conformation of the methoxy group relative to the aromatic ring. According to our results, in the planar conformation anisole is a stronger base than phenol, and protonation can occur either on the ring or on the substituent. The rotation of the methoxy group increases the basicity of anisole, which behaves as an oxygen base. This fact could be responsible for the absence of deuterium exchange in anisole, pointed out by Beauchamp.[6]

Our results bring out, once more, the problem of the conformation of anisole and they ratify, to some extent, the INDO results, though no definitive answer can be given on this particular point. The full geometry optimization at the ab initio level, which would settle the question, would require the use of an optimization procedure similar to that employed to obtain our INDO results, which would be too expensive.

**Acknowledgments.** All calculations were performed in the IBM 360/65 computer at the UAM/IBM Center (Madrid). We would like to thank our referees for helpful criticism.

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# An ab Initio Study of the Cis–Trans Photoisomerization of Stilbene

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**Abstract:** The molecular energies of the ground and lowest excited $\pi\pi^*$ states for the cis and trans isomers of stilbene and for the twisted geometry of the molecule have been evaluated by the SCF method followed by configuration mixing. The orbital basis is a minimal basis of STO/3G orbitals and the CI includes all relevant second-order interactions of the ground and lowest excited configurations. Two-term Fourier interpolations of the computed energies have provided potential energy curves along the coordinate of internal rotation. The potential curves support the adiabatic mechanism for the trans–cis thermal conversion in the ground state and for the sensitized photoconversion in the lowest triplet state and a nonadiabatic mechanism for the direct photoisomerization in the lowest excited singlet state.

## Introduction

Several mechanisms have been proposed for the direct cis-trans photoisomerization of stilbene and of the related $\alpha,\omega$-diphenylpolyenes.[2,3] Given the correlation diagram of the orbital levels in *cis*- and *trans*-stilbene (Figure 1), the isomerization reaction, after Woodward–Hoffmann,[4] is allowed in the lowest excited B ($S_1$, $T_1$) and A ($S_2$) states. The excitations to the B and A states are essentially described as (4a) → (4b) and $(4a)^2 \rightarrow (4b)^2$, respectively. An alternative description of the $S_1$, $T_1$, and $S_2$ states can be given in terms of biradicaloid states.[5]

Experimentally it has been possible to prove that the direct photoreaction does not follow the triplet pathway.[3] Among the mechanisms involving states in the singlet manifold, it was first proposed that the optical excitation to the $S_1$ state is followed by adiabatic motion on the $S_1$ energy curve to a minimum located at the twisted geometry ($\varphi = 90^\circ$) and by deactivation onto the ground potential energy surface. This mechanism contrasts with the results of a spectroscopic investigation[6] where it was deduced that the $S_1$ state has in fact a barrier at $\varphi = 90^\circ$ high enough to make the state inactive in the photoreaction. For this reason a second mechanism was postulated,[7] where the molecule, before deactivation, undergoes a nonadiabatic crossing from the $S_1$ to the $S_2$ potential surface, which has a minimum at $\varphi = 90^\circ$.

The $S_2$ state, owing to its forbidden character, has not been observed by conventional one-photon spectroscopy. The overall experimental knowledge of the $S_1$ potential curve is also rather limited.

The validity of the one-electron model, on which the

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Woodward-Hoffmann correlation diagrams are based, for inferring the qualitative shape of the $S_1$ and $S_2$ potential curves may in principle be established by actual computations within the framework of molecular orbital theories. In addition, theoretical computations may provide estimates of the relative energies of the $S_1$ and $S_2$ states and of the potential barrier hindering the internal rotation in the $S_1$ state.

The results of the theoretical treatments reported so far[8-10] are, in some respects, conflicting since the shape of the $S_1$ and $S_2$ potential curves and the relative energies of the two states proved to be sensitive to the empirical model Hamiltonian adopted in the computations (in most cases of Pariser-Parr-Pople type) and to the amount of configuration mixing included in the treatment.

Following a similar calculation on styrene,[11a] to which we refer for the details of the computational procedure, we have reinvestigated the problem by using an ab initio approach. A more efficient coding of all computer programs needed in the CI computations has allowed the explicit inclusion of all 96 electrons of the molecule in the molecular wave functions.

