Theoretical Study of the Electronic Spectrum of *trans*-Stilbene

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The electronic spectrum of *trans*-stilbene in the energy range up to 6 eV has been studied using multiconfigurational second-order perturbation theory (CASPT2). The study includes a geometry determination of the ground state. In all, 12 singlet and one triplet excited states were studied. The calculated spectrum makes it possible to assign the valence excited singlet states corresponding to the three bands observed in the low-energy region of the one-photon absorption spectrum. The most intense feature of the calculated spectrum corresponds to the $1^1A_g \rightarrow 2^1B_u$ transition at 4.07 eV. The weakly allowed 1^1B_u state was found 0.3 eV below 2^1B_u. Transition to the 3^1A_g state, computed at 4.95 eV, is responsible for the main band observed in the two-photon absorption spectrum. This state has a large weight (around 43%) of doubly excited configurations. The first singlet−singlet Rydberg transition (3*s*) appears at 5.33 eV and is weak. Implications of the present findings on the trans → cis photoisomerization process in the singlet manifold are discussed. A photoadibatic reaction involving the two lowest states of B_u symmetry seems to be the most plausible mechanism to explain the origin of the small barrier observed on the S_1 surface.

1. Introduction

Stilbenoid compounds have been studied for more than 60 years. Because of their important role in many areas of chemistry, the interest in the field remains. The number of publications appearing each year has progressively grown. Several reviews covering different aspects of the photochemistry and photophysics of stilbene-like systems, as well as their impact on materials technology, have been published recently.[1−6]

Stilbene (1,2-diphenylethylene) can be considered the prototype molecule for studying photochemical trans−cis isomerization and has been investigated in great detail by many groups. The most stable conformer,[3] *trans*-stilbene (or *E*-stilbene), has probably been most extensively studied both experimentally and theoretically. Champagne *et al.*[7] have concluded using ultracold jet conditions that this form of stilbene, with no excess of vibrational energy, is planar in the ground state. This conclusion is supported by the vibronic structure of the low-frequency modes of stilbene.[2,8] There is, however, additional experimental evidence based on features of the vibrational spectrum of stilbene in solids, liquids, and in gas phase consistent with an out-of-plane C_1−phenyl torsional angle (ϕ) (see Figure 1).[2,9,10] Previous theoretical works have found a shallow potential energy curve with respect to variations in ϕ around the equilibrium geometry.[11−13]

A large amoung of spectroscopic information is available. The ultraviolet spectrum of *trans*-stilbene (TSB hereafter) has been known for a long time.[14−16] Interpretation of its bands has been attempted by many workers, mostly with the aid of results from semiempirical calculations.[2,17−19] There are three major bands in the low-energy part of the absorption spectrum of TSB, which are commonly labeled A, B, and C. The three bands are fairly strong. The lowest energy band (the A band) is the most intense, with the maximum located at 3.98 eV in benzene and 4.22 eV in *n*-heptane solvents. The two other bands are centered (in *n*-heptane) at 5.43 eV (the B band) and at 6.15 eV (the C band). The relative intensities of the B and C bands with respect to the A band are about 58% and 85%, respectively.[15] A variety of experimental techniques have been used to determine the polarization of the bands. The A and C bands have been found to be polarized mainly along the long axis of the molecule, whereas the B band has been shown to have a mixed character.[18−20] Spectroscopic evidence for the existence of multiple transitions in the A band has also been presented.[21] Additional information about the singlet states has been obtained from the two-photon spectra.[18,22,23] The most intense two-photon band has been observed around 5 eV, between the one-photon A and B bands. The triplet states have also been studied extensively (for a recent review see ref 6). In particular, the triplet energy of T_1 has been placed at 2.21 eV for TSB by using oxygen perturbed absorption techniques.[24] This is slightly above the phosphorescence origin (2.13 eV) and the vibrational origin of the $S_0 \rightarrow T_1$ absorption band (2.15 eV),[25] but below the vertical transition energy. A combined theoretical and experimental determination of the molecular structure of stilbene in the T_1 state is also available.[26]

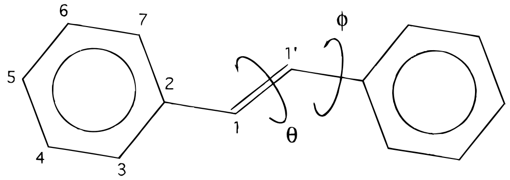

Figure 1. *trans*-Stilbene atom labeling.

