

- comes from the fact that the two lowest energy π electrons occupy an MO composed of more contracted AOs than do the remaining pair of π electrons, so interorbital electron repulsion is smaller at the SCF level.
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The Lowest Energy Excited Singlet States and the Cis-Trans Photoisomerization of Styrene

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Abstract: Potential energy curves, as functions of the torsional angle around the ethylenic bond, were obtained for the ground and for a few singlet excited states of styrene by ab initio configuration interaction methods and an STO/3G minimal basis set of Gaussian atomic orbitals. Limited and more extended CI computations were performed to investigate the stability of the computed potential energy curves with respect to the size of the CI expansion and to the inclusion of $\sigma\pi^*$ and $\pi\sigma^*$ electronic configurations. The computed level ordering and oscillator strengths are in agreement with the available experimental data and the first excited state is predicted to have a potential curve with a minimum at $\theta = 0^\circ$ (planar geometry). The inclusion of doubly excited configurations and the variation of the C-C bond lengths in the vinyl group during internal rotation are found to affect significantly the shape of the potential energy curves. The relevance of the theoretical results to the theory of the cis-trans isomerization is briefly discussed.

A number of spectral properties of diphenylpolyenes have been recently determined.⁴⁻⁵ In particular, the fluorescence lifetimes of these molecules were found to be much larger than the values estimated from the measured absorption intensities. Moreover, the apparent origins of the absorption and of the emission spectra of diphenylpolyenes are not coincident and have different shifts in solution. All these properties suggest that in these molecules the emission originates from an optically forbidden state lying just below the allowed state responsible for absorption.

Experimentally, direct evidence for the existence of such a forbidden state has been found for diphenyloctatetraene⁴, diphenylbutadiene,⁶ and the visual chromophore retinal.⁵

Theoretically, Pariser-Parr-Pople type computations on the first members of the polyene series, i.e., butadiene, hexatriene, and octatetraene,⁷ support this assignment. In fact, when doubly excited (DE) configurations are included in the configuration interaction (CI) treatment, a singlet state of A_g symmetry, with dominant contributions from DE configurations, is predicted to be the lowest singlet state and to lie just below the optically active singly excited (SE) B_u state. Nonempirical computations on butadiene⁸ and benzene⁹ also gave a similar sequence for the singlet states.

Subsequently, DE states were proposed to play an important role in the photoisomerization reaction of stilbene.¹⁰ According to this model, in analogy with the results of van der Lugt and Oosterhoff on the butadiene photocyclization,¹¹ the DE 1A_g state, which in this molecule arises from an electronic excitation mainly localized in the ethylenic fragment, has higher energy than the lowest B_u state for planar geometry but lower energy for twisted geometries, thus becoming instrumental in the process of direct photoisomerization.

In order to verify this hypothesis and to investigate the role of DE configurations in determining the order of the excited states, we have performed CI computations on styrene and obtained theoretically the potential energy curves for torsion around the double bond for the ground and for the lowest excited singlet states. Styrene was chosen rather than stilbene, since this molecule, being smaller, makes it possible to examine the main features of the cis-trans isomerization by more accurate theoretical procedures.

Method of Computation

The bond lengths of the benzene ring and all bond angles were fixed to standard values ($R_{CC} = 1.397 \text{ \AA}$, $R_{CH} = 1.084 \text{ \AA}$, $\angle CCC = \angle HCC = 120^\circ$). The torsional coordinate θ of the methylene around the double bond and the C-C (R_s) and C=C (R_d) bond distances¹² in the vinyl group were allowed to vary by taking

$$\begin{aligned} \theta &= 0, 40, 80^\circ \\ R_s &= 1.467 \text{ \AA} - \Delta R \\ R_d &= 1.344 \text{ \AA} + \Delta R \\ \Delta R &= 0, 0.04, 0.08 \text{ \AA} \end{aligned} \quad (1)$$

The three ΔR values are appropriate respectively to the ground, to the first SE state,¹² and to the DE state of ethylenic type, where the molecule is better described as $\text{Ar}::\text{CH}::\text{CH}_2$. The molecular orbitals (MOs) were expressed as linear combinations of STO/3G atomic orbitals.¹³ CI energies of two levels of accuracy were next computed for nine molecular geometries in order to obtain two-dimensional sections of the potential energy surfaces of the ground and lowest excited

