terms of group orbital configurations ("VB-structures") $|A^2\rangle$ (I) and $|B^2\rangle$ (III) (see eqns (4) and (5)) as a function of the twist angle θ . Wavefunctions from a 3M/3R $T = 10 \mu h$, T-MO-CI treatment.

It is to be expected that the energies of the state obtained from the CI employing the natural orbitals of the same state have lowest values because the correlation effects are considered in the most proper manner. Notice that the 3M/3R T-MO-CI and the corresponding NO-CI calculations for each state yield nearly the same energy gap between the singlet excited states S_2 and S_1 (see Table 3). We conclude that the T-MO-CI treatment is convenient for the determination of the energy difference between both singlet excited states while the S-MO-CI should be used with caution

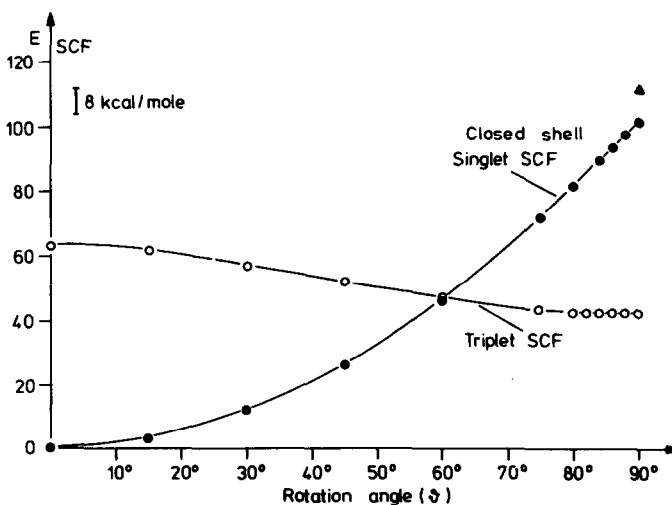


Fig. 4. Singlet (●) and Triplet SCF (○) energies of propylene as a function of the twist angle θ . At $\theta = 90^\circ$ the closed shell singlet SCF solution yields a symmetry-unadapted solution (●) which lies lower than the symmetry-adapted solution (▲) obtained imposing symmetry constraints in the iterative procedure.

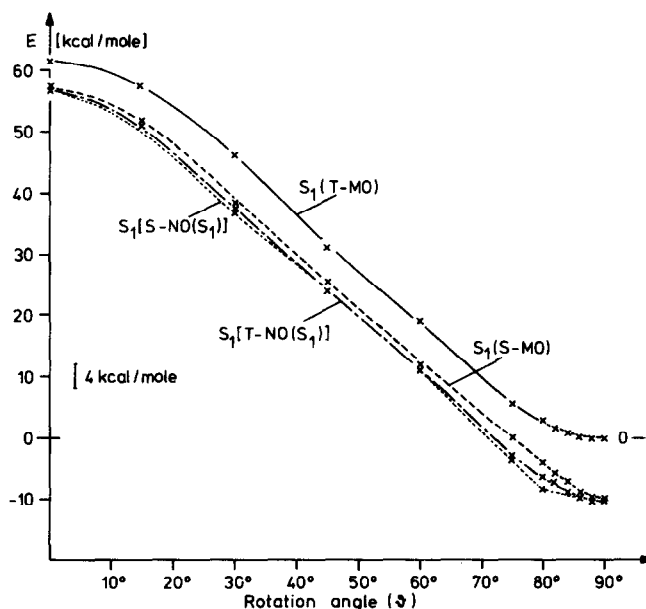


Fig. 5. Detail of Fig. 1: Pure torsion potential curves for the lowest excited singlet state S_1 of propylene obtained in a CI 3M/3R treatment with configuration selection threshold $T = 10 \mu\text{h}$ employing different one-electron functions: T-MO, —; S-MO, ----; S-NO(S_1), ····; T-NO(S_1), -.-.

Table 3. The energy differences for the 90° twisted propylene obtained from different treatments

	$\Delta E_1 = E(S_0) - E(S_1)$ (Kcal/mole)	$\Delta E_2 = E(S_1) - E(S_2)$ Kcal/mole
S-MO-CI	-55.38	-40.07
T-MO-CI	-72.75	-26.34
NO-CI for each Root	-61.9	-26.15

because it yields description of different qualities for these two states.