## Atomic Orbitals and Electronic Configurations

Any theoretical description of a conjugated molecule as large as stilbene inevitably suffers from limitations in the choice of the orbital basis and of the electronic configurations. The results hereafter presented have been obtained with a minimal basis set of STO/3G orbitals[12] by using a CI procedure[13] which includes all important excitations within the subspace of the $\pi$ orbitals of the molecule. The assumption inherent in the choice of the orbital basis, which does not allow an adequate description of the Rydberg states, is that the lowest excited states of the molecule have a definite valence character. On physical grounds, this assumption appears to be justified since the lowest $\pi\pi^*$ configurations are, in this molecule, well below the ionization limit and, therefore, unlikely to interact strongly with Rydberg configurations.[14] In order to determine the amount of Rydberg character of the lowest $\pi\pi^*$ states of stilbene, a preliminary investigation has been undertaken on the closely related molecule styrene, with orbital bases of increasing size and flexibility.[11b] The results have indicated that the electronic states relevant to the present discussion ($S_1$, $S_2$, $S_3$) have in fact a definite valence character.

The truncation of the CI expansion amounts to neglecting entirely the correlation between $\sigma$ and $\pi$ electrons. Actual computations of potential energy curves for the cis-trans isomerization processes of ethylene derivatives have been performed, in a few cases,[11b,15] by ab initio CI procedures, which include the excitations from the highest occupied to the lowest virtual $\sigma$ MOs, mostly distributed in the C-H bond region, and the relevant energy terms were not found important for a qualitative description of the potential energy curves. The inclusion of the $\sigma$-$\pi$ correlation in the C-C bond region, on the other hand, requires the inclusion of $\pi\sigma^*$ and $\sigma\pi^*$ configurations with higher energy. A detailed analysis is available for the $B_{1u}$ state of ethylene, which clearly shows that the $\sigma$-$\pi$ correlation in this molecular region is mainly of left-right type and is related to the ionic character of the state.[14] Since the ionic character of $S_1$ does not depend on the $\pi\pi$ overlap and on the degree of torsion around the double bond,[5] we expect that these energy terms are nearly constant along the torsional coordinate in $S_1$. On similar grounds, the $\sigma$-$\pi$ correlation is expected to have similar values in $S_1$ and $S_2$ at the twisted geometry, since both states are zwitterionic states at this geometry.[5]

## Results and Discussion

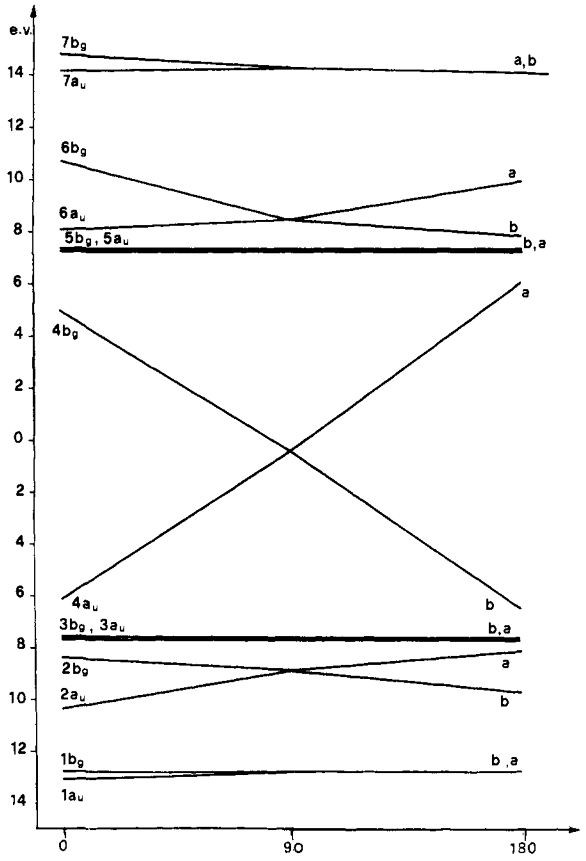

Figure 1. Correlation diagram of the orbital levels of *trans*- ($\varphi = 0°$) and *cis*- ($\varphi = 180°$) stilbene. The orbital energies at $\varphi = 90°$ have been obtained for the triplet state, where the 4a and 4b orbitals are singly occupied.

**Ordering of the Electronic States.** The configuration interaction energies, which have been obtained for the trans isomer and the twisted geometry ($\varphi = 90°$), are listed in detail in Table II. The approximate expressions of the molecular orbitals (MOs) and of the CI wave functions are given in Table I, where the orbitals and the excited states of stilbene are directly related to the orbitals and to the excited states of benzene and ethylene. The potential energy curves in Figures 2a and 2b have been drawn by interpolating the computed energies by two-term Fourier expansions.