Table I. Relative Energies (au) of S_0 , S_1 , S_2 , and S_3 States of Styrene and Major Contribution to the CI Wave Functions^a

State	Energies		Wave functions
	Limited CI	Extended CI	
(a) S_0	0.0 (-303.881 50)	0.0 (-303.959 30)	[0]
S_1	0.289 60	0.205 94	0.56 [28,30] - 0.59[27,29]
S_2	0.361 13	0.291 60	0.38 [28,31] - 0.43[26,29] + 0.55[28 28,29 29]
S_3	0.345 44	0.348 91	[28,29]
(b) S_0	0.116 51	0.105 79	0.85[0] - 0.46[28 28,29 29]
S_1	0.307 26	0.269 26	0.54[28,30] + 0.38[27,29] - 0.53[28 28,29 30]
			- 0.35[27 28,29 29] + 0.57[26 28,29 30]
S_2	0.323 14	0.271 14	0.37[0] - 0.26[28,31] + 0.35[26,29] + 0.67[28 28,29 29]
			+ 0.31[27 28,29 30]
S_3	0.356 24	0.354 08	[28,29]
(c) S_0	0.116 22	0.104 07	
S_1	0.307 24	0.266 33	
S_2	0.323 01	0.274 37	
S_3	0.352 16	0.347 54	

^a (a) $\Delta R = 0$, $\theta = 0^\circ$; (b) $\Delta R = 0.08 \text{ \AA}$, $\theta = 80^\circ$; (c) $\Delta R = 0.08 \text{ \AA}$, $\theta = 80^\circ$ with $\sigma\pi^*$ and $\pi\sigma^*$ configurations included. In parentheses the total molecular energy of the S_0 state.

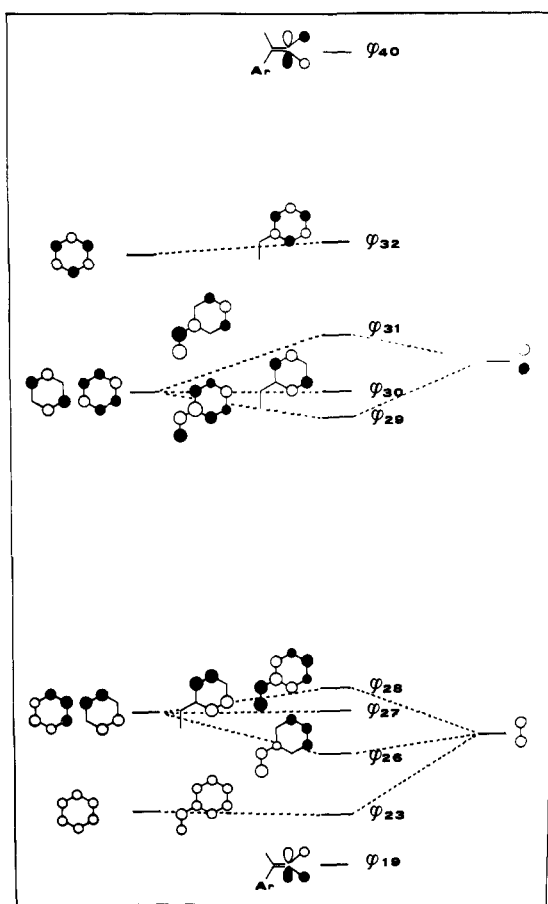


Figure 1. Correlation diagram of the highest occupied and of the lowest virtual MOs of the styrene with the MOs of benzene and ethylene.

electronic states in the Born-Oppenheimer approximation. The simpler CI expansion includes the SE and DE configurations of lower energies involving electronic excitations from the six highest occupied to the five lowest virtual MOs. The more accurate CI includes all second-order interactions larger than 5×10^{-5} .¹⁴ For twisted geometries, the separation of the MOs into σ and π symmetries is no longer possible and therefore $\sigma\pi^*$ and $\pi\sigma^*$ configurations contribute to the potential energy of the molecule. The importance of these effects has been estimated by including in the CI expansion the excitations from the bonding and to the antibonding σ MOs localized in the vinyl group. The number of configurations employed is ~ 70

in the simpler CI and ~ 700 in the more accurate description. The approximate procedure described in ref 14 was used to solve the secular equation.