The occupation numbers of natural orbitals of the ground state S_0 are very useful as a measure of biradical character: If a couple of occupation numbers n and n' ($n < n'$) of natural orbitals, which are the correlated analogues to HOMO and LUMO, deviate appreciably from the values 0 and 2, the molecule can be classified as a biradicaloid.²⁷ If n and n' are very close to 1 the molecule is a biradical. It is worth mentioning that the development of the biradical character in propylene upon twisting is slow up to about 70° and then is rapid in the remaining interval to 90° for which the two energy surfaces of S_1 and S_2 approach considerably each other (see Fig. 6).

(c) Dipole moments curves

The dipole moments of the excited singlet states S_1 and S_2 are mostly determined by the weights of the ionic configurations $|A^2\rangle$ and $|B^2\rangle$ (I and II). Each singlet state containing a large contribution from $|A^2\rangle$, which is especially the case of S_1 , should have a positive dipole moment in the double bond direction oriented towards the Me substituted vinylic C atom. The dipole moment of the second excited state S_2 , which has a large $|B^2\rangle$ contribution, is smaller in the absolute value and

oppositely directed indicating charge flow towards the substituted end. Of course, the effect of σ -donation diminishes these effects.

The dipole moment curves obtained from the CI treatments are given in Fig. 7. Dipole moments in the first excited state are fairly independent of the treatment employed, exhibiting almost constant values for twist angles below 40° and substantial increase in polarity for a broad interval of large twist angles. Dipole moments in the second excited state S_2 have indeed smaller absolute

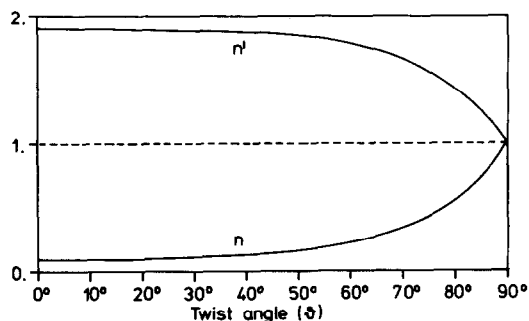


Fig. 6. Occupation numbers of two natural orbitals n, n' of the S_0 state of propylene as a function of the twist angle θ . The 3M/3R, $T = 10 \mu\text{h}$, T-MO-CI treatment was employed.

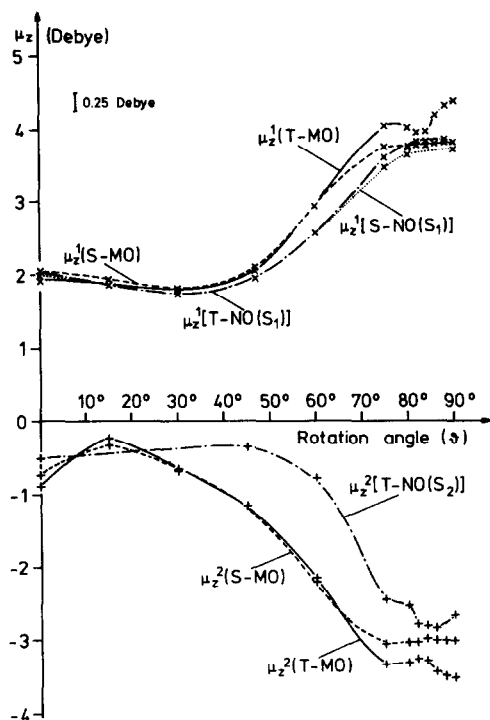


Fig. 7. The μ_z^1 and μ_z^2 components of the dipole moments (in the direction of the double C=C bond) of the S_1 and S_2 states of propylene as a function of the twist angle θ for the same treatments as in Fig. 1.

values than in the S_1 state, mainly if the S_2 -NO's are employed for constructing the CI space. The effect of strong charge separation in both excited states is not very sudden due to the relatively strong substituent effect.

3. EFFECTS OF PYRAMIDALIZATION AT ONE OF THE VINYLIC CARBON ATOMS OF 90° TWISTED PROPYLENE

Pyramidalization at the unsubstituted carbon atom C_2 stabilizes further the $|A^2\rangle$ configuration with extra electronic charge at C_2 because an empty developing sp^3 orbital has a higher electronegativity than a pure p orbital and attracts charge more strongly, so that the π -donating effect of the Me group which shifts charge towards C_2 is reinforced. Therefore, the energy of the first excited state S_1 is lowered by pyramidalization at C_2 while the energy of the S_2 state increases drastically (see Fig. 8). The corresponding dipole moment values increase negligibly in respect to the values for the 90° twisted unpyramidalized geometry.