The two lowest excited states of *trans*-stilbene are $B_u$ states: the one at lower energy, $S_1$ (B), correlates with the $B_{1u}$ and $E_{1u}$ states of benzene, while the second state, $S_3$ ($G^-$), lying about 0.25 eV above the former, correlates with the benzenic $B_{2u}$ states.

These results and the observation that the G state is in fact the lowest excited state of styrene, as shown by the very different intensities and vibrational structure of the lowest UV absorptions of stilbene[6] and styrene,[19] indicates, in agreement with previous assignments,[20] that the A band of the *trans*-stilbene UV spectrum may encompass both $^1B \leftarrow {}^1A$ and $^1G \leftarrow {}^1A$ transitions. In stilbene the first transition dominates the intensity and the polarization (long axis) of this absorption (see Table III), but when the benzene rings lose their axial symmetry because of distortions or of substitution the second transition acquires some oscillator strength.[21] The energy difference of the B, $G^-$ states is very sensitive to the amount of conjugation[22] in the $\pi$-electron system. By increasing the length of the ethylenic bond and by reducing the length of the phenyl-ethylene "single" bonds, the B state is stabilized with respect to the G state. Conversely, by twisting the two rings around the single bonds, the G state tends to become the lowest. In fact we find that the G state is the lowest excited state for the cis form, where the rings have been taken symmetrically twisted by 45° with respect to the plane of the ethylenic unit.[23]

**Table I.** Configuration Interaction Wave Functions for *trans*-Stilbene[a]

| molecular orbitals | electronic states |
|---|---|
| | A. Singlets |
| $1a_u \simeq \pi + a_{2u}{}^+$ | $1^1A_g \simeq$ ground configuration |
| $1b_g \simeq a_{2u}{}^-$ | $1^1B_u(B) \simeq B_{1u}(\text{ethyl}) + B_{1u}(L_a) + E_{1u}{}^-(B_a)$ |
| $2a_u \simeq \pi + e_{1g}{}^+$ | $+ \text{CT}$ |
| $2b_g \simeq e_{1g}{}^-$ | $2^1B_u(G^-) \simeq B_{2u}{}^-(L_b) + \text{CT}$ |
| $3b_g \simeq e'_{1g}{}^-$ | $2^1A_g(G^-) \simeq B_{2u}{}^+(L_b) + \text{CT}$ |
| $3a_u \simeq e'_{1g}{}^+$ | $3^1A_g(C,H^+) \simeq B_{1u}{}^+(L_a) + E_{1u}{}^+(B_a)$ |
| $4a_u \simeq \pi - e_{1g}{}^+$ | $+ {}^3B_{1u}(\text{ethyl}){}^3B_{1u}{}^-(L_a)$ |
| $4b_g \simeq \pi^* + e_{2u}{}^-$ | $+ {}^3B_{1u}(\text{ethyl}){}^3E_{1u}{}^-(B_a) + A_g + E_{2g}{}^+ + \text{CT}$ |
| $5b_g \simeq e'_{2u}{}^-$ | $4^1A_g(C,H^+) \simeq B_{1u}{}^+(L_a) + E_{1u}{}^+(B_a) + \text{CT}$ |
| $5a_u \simeq e'_{2u}{}^+$ | $5^1A_g(G^+) \simeq E_{1u}{}^+(B_b) + \text{CT}$ |
| $6a_u \simeq e_{2u}{}^+$ | $3^1B_u(G^+) \simeq E_{1u}(B_b) + \text{CT}$ |
| $6b_g \simeq \pi^* - e_{2u}{}^-$ | $4^1B_u(H^+) \simeq B_{1u}(\text{ethyl}) - B_{1u}{}^-(L_a)$ |
| $7b_g \simeq b_{2g}{}^+$ | $- E_{1u}{}^-(B_a) + \text{CT}$ |
| $7a_u \simeq \pi^* + b_{2g}{}^-$ | |
| | B. Triplets |
| | $1^3B_u(B) \simeq B_{1u}(\text{ethyl}) + B_{1u}{}^-(L_a) + E_{1u}{}^-(B_a)$ |
| | $+ \text{CT}$ |
| | $1^3A_g \simeq E_{1u}{}^+(B_a) + \text{CT}$ |
| | $2^3B_u \simeq B_{1u}{}^-(L_a) + \text{CT}$ |
| | $3^3B_u \simeq E_{1u}{}^-(B_b) + \text{CT}$ |
| | $3^3A_g \simeq E_{1u}{}^+(B_b) + \text{CT}$ |