Although transition energies computed with minimal orbital bases are generally much higher than the experimental values, the energy sequence and the energy difference between the lowest SE and DE states in Table I is believed to be correct. For the benzene molecule the energy difference between the lowest SE ${}^1B_{2u}$ and DE ${}^1E_{2g}$ states, which is estimated as 3.36 eV in the minimal basis description,¹⁵ becomes 3.33 eV in the more accurate computation with an extended set of atomic orbitals by Hay and Shavitt.¹⁶

Results

A. Ground State Molecular Orbitals. As in Hückel-type calculations the MOs $\{\varphi\}$ of styrene have the C_{2v} pseudosymmetry of the monosubstituted benzene derivatives. Only one of the two E_{1g} MOs of the benzene molecule may interact with the ethylenic π bonding MO and the two resulting MOs describe the conjugation between the benzene ring and the substituent. φ_{28} is mainly localized on the ring and the φ_{26} on the ethylenic fragment. Similarly the interaction of one of the two E_{2u} benzene MOs and the π^* ethylene MO generates in styrene two MOs with bonding and antibonding character with respect to the aryl-ethylene bond. All remaining π MOs of benzene keep their identity in styrene. The orbital scheme in Figure 1 is consistent with the photoelectron spectrum of the molecule.¹⁷ φ_{19} and φ_{40} are the highest occupied and the lowest virtual σ MOs of the terminal methylene group. The electronic excitations from/to these MOs are expected, for energy and symmetry reasons, to contribute to the potential curves of the molecule more than all remaining $\sigma\pi^*$ and $\pi\sigma^*$ configurations.

B. Single Configuration Energies. The potential curves of the singlet configurations with lowest energy are plotted in Figure 2 as functions of the torsional angle and of the bond lengths variation ΔR , since they provide a better understanding of the CI effects to be discussed below. The first excited configuration is [28,29].¹⁸ This is mainly a $\pi \rightarrow \pi^*$ excitation in the ethylenic double bond region with a strong reduction of the relevant bond order as shown by its flat potential curve. The SE configurations [27,29] and [28,30] do not affect the bond order of the ethylene moiety and, therefore, exhibit torsional behavior similar to that of the ground configuration. The DE configuration [28 28,29 29] is correlated with the ground configuration, the two being degenerate at 90° . The energy variation of the two configurations with θ is similar to that observed for the corresponding configurations in ethylene and

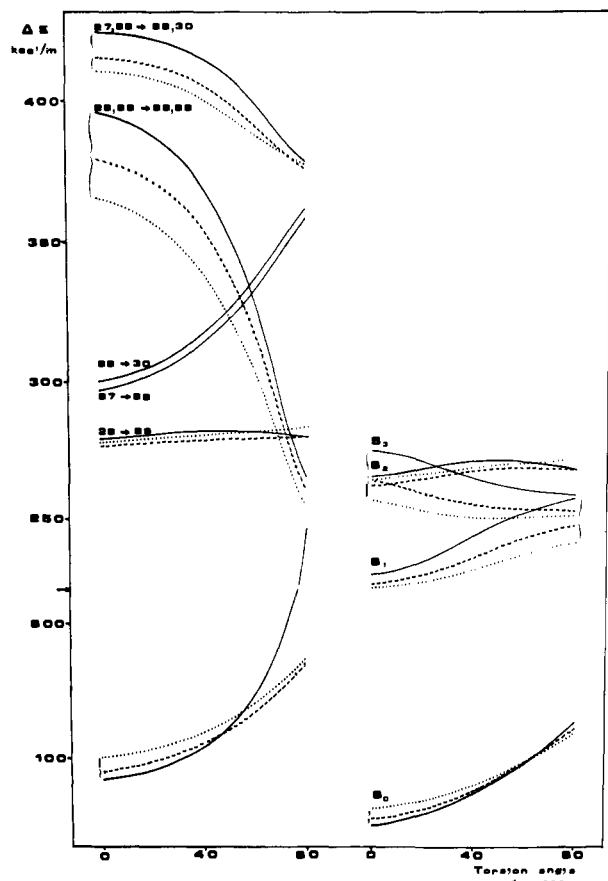


Figure 2. Potential curves for single determinant (left) and CI wave functions. Curves within the same bracket refer to the same state for different C-C bond lengths in the vinyl group: $\Delta R = 0$ full line; $\Delta R = 0.04$ Å, dashed line; $\Delta R = 0.08$ Å, dotted line. Two different scales are adopted in the lower and in the upper part of the figure.

their behavior may be similarly explained. Other DE configurations show an energy minimum at $\theta = 90^\circ$, but this is less pronounced than that observed for the [28 28, 29 29] configuration.