In contrast, pyramidalization at the substituted carbon atom C_1 causes an avoided crossing between the two excited states at about 40° pyramidalization. Since the sp^3 orbital which develops in the course of pyramidalization acts as an acceptor, it opposes the stabilization of positive charge by the Me group, at first causing a decrease of the dipoles of the S_1 and S_2 states. For larger pyramidalization angles the increasing electronegativity of the sp^3 orbital overpowers the positive-charge stabilizing effect of the Me and produces a switch of dipole moment directions in both excited states (see Fig. 8). The pyramidalization at the atoms C_1 or C_2 is energetically

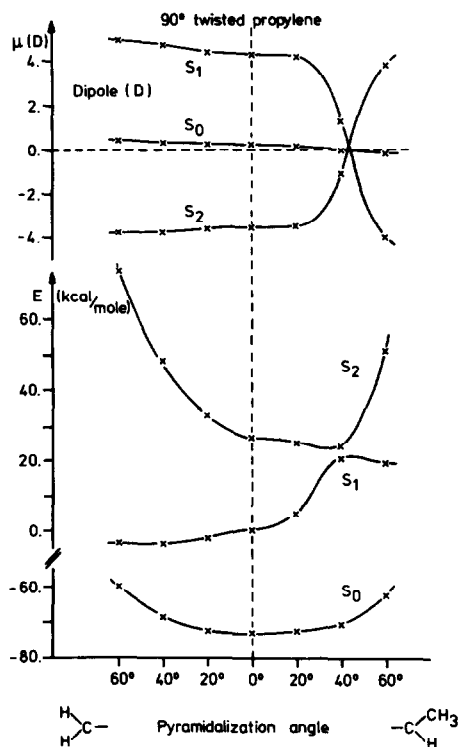


Fig. 8. Potential curves and dipole moments for S_0 , S_1 and S_2 states of the 90° twisted propylene as a function of the pyramidalization angles at one of the two different vinylic carbon atoms (right, at the substituted carbon; left, at the unsubstituted carbon). The 3M/3R, $T = 10 \mu\text{h}$, T-MO-CI treatment was used. Pyramidalization angle is defined as the angle between the C=C

bond and the plane of $\begin{matrix} \text{H} \\ | \\ \text{H}-\text{C} \\ | \\ \text{H} \end{matrix}$ or $\begin{matrix} \text{H} \\ | \\ \text{C}-\text{CH}_3 \\ | \\ \text{H} \end{matrix}$. The HCH and H_3CCH angles are kept constant.

unfavorable in the S_0 state, and the small magnitude of the dipole moments in this state remains almost unchanged during this geometrical change.

This example clearly demonstrates the influence of donor and acceptor substitution on the energies and polarities of the various singlet states for biradicaloid geometries. Overall effects obtained by the large-scale CI treatment agree with the results of the study of substitution effects at different positions of the diallylic skeleton which were carried out earlier employing only CI among configurations $|a^2\rangle$, $|b^2\rangle$ and $|ab\rangle$.

4. VIBRONIC STATES AND THE BORN-OPPENHEIMER APPROXIMATION

Ideally, a prediction of photochemical and spectroscopic properties should be supported by an evaluation of the nature of the vibronic states concerned, and of their dynamical behavior. Previous contributions in this direction were based either on different models of the three interacting singlets,^{28,29} on semiempirical calculations³⁰ or on a very simple *ab initio* treatment.³¹ The experience gained from simpler methods, together with common chemical intuition, makes it possible to characterize the vibronic excited states of olefins, once the basic information on electronic energies, dipoles, and

nonadiabatic coupling matrix elements

$$g_{KL} = \left\langle \Psi_K \left| \frac{\partial}{\partial \theta} \right| \Psi_L \right\rangle \quad (8)$$

is obtained from an accurate calculation.

Work is in progress³² to determine the shape of the g_{KL} matrix elements as functions of twisting angle θ for ethylene (with different pyramidalization of the $-\text{CH}_2$ ends) as well as for propylene at the same *ab initio* level as employed in the present paper for determination of energy surfaces and dipole moments. The $g_{KL}(\theta)$ curves have typical shapes, an example of which is shown in Fig. 9 for the case of propylene (for details of the calculation see Ref. 33).

The general features of the vibronic problem can be summarized as follows. In the Born–Oppenheimer approximation the S_1 and S_2 potential surfaces support two sets of vibrational states with opposite average dipoles (μ_z), whose magnitudes generally decrease with the increasing quantum number of the twisting vibration; when high polarity is present in a broad range of twisting angles, then for several lowest vibrational states (μ_z) is approximately equal to the value of the dipole moment at $\theta = 90^\circ$.