[a] $\pi$ MOs belong to $a_u$ and $b_g$ symmetry. Their approximate expression as linear combinations of benzene (16) and ethylene MOs is given in the table. e and e′ are the two components of the degenerate pair of MOs, ± specifies the linear combinations where the MOs of the two benzene rings are combined in phase and out of phase, respectively, and $\pi$, $\pi^*$ are the bonding and antibonding MOs of the ethylene fragment. The notation for the electronic states is consistent with the orbital designation. $B_{1u}$(ethyl) and $A_g$ are the lowest excited states of ethylene with orbital configurations $\pi\pi^*$ and $\pi^*\pi^*$; $E_{2g}$ is the excited state of benzene generated by the double excitation $e_{1g}{}^2 \rightarrow e_{2u}{}^2$. ${}^3B_{1u}(\text{ethyl}){}^3B_{1u}$ and ${}^3B_{1u}(\text{ethyl}){}^3E_{1u}$ are the electronic states where both the ethylenic and the benzenic units are excited to triplet states. The charge-transfer components of the CI wave functions are not specified and include the excitations from the occupied MOs of the benzene rings and the ethylenic unit to the virtual MOs of the ethylene and benzene rings, respectively. Platt's notation[16,17] for the electronic states and for their components is given in parentheses. The labeling of the states is as follows: $S_1 = 1^1B_u(B)$, $S_2 = 3^1A_g(C,H^+)$, $S_3 = 2^1B_u(G^-)$, $S_4 = 2^1A_g(G^-)$.

Even by allowing for the insufficient optimization of the cis geometry, the appearance of the benzenic G state in the same energy region of the B state fits well with the experimental observation of the broad absorption band[6] of the cis form and could be related to the lower efficiency of emission at room temperature and to the large red shift[24] of the fluorescence spectrum of the cis isomer. The current interpretation[23,25,26] is that the very different absorption contours and intensities of the trans and cis isomer and the red shift of the emission of the cis isomer are essentially due to Franck-Condon effects.

At higher energies we found two allowed $B_u$ states (${}^1G^+$, ${}^1H^+$). The ${}^1G^+$ state is complementary to the ${}^1B$ state and ${}^1H^+$ is the linear combination of two $E_{1u}$ benzenic states. Given the absolute intensities of the ${}^1G^+ \leftarrow {}^1A$ transition and ${}^1H^+ \leftarrow {}^1A$ transition (Table III), the two states are the most likely candidates for the B and C absorptions of *trans*-stilbene. To discriminate between the two possible assignments polarization data for the two absorptions would be required (see Table III).

For the states of $A_g$ symmetry the only available information is provided by a recent investigation by two-photon spectroscopy.[27] This study shows a strongly allowed excitation band lying between the one-photon A and B bands, with the intensity maximum at about 1 eV above the origin of the $S_1 \leftarrow S_0$ one-photon absorption, which for its intensity distribution must be attributed to a state whose geometry is strongly displaced and/or distorted with respect to the ground-state equilibrium geometry. According to the present calculation this band is to be attributed to the $3^1A_g$ state, which we label $S_2$ as in ref 7. In fact, most of the $A_g$ states in Table I have the character of benzenic excited states. For all of them the displacements of the ring coordinates from the ground-state equilibrium values are expected to be small as found for benzene and torsional barriers are likely to be found at the twisted geometry. Selected examples are shown in Figures 2a and 2b. In this respect the only exception is the $S_2$ state, where the ethylenic unit and the benzene rings are both partially excited to triplet states. The relative weight of these components of the molecular wave function increases to 50% at the twisted geometry, when the $\pi$ interaction in the central bond vanishes by symmetry. This state has a higher energy than the ${}^1B$ and ${}^1G^-$ states in the trans and cis isomers, but becomes the lowest at the twisted configuration ($\varphi = 90°$), where it exhibits a deep relative minimum. The minimum of the potential energy curve along the torsional coordinate is therefore highly displaced with respect to the ground state. Thus $S_2$ appears to be the only $A_g$ state in the proper energy region and with the proper potential energy curve compatible with the spectroscopic findings of ref 27.