C. Configuration Interaction Energies. The CI mixes states with identical pseudosymmetry leading to the potential curves displayed in Figure 2. The ground and the [28 28, 29 29] DE configurations have the largest interaction within "A₁" configurations. The resulting barrier to the internal rotation in the ground state is much smaller than in the single configuration description. The complementary state, [28 28, 29 29], with minor contributions from [28, 31], [26, 29], and [27 28, 29 30] configurations, is the second excited state (S_2) and has a twisted equilibrium geometry with $\theta = 90^\circ$, where it is nearly degenerate with S_1 . The first excited state S_1 is the linear combination of the two "B₂" configurations [27, 29] and [28, 30] with important contributions from DE configurations [28 28, 29 30] and [27 28, 29 30] and [27 28, 29 29]. The potential energy curve of S_1 has only a shallow minimum at $\theta = 0^\circ$, since SE and DE energy curves have opposite behavior with θ . The description of the first excited singlet states and the potential curves are sufficiently stable with respect to the size of the CI expansion. For comparison, essential numerical data concerning the restricted and the more extended CI are reported in Table I for two geometries. The variation of the bond lengths in the vinyl group has large effects on the computed transition energies and on the torsional energies of the molecule, which, in the ground state, is reduced by as much as 20 kcal/mol, by changing ΔR .

D. Effect of $\sigma\pi^*$ and $\pi\sigma^*$ Configurations. The main features of the potential curves along the torsional coordinate in con-

jugated molecules are generally believed to be governed by the $\pi \rightarrow \pi^*$ electronic excitations. For this reason, most ab initio and semiempirical computations of torsional barriers in these molecules were performed under the assumption of a complete σ/π separability. In this respect, an exception is the calculation on styrene by Bruni et al.,¹⁹ based on the CIPSI method²⁰ and on the CNDO parametrization, which indicates that $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ excitations affect substantially the potential curves of the ground and lowest excited states. To investigate this point, excitations involving the MOs φ_{19} and φ_{40} were added to the configurational bases. As shown by the comparison with the previous CI results (Table I) the energy variation due to the added configurations is less than 2 kcal/mol in the ground state, and has similar values in the S_1 and S_2 states and a slightly larger value in S_3 . Since we have estimated from the MO coefficients that 40% of the relevant $\sigma\pi^*$ and $\pi\sigma^*$ configurations have been included by this procedure, we conclude that their contributions to the torsional barriers of the molecule are similar in the S_0 , S_1 , and S_2 states and not higher than 10 kcal/mol. Therefore, these energy terms cannot produce either a crossing of the potential energy curves S_1 and S_2 or an absolute minimum at the twisted geometry in the S_1 potential curve.

Discussion

The barrier to the internal rotation of styrene in the ground state is evaluated to be 71 kcal/mol, which should be compared to the measured torsional barriers of ethylene (63 kcal/mol)²¹ and stilbene (48 kcal/mol).²² The equilibrium geometry of S_1 is estimated to be planar and the geometry of the vinyl group in the excited state S_1 corresponds to $\Delta R = 0.04$ Å.

These results are in agreement with the rotational contour analysis of the 0-0 band in the $S_1 \leftarrow S_0$ transition^{12,23} but not with the potential curve hypothesized by Hui and Rice.²⁴ These authors have been able to measure the fluorescence lifetimes from single vibronic levels of S_1 . With the assumption that the rate of nonradiative process may be taken equal to that of a similar molecule not showing rotational isomerism (ethynylbenzene), the isomerization rate constant was estimated to be $2 \times 10^7 \text{ s}^{-1}$, to be independent of the vibrational energy excess, and to exhibit a weak inverse deuterium effect.

These results have been interpreted²⁴ by assuming a potential curve in the S_1 state with an absolute minimum at $\theta = 90^\circ$ and a relative minimum at $\theta = 0^\circ$. The Stoke's shift (518 cm^{-1}) measured in solution between the origins of the $S_1 \leftarrow S_0$ absorption and of the $S_0 \leftarrow S_1$ emission was taken in support of the proposed potential curve.