The coupling between the zwitterionic states (g_{12}) is large in the regions of steeply developing polarity^{28,29,31} and vanishes by symmetry at $\theta = 90^\circ$. Its importance in mixing the lowest vibrational states of S_1 with those of S_2 is limited to the cases of extremely “sudden” polarization and small S_1 – S_2 energy gap; only higher lying vibrational states, of spectroscopic interest, are normally affected.

A fast internal conversion from S_1 or S_2 to S_0 , which was proposed in order to explain the high quantum yields of some photoisomerizations,³⁰ would require g_{01} or g_{02} functions sharply peaked around $\theta = 90^\circ$. The presently

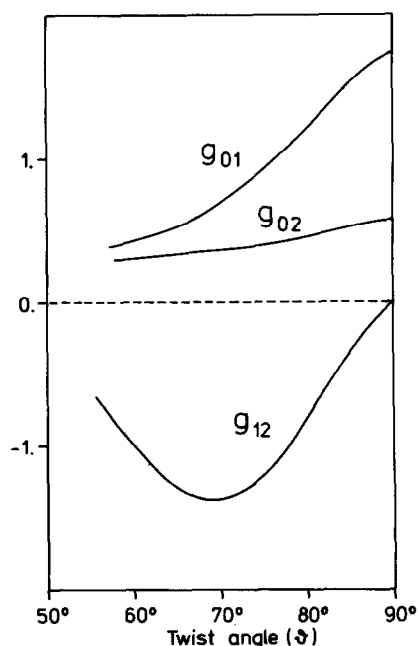


Fig. 9. Coupling matrix elements g_{01} , g_{02} and g_{12} (see eqn (8)) between S_0 and S_1 , between S_0 and S_2 and between S_1 and S_2 of propylene, respectively, as a function of the twist angle θ . The 3M/3R, T = 10 μ h, S–MO–CI treatment was used.

determined shapes of coupling matrix elements g_{01} and g_{02} as a function of θ (see Fig. 9) indicate that the vibronic coupling between the ground state and the excited states S_1 or S_2 is too small to support the proposal of reference 30 (see also Ref. 31).

5. QUALITATIVE SUMMARY

The singlet ground state of propylene is of prevailing covalent nature (VB structure III) throughout the twisting interval 0–90°. At the planar geometry both excited states S_1 and S_2 contain relatively large ionic contributions (VB structures I and II). The weights of these two configurations are unequal but comparable in magnitude giving rise to dipole moments of a moderate size and opposite direction, but also to a high polarizability. This comes into play as the two states approach each other in energy during the geometrical relaxation, so that the twist around the double bond with “unequal ends” provokes a high polarity of these two states. This is due to a *strong decrease* in the smaller contribution of the VB ionic structure in each state, while the larger contribution of the other VB ionic structure *does not decrease* in the course of the twisting. Consequently, for twisted geometries each excited state S_1 and S_2 contains primarily one of the ionic structures and therefore, large dipole moments of opposite direction.

In general, the energy lowering of the second excited state S_2 due to the twist is larger than the energy lowering of first excited state S_1 . The avoided crossing between these two states occurs near $\theta = 75^\circ$ and is reflected in a change of sign of the smaller VB ionic contribution in each state. The directions of dipole moments after the avoided crossing are not changed because they are determined by the larger ionic VB contribution. The avoided crossing between S_1 and S_2 is obtained only when the large-scale CI treatment is employed, because the interaction with the configurations describing $\pi \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ excitations³⁴ is sufficiently taken into account. Apparently, excitations of this kind affect more the energy of the state which contains a large contribution of the doubly excited configuration than the energy of the other excited state. The configuration interaction among the most important VB structures (3 \times 3 CI) does not yield the avoided crossing and gives rise to the exaggerated dipole moments because it does not allow the σ -electrons to compensate partly the shift of π electrons.

In the case of propylene and similarly, of ethylene strongly pyramidalized at one end, charge separation in the two excited states occurs in a broad interval of the relaxation coordinate. The energy gap between the two singlet excited states with opposite dipole moments is not smaller than 26 kcal/mole because of the relatively large substitution effect of the Me group. Due to this substantial separation of the energy surfaces and due to the relatively smooth change of the wavefunction, vibronic–electronic coupling does not substantially diminish the dipole moments in the two singlet excited states.

The opposite influence of the donor and acceptor substitution on the dipole moments in excited states is shown on the example of the twisted propylene pyramidalized at the vinylic carbon atom next to the methyl group. In this case these competing substitution effects diminish dipole moments in the excited states and can lead to reversal of dipole moment directions.

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