The intensity of the two-identical-photon transition $0 \rightarrow f$, where 0 and f label the initial and the final states of the transition, is proportional to the square of the elements of the tensor $S_{0f}$:[28]

$$S_{0f} = \sum_i \langle o|\mathbf{p}|i\rangle\langle i|\mathbf{p}|f\rangle/(E_i - \hbar\omega) \qquad (1)$$

where $\mathbf{p}$ is the dipole moment operator, $i$ and $E_i$ are the intermediate electronic states and their energies, and $\hbar\omega$ is the photon energy.

In a molecular orbital expansion, the $S_2$ state is described by electronic configurations which are doubly excited with respect to the ground state. Among these, the $(4a)^2 \rightarrow (4b)^2$ configuration has the largest coefficient (0.593 for the trans isomer and 0.671 for the twisted geometry). The $S_1$ state, which is strongly allowed in the one-photon spectra, is essentially described by the $(4a) \rightarrow (4b)$ configuration. Thus, by using eq 1 for the $S_2 \leftarrow S_0$ two-photon transition, the $S_1$ state appears to provide a large contribution to the transition intensity, since both transition moments $\langle S_0|\mathbf{p}|S_1\rangle$ and $\langle S_1|\mathbf{p}|S_2\rangle$ are large with approximate values $\langle 4a|\mathbf{p}|4b\rangle$, while the energy difference at the denominator has the smallest possible value, being $S_1$, the lowest excited state. A similar analysis reveals that the other $A_g$ states in the same energy range, notably the $2^1A_g$ and $4^1A_g$, have much lower intensity. Thus the attribution to $S_2$ of the observed two-photon band is consistent with the intensity of the two-photon absorption.

The full inclusion of double and higher order excitations is therefore essential for a proper description of the $S_2$ state. The effect of the extension of the configuration mixing on molecular energies is most clearly seen by comparing the $S_2$ potential curves in Figures 2a and 2b. The geometry of the ethylenic unit is also very important for the accurate prediction of the $S_2$ potential curve (compare the full and dashed $S_2$ curves in Figure 2b).

## Potential Energy Curves

**Ground State.** In agreement with previous estimates,[9] which indicate that the theoretical value of the trans to cis barrier hindering internal rotation in the ground state should be of the order 100–130 kcal/mol at the SCF level, our SCF values are in the range 105–112 kcal/mol for the different geometries which have been considered in the computations. The corresponding CI results are 88–90 kcal/mol in the limited CI and ~70 kcal/mol in the more extended CI. The limit of a full CI