In our opinion, the Stoke's shift is not by itself a proof of the existence of a second minimum of the potential curve. It could be due to solute-solvent interactions, since the shift is not observed in the gaseous phase. In fact, the 0-0 band of the fluorescence vapor spectrum has been assigned to the 347 56- cm^{-1} band,²⁵ which is nearly coincident with the 347 59- cm^{-1} 0-0 absorption band.

A potential curve for S_1 with a low torsional barrier at $\theta = 90^\circ$ is an alternative hypothesis which accounts for the intensity distribution in the $S_1 \leftarrow S_0$ absorption spectrum and explains, according to the theory of radiationless transitions,²⁶ the lack of a direct isotope effect in the isomerization rate constant in the high-temperature limit ($h\nu < kT$). The value of the isomerization rate constant, which is 10^5 smaller than the usual preexponential factor for motions on the same energy curve, does indeed suggest a small barrier of the order of 6 kcal/mol. Since entropy effects may contribute substantially to the free-energy change of the molecule upon torsion,²⁷ and since the use of a more flexible orbital basis in the CI computations, together with a more complete geometry optimization and the full inclusion of the $\sigma\pi^*$ and $\pi\sigma^*$ configurations, is

Table II. (a) Computed and (b) Experimental Oscillator Strengths for the $S_1 \leftarrow S_0$, $S_2 \leftarrow S_0$, and $S_3 \leftarrow S_0$ Transitions

Transition	Oscillator strengths		Polarization
	a	b	
$S_1 \leftarrow S_0$	8.3×10^{-3}	2.0×10^{-2}	Long axis ³⁰
$S_2 \leftarrow S_0$	5.0×10^{-4}		
$S_3 \leftarrow S_0$	0.61 ³¹	0.24	

likely to reduce the computed torsional barriers in the ground and first excited states, the value of the barrier obtained in the present study (16 kcal/mol) for the S_1 state is compatible with the hypothesis of a low torsional barrier in this state.

The ethylenic SE state is not involved in the isomerization process of styrene as it lies at higher energies for all geometries. In this connection, the most important difference with respect to the semiempirical energies and wave functions of ref 19 is the almost pure character of the ethylenic SE state S_3 , while benzene- and ethylene-like excitations are strongly mixed in the CIPSI wave functions. Since all essential interactions are believed to be included in the present treatment, we attribute the difference to the empirical parametrization used in ref 19, where standard CNDO/2 parameters have been adopted.

The transition moments and the polarizations of the lowest transitions provide a sensitive test of the accuracy of the description of the excited states. It is well known that standard calculations including only SE configurations yield the wrong polarization ratio for the lowest weak electronic transition of styrene.²⁹ Theoretical and experimental values for the oscillator strengths of the lowest energy transitions of styrene are given in Table II. Both the magnitudes of the oscillator strengths and the polarizations of the two transitions $S_1 \leftarrow S_0$, $S_3 \leftarrow S_0$ are correctly predicted. The $S_2 \leftarrow S_0$ transition has not been observed experimentally since it is weak and conceivably hidden by the strong $S_3 \leftarrow S_0$ transition. The long axis polarization of the $S_1 \leftarrow S_0$ transition deserves some comments, since it contrasts with the local " B_2 " symmetry of the excited state. In fact, the two components of the S_1 state (see Table I) give contributions of nearly equal magnitude and opposite sign to the short axis component of the transition dipole. Therefore charge transfer from or to the substituent determines the long axis polarization of the transition dipole. It should be also noticed that the corresponding transition in D_{6h} symmetry is forbidden.

As to the general problem of the role of DE configurations in describing the lowest excited states and, therefore, the photochemical behavior of these molecules, these calculations show, in agreement with previous work,³² that DE configurations are essential in this connection. In the specific case considered, the mixing of the DE configurations strongly affects the nature of the lowest excited state and its barrier height. Even if the covalent DE S_2 state lies in the region of the lowest singlet state as found for polyenes, the involvement of the S_2 energy surface in the isomerization reaction is not re-

quired by our energy diagram. However, given the small energy difference involved it is possible that in similar molecules, as found for diphenylpolyenes, the S_2 state becomes the lowest excited singlet state. Its role in cis-trans isomerization is expected to become important, especially when the S_1 potential energy curve exhibits a higher barrier at $\theta = 90^\circ$. Stilbene, for which low-temperature high-resolution spectra³³ suggest a barrier of 30–40 kcal/mol at $\theta = 90^\circ$ for the S_1 state, could belong to this class of molecules.

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