The low-lying excited states of TSB have been studied as a way to understand the possible pathways taking place in the light-induced isomerization process to the *cis* form (for a historical background see refs 2, 6, and 27). A key issue has been the characterization of the S_1 excited-state surface. A trans−cis barrier to isomerization on the S_1 surface of about 0.15 eV has been determined from studies of the dynamics of the process.[28] The influence of the environment on the barrier has also been analyzed.[29,30] Speculations of the origin of this behavior have attracted much interest. The currently accepted rationalization is based on the proposal of Orlandi and Siebrand.[31] They considered two interacting benzyl radicals in the π-electron approximation. The interaction between the two unpaired electrons of the ground state of the benzyl moieties in

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the planar configuration gives rise to four electronic states S_0, S_1, S_2, and T_1, analogues to the corresponding N, V, Z, and T states of ethylene.[32] In this scheme, the barrier in the excited state is assumed to be the result of a curve crossing between S_1 and S_2. The latter, which has a doubly excited character that correlates diabatically with the ground state of the *cis* conformer, exhibits a minimum at a perpendicular conformation of the torsion around the C═C ethylenic double bond of stilbene.[33] The scheme has been subsequently modified by Hohlneicher and Dick, involving a number of additional avoided crossings.[18] The discussion of the nature of the experimentally observed barrier has been focused on whether the photoisomerization reaction along the S_1 surface involves a nonadiabatic crossing of the lowest B_u and A_g states or not. An important prerequisite for solving questions of this type is an accurate characterization of the potential curves for the low-lying excited states of stilbene. As shall be discussed below, the trans → cis barrier in the photoisomerization process along the S_1 surface can be rationalized by involving the two lowest excited states of B_u symmetry.

As a first step toward a theoretical study of the photoisomerization reaction of stilbene, the vertical transition properties of the low-lying excited states of TSB are examined in the present contribution. The study includes a geometry characterization of the ground state and the lowest excited state of ^1B_u symmetry. The singlet excited states below 6 eV, including the first Rydberg transitions, as well as the lowest triplet state have been computed using multiconfigurational SCF and second-order perturbation theory, the CASSCF/CASPT2 method.[34,35] The successful performance of the CASPT2 approach in computing differential correlation effects for excitation energies has been illustrated in a number of earlier applications.[36,37] Closely related to the present work are the CASPT2 studies performed on the electronic spectra of benzene,[38,39] naphthalene,[40] ethylene and polyenes,[41−43] and biphenyl.[44−46]

2. Methods and Computational Details

Generally contracted basis sets of atomic natural orbital (ANO) type were used to expand the molecular orbitals. They were built from the C(14s9p4d)/H(8s) primitive sets.[47] The contraction scheme C[3s2p1d]/H[2s] was employed. It has proved its efficiency in previous studies of valence excited states of related systems such as naphthalene[40] and biphenyl.[45] In order to include in the spectroscopic study of stilbene the lowest 3*s* and 3*p* Rydberg states, the basis set was supplemented with two *s*- and two *p*-type diffuse functions (see exponents in refs 40 and 45) placed at the inversion center of the molecule.

The basis set used for the geometry optimizations was the valence contraction of the (9s5p) Dunning primitive set for the carbon atoms with one set of 3d-type polarization functions, and a double-ζ contraction of the (4s) primitive set for the hydrogen atoms (this basis set will hereafter be called VZP). The corresponding exponents and coefficients for the carbon and hydrogen atoms were taken from the compilation reported by Dunning and Hay.[48] Full geometry optimization for the ground state was carried out at the Hartree−Fock (HF) level within the C_{2h} (planar molecule), C_2 (disrotatory motion of the phenyl groups out of the plane), and S_2 symmetries (conrotatory motion of the phenyl groups). In addition, the ground-state planar structure (C_{2h} symmetry) was optimized at the CASSCF level.