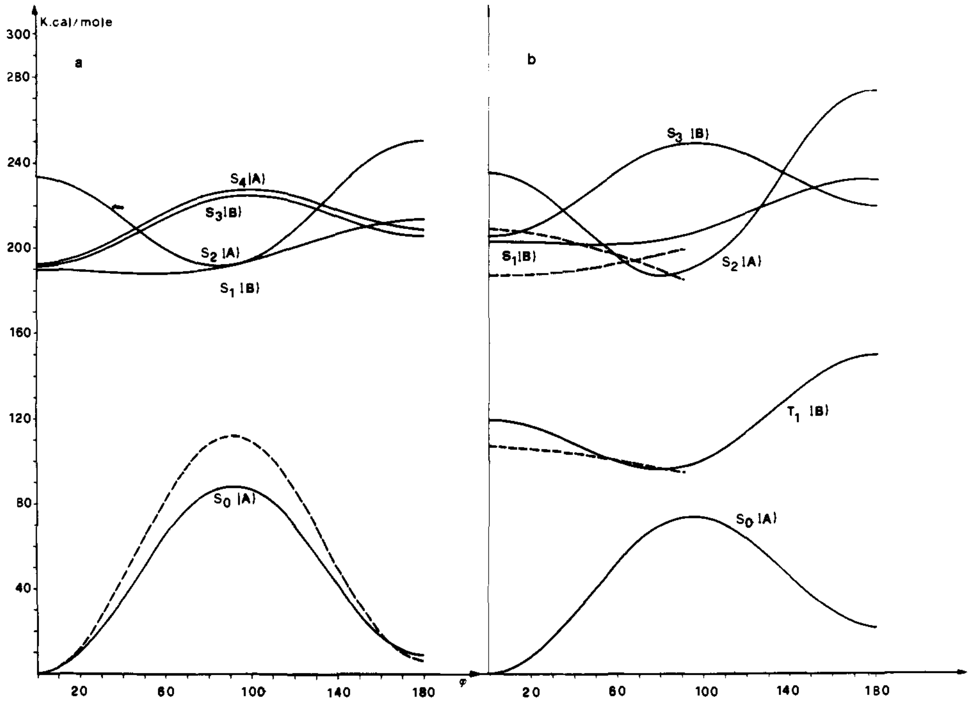

**Figure 2.** Potential energy curves for the ground and lowest triplet and singlet excited states of stilbene. Following the notation of ref 7, the $3^1A_g$ state of Table I is designated as $S_2$. $S_1$, $S_3$, and $S_4$ are the $1^1B_u$, $2^1B_u$, and $2^1A_g$ states, respectively: (a) limited CI; (b) extended CI. The dashed curve in Figure 2a is the ground-state SCF potential energy curve. The dashed curves in Figure 2b are the $T_1$, $S_1$, and $S_2$ potential curves which have been computed with bond lengths in the ethylenic fragment appropriate to the $S_1$ and the $S_2$ states.

**Table II.** Configuration Interaction Energies for the Ground and Lowest Excited Singlet and Triplet $\pi\pi^*$ States for $\varphi = 0°$ and $\varphi = 90°$[a]

| $\varphi = 0°$ | (a) | (b) | $\varphi = 90°$ | (a) | (b) |
|---|---|---|---|---|---|
| | | | Singlet States | | |
| $A_g$ | −530.629 250 | −530.727 225 | A | −530.495 708 | −530.616 769 |
| $B_u$ | −530.349 005 | −530.429 341 | A | −530.333 630 | −530.433 825 |
| $B_u$ | −530.334 567 | −530.420 707 | B | −530.336 252 | −530.411 501 |
| $A_g$ | −530.334 285 | −530.419 237 | A | −530.269 417 | −530.366 348 |
| $A_g$ | −530.276 859 | −530.396 745 | B | −530.269 993 | −530.362 341 |
| $A_g$ | −530.253 860 | | B | −530.240 483 | |
| $A_g$ | −530.244 191 | | B | −530.207 338 | |
| $B_u$ | −530.244 159 | | B | −530.206 143 | |
| $B_u$ | −530.229 289 | | A | −530.205 751 | |
| | | | Triplet States | | |
| $B_u$ | | −530.557 264 | B | | −530.577 315 |
| $A_g$ | | −530.491 966 | B | | −530.366 240 |
| $B_u$ | | −530.463 314 | A | | −530.357 116 |
| $B_u$ | | −530.418 129 | A | | −530.346 675 |
| $A_g$ | | −530.417 563 | B | | −530.345 129 |

[a] The CI energies were obtained by (a) a limited CI treatment which includes all single and double excitations with lowest energy within the subspace of the π orbitals in Table I; (b) a more extended CI treatment which includes higher order excitations. The geometry of the stilbene molecule is appropriate to the lowest $B_{1u}$ state.[16] At $\varphi = 90°$ the lowest excited A and B states correlate with the electronic states $1^1B_u$ and $3^1A_g$ of Table I.

**Table III.** Absolute Intensities ($f$) and Polarizations of ${}^1B_u \leftarrow {}^1A_g$ Transitions of Stilbene. Limited CI Results

| excited state | $f$ | polarization |
|---|---|---|
| $1^1B_u$ | 1.5 | long axis |
| $2^1B_u$ | 0. | |
| $3^1B_u$ | 0.4 | perpendicular to long axis |
| $4^1B_u$ | 0.3 | long axis |

treatment over the π orbital basis was estimated with a more extended CI treatment including all single and double excitations arising from the ground and the $(4a)^2 \rightarrow (4b)^2$ configurations.[29] The height of the barrier was found again to be ~70 kcal/mol, which should be compared with the experimental value of ~50 kcal/mol.[30] It appears that the electronic correlation within the π-electron system accounts for most of the difference between the SCF and the experimental value[30] of the barrier to internal rotation.

The computed cis-trans energy difference is 5.7 kcal/mol at the SCF level, and is larger (20 kcal/mol) with the CI treatment described in ref 11a. With the inclusion of all single and double excitations from the ground configuration the cis-trans energy difference becomes 5.4 kcal/mol, in close agreement with the experimental value,[31] thus suggesting that σπ configurations are unlikely to give large contributions to the conformational energy of the molecule.

**Lowest Triplet State.** For all values of the torsional coordinate φ, the lowest triplet state lies well above the ground state potential curve. The nonadiabatic model for the thermal trans-cis isomerization in the ground state, involving intersystem crossing to the $^3$B state, which was suggested by the results of previous theoretical investigations,[9,32] does not receive support by our results and is not required to explain the activation energy of the process.

The $T_1$ potential curve has a minimum at the twisted geometry, which becomes less pronounced by a more appropriate choice of the geometry of the trans isomer, and maxima at the cis and trans geometries. The picture is therefore consistent with the model proposed by Hammond et al.[33] to interpret the cis–trans photosensitized isomerization. According to this model the trans ($T_t$), the cis ($T_c$), and the "phantom" ($T_p$) triplets would be different points of the same adiabatic energy curve with relative energies $E(T_p) < E(T_t) < E(T_c)$.

**Lowest Singlet Excited States.** The potential energy curve of $S_2$, which is the lowest excited singlet state for values of the $\varphi$ coordinate close to 90°, has been discussed in a previous section. The energy curve of the singlet state (B), which is rather flat and monotonically increasing going from the trans to the cis form, does not present the high barrier to torsion[34] which was derived by Dyck and McClure[6] by spectroscopic measurements. Their estimate was based on the observation that, in the A region of the absorption spectrum of the trans isomer, the frequency of the leading vibration (1635 cm$^{-1}$), which was assigned to the ethylenic double bond stretching, does not generate long progressions in the spectrum and is apparently unchanged (1599 cm$^{-1}$) after excitation. An empirical correlation between the double bond stretching frequency and the torsional barrier was then used to make the estimate of the barrier (~40 kcal/mol) in the singlet B state. We notice that long progressions of vibrational frequencies are missing in the solid-state spectra, where internal rotation is prevented by intermolecular forces,[35] but is present in low-temperature solution spectra,[36] where a five-term progression has been observed and attributed to the double-bond vibration.[36] The displacement parameter $j$,[37] which is deduced from the intensity distribution of the vibrational peaks in the progression, is $\geqslant 1.5$ and would indicate that the bond length of the central bond $R_{CC}$ is greater than 1.43 Å in the singlet state B, which clearly contrasts with Dyck and McClure's estimates.[6]

We interpret these apparently contradicting spectroscopic observations by admitting, in agreement with the computed CI energies, that the C—C and C═C stretching vibrations in the ethylenic unit ($\nu_2$, $\nu_4$ in ref 6) are strongly coupled in the excited state. The empirical correlation between the double-bond character and the vibrational frequency does not hold, in this case, for the large variation of the vibrational coordinate in the excited state.

The mechanism, emerging from the computed levels and potential energy curves in Figure 2a, for the main route of the decay of the optically excited $S_1$ state and of the direct photoisomerization is that proposed in ref 7. The excitation to the B state is followed by internal rotation about the central bond leading to a temperature-dependent $S_1 \rightsquigarrow S_2$ internal conversion. The preexponential factor found experimentally[6,39-41] is $10^{12}$ s$^{-1}$ and is typical for spin-allowed radiationless processes.[35] The activation energy has been found theoretically (Figure 2a) to be very small for the trans isomer and vanishing for the cis isomer. Experimentally, it has been estimated to be 2.5–4.0 kcal/mol[6,39-41] for the trans isomer and must be vanishingly small for the cis isomer, since its excited singlet has a lifetime of 7 ps.[33] In view of the different symmetry of the $S_1$ and $S_2$ states, the actual crossing between $S_1$ and $S_2$ is vibronically induced by a B symmetry type vibration, conceivably localized in the ethylenic moiety. Once the molecule is in the $S_2$ state, after vibrational relaxation, it undergoes internal conversion $S_2 \rightsquigarrow S_0$ in the twisted geometry producing both isomers and thereby isomerization.

We note that the lack of any observation by single-photon spectroscopy of the biradicaloid state with the minimum at $\varphi = 90°$, i.e., a weak absorption on the red edge of the $S_1 \leftarrow S_0$ absorption and a broad red-shifted emission, indirectly supports the assignment to the optically forbidden $S_2$ state.