With the molecule placed in the *xy* plane, the π orbitals belong to the a_u and b_g irreducible representations of the C_{2h} symmetry group. The active space used in the CASSCF geometry optimization comprised 12 active π MO's, six in each of the two symmetries, with 10 electrons active. The two lowest π MO's were kept inactive. The number of configurations involved in the CASSCF (12MO's/10e) wave function of the 1^1A_g state is 85 092. The optimal ground-state structure obtained at the CASSCF(12MO's/10e) level was subsequently employed for the spectroscopic study. A full geometry optimization was performed by assuming a planar molecule with C_{2h} symmetry.

The vertical electronically excited states of TSB were studied by using CASSCF wave functions with dynamic electron correlation effects estimated by multiconfigurational second-order perturbation theory through the CASPT2 method,[34,35] which uses the CASSCF wave function as a reference. A number of earlier applications have illustrated the ability of the CASPT2 method to yield accurate excitation energies (for recent reviews, see refs 36 and 37). In most cases the agreement is within 0.2 eV for excitation energies where comparison with experimental data is possible. Of course, flexible one-electron basis sets, which describe both valence and Rydberg states, and an appropriate active space have to be provided.

The reference function, determined at the CASSCF level, represents the natural bottleneck of the CASPT2 method. It is not unusual that the active space has to be enlarged in order to overcome problems with intruder states. When the intruder states are weakly interacting with the reference function, they can be effectively removed by a level shift corrected perturbation (LS-CASPT2) theory.[36,49] A different situation obtains, however, when the obvious choice of the smallest number of active orbitals and active electrons becomes too large to be handled technically. The stilbene molecule, with 14 valence π MO's and 14 π electrons, is an example of such a challenging case, where the full π-valence CASSCF calculation cannot currently be performed. The possibility of moving either the lowest two occupied π-MO's or the highest two unoccupied π MO's out of the active space (to the inactive or virtual subspaces, respectively), still keeping a reasonable description of the low-lying excited states of TSB, was recently investigated with the LS-CASPT2 method and level shifts in the range 0.0−0.5 au.[50] Examination of the results showed that a level shift of 0.3 au removes all intruder states and stabilizes the excitation energies for all states of interest. Comparative calculations also showed that the intruder state problem is less severe when the two highest unoccupied MO's are left out of the active space. In the present paper, the spectroscopy related to the valence singlet states and the lowest triplet state of TSB is analyzed on the basis of the CASSCF (12MO's/14e) and the LS-CASPT2(0.3) results. As can be seen in detail elsewhere,[50] the quantitative predictive character of the results is not significantly affected when larger LS values are applied. Therefore, the LS technique has made it feasible to study the electronic spectroscopy of molecules with extended π-systems, like stilbene. It has, however, to be emphasized that, in general, the LS technique is not the recommended procedure for removing intruder states that involve valence orbitals. Intruder states of valence character are usually strong perturbers, with a large interaction with the reference function. Within the framework of low-order perturbation theory they should preferably be moved to the CASSCF reference function.

The lowest Rydberg states resulting from excitation from the highest occupied molecular orbital (HOMO) have been also considered. No level shift was needed in the calculation of the Rydberg states. For the computation of the HOMO($4a_u$) → 3s,-3p Rydberg states, the CASSCF(12MO's/14e) active space was accordingly enlarged, including the corresponding Rydberg orbital of interest.

The dipole transition moments were computed by using the CASSCF state interaction (CASSI) method, which enables an efficient calculation of the transition properties for nonorthogonal state functions.[51,52] Energy differences corrected by CASPT2 were used in the oscillator strength formula.

All calculations have been performed on IBM RS/6000 workstations at the University of Valencia using the MOLCAS-3 quantum chemistry software.[53]

3. Results and Discussion

In this section we shall present and discuss the results for TSB. The present findings will be compared with previous theoretical results and available experimental data. The geometry of ground-state TSB is first considered. The vertical excitation energies are next analyzed. Finally, the possible implications of the present results on the trans−cis photoisomerization process of stilbene in the singlet manifold are discussed.

3.1. Geometry Determination of Ground-State *trans*-Stilbene. Characterization of the ground-state geometry of TSB to be employed in the spectroscopic study is considered in this section. All geometry optimizations have been performed with the VZP basis set. In a first step, a full geometry optimization for the lowest singlet state was carried out at the HF level within the constraints of C_{2h}, C_2, and S_2 symmetries, as explained above.

Actually, the S_2 structure collapses to the optimized C_{2h} geometry, which is only 0.06 kcal/mol above the most stable C_2 minimum. The result is in line with previous theoretical conclusions obtained at the HF level, employing the less flexible 3-21G split-valence basis set.[11−13] Thus, we conclude that the relative improvement of the valence basis set and the inclusion of polarization functions on the carbon atoms do not affect the relative energy ordering previously found at the HF level for these two conformations of stilbene. As pointed out by Lhost and Brédas,[11] essentially free rotation of the phenyl rings about the single bonds occurs in stilbene at room temperature. Based on the experience obtained from the study of the internal rotational barrier of biphenyl,[44] it is not expected that further refinements of the geometry and the level of theory, with inclusion of electron correlation, would change this conclusion. Thus, due to the topology of the ground-state surface of stilbene, a planar C_{2h} structure can safely be employed in the spectroscopic study.

In cases where the surface of the excited state is very different from that of the ground state, the computed vertical excitation energies may, however, be sensitive to the geometry employed for the ground state. Such a situation has been previously found in long polyenes.[42] Thus, an accurate determination of the gas-phase spectrum on theoretical grounds has to be preceded by a reliable characterization of the ground-state geometry. The use of the correct length in the ethylene bond is for stilbene particularly relevant. In order to check the influence of the main effects related to the valence electron correlation contributions, a full geometry optimization of ground-state planar stilbene has been carried out at the CASSCF level (12 active MO's/10 active electrons, see section 2). Table 1 collects the computed bond distances and a few selected bond angles for planar TSB. Experimental gas-phase electron diffraction and crystal X-ray data are also included.

TABLE 1: Geometrical Parameters for the Ground State of *trans*-Stilbene Obtained from the Full Geometry Optimization of the Planar System (C_{2h} Symmetry) Computed at the Hartree−Fock and the CASSCF(12MO's/10e) Levels[a]

			exptl		
parameter[b]	HF	CASSCF	ED[c]	X-ray[d]	
$r(\mathrm{C_1{-}C_{1'}})$	1.332	1.351	1.33	1.326	(1.35−1.36)[e]
$r(\mathrm{C_1{-}C_2})$	1.479	1.479	1.48	1.471	
$r(\mathrm{C_2{-}C_3})$	1.396	1.388	1.398	1.392	
$r(\mathrm{C_3{-}C_4})$	1.391	1.399	1.398	1.384	
$r(\mathrm{C_4{-}C_5})$	1.387	1.392	1.398	1.381	
$r(\mathrm{C_5{-}C_6})$	1.393	1.403	1.398	1.383	
$r(\mathrm{C_6{-}C_7})$	1.385	1.390	1.398	1.381	
$r(\mathrm{C_2{-}C_7})$	1.401	1.410	1.398	1.397	
$\angle(\mathrm{C_{1'}C_1C_2})$	126.9	126.7	128	126.4	
$\angle(\mathrm{C_1C_2C_3})$	118.4	118.6		119.0	
$\angle(\mathrm{C_1C_2C_7})$	123.7	123.3		123.2	

[a] The VZP basis set was used (see text). [b] Bond distances in Å and angles in degrees (see Figure 1 for atom labeling). [c] Gas-phase electron diffraction data reported by Traetteberg *et al.* (1975).[9] [d] X-ray data; Bouwstra *et al.* (1984).[54] [e] Recent X-ray crystallographic estimate of the ethylene bond in *trans*-