## Conclusion

The present results explain the available experimental data, provided by spectroscopic, photophysical, and photochemical studies. In particular, the two-photon band observed by Stachelek et al.[27] is attributed to the $S_2$ state, whose potential energy curve has a minimum at $\varphi = 90°$. The largest component of the CI wave function for this state is provided by the doubly excited configuration $(4a)^2 \rightarrow (4b)^2$, which correlates with the ground configuration of the cis isomer. The present results support a nonadiabatic mechanism of the cis–trans isomerization, where the $S_2$ state is the intermediate state of the $S_1$ deactivation.

**Acknowledgments.** After this work was completed we were informed that Drs. P. Tavan and K. Schulten have studied theoretically the excited states of stilbene with the Pariser–Parr–Pople method, arriving at similar conclusions. We thank Dr. Schulten for giving us a preprint of his paper. P.P. acknowledges financial support from CNR (Rome) and G.O. a fellowship from A. von Humboldt Stiftung, during which this work was completed, and the support from NATO (Grant 1190).

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# Ab Initio Investigation of the Electronic Properties of Cyclopropyl, α-Fluorocyclopropyl, and α-Chlorocyclopropyl Anions

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**Abstract:** Electronic structure calculations using a 4-31G basis set have been carried out on cyclopropyl and α-halocyclopropyl anions. The results show substantial barriers to inversion of the X atom in the species $C_3H_4X^-$ about the plane of the cyclopropyl ring. Substitution of halogens for hydrogen in the α position does not appear to stabilize the anion.

## Introduction

Meyers et al.[1a-g] have shown that α-halo ketones may follow a variety of reaction pathways when treated with powdered potassium hydroxide in *tert*-butyl alcohol, depending on the nature of the α-halo ketone. A striking example is the contrast between α-haloisopropyl ketones and α-halocyclopropyl ketones. At 25 °C α-bromo- and α-chloroisopropyl phenyl ketone are rapidly converted into α-hydroxyisopropyl phenyl ketone. Under identical conditions α-chlorocyclopropyl phenyl ketone is quantitatively cleaved within 2.5 h into chlorocyclopropane and potassium benzoate, and α-bromocyclopropyl phenyl ketone with 2 h quantitatively undergoes 50% cleavage into bromocyclopropane and potassium benzoate and 50% dehydrobromination. Likewise, mono- and bis(α-chlorocyclopropyl) ketone are quantitatively cleaved into chlorocyclopropane and, respectively, potassium cyclopropanoate and potassium α-chlorocyclopropanoate. On the other hand, cyclopropyl phenyl ketone and α-methylcyclopropyl phenyl ketone were quantitatively *recovered* after similar treatment even after many hours under reflux (82 °C). Meyers suggested that the facile cleavage reactions reflect the low transition energy associated with the substantial stability of the α-chloro- and α-bromocyclopropyl anions (or the metal–anion pairs) formed in this process. This suggestion has been supported by preliminary calculations.[1c,e,h]

It has also been shown[2,3] that cleavage of optically active cyclopropanes involves the chiral anion as an intermediate but that the resulting cyclopropanes retain their original configuration. This would suggest the possibility of a significant barrier to inversion about the plane of the cyclopropyl ring for the anion. Koeppl[4] has used valence force field methods to estimate a barrier to inversion for the cyclopropyl anion of 19 kcal/mol. On the other hand, Clark and Armstrong[5] using a small Gaussian-type basis set have determined the energy difference between the bent and planar cyclopropyl anion to be only 1.66 kcal/mol.

The purpose of the present study is to determine the relative energies of the planar and bent $C_3H_4X^-$ anions where X is H, F, or Cl and thus to determine the barrier to inversion in these anions. We further wish to determine the stabilizing effect, if any, of substitution of fluorine or chlorine for hydrogen at the α position. For this purpose we use the method of "isodesmic" reactions and also compare the electron population distributions in the three anions.

## Method and Results

Calculations were first carried out using the semiempirical MINDO/3 program[6] to obtain optimized geometries for the α-halocyclopropyl anions. For comparative purposes similar calculations were carried out on the related halocyclopropanes and cyclopropane and the geometries obtained compared, where possible, with experimental data. The MINDO/3 program was also used to optimize the geometries of the species $CH_3\bar{C}XCH_3$ where again X is hydrogen, fluorine, or chlorine.

Using the optimized geometries for the cyclopropyl anions obtained using the MINDO/3 program a series of calculations were carried out for each anion using the GAUSSIAN 70 ab initio program[7] and a 4-31G basis set. In these calculations the dihedral angle XCCC was varied from 90° through 180° op-

0002-7863/79/1501-3497$01.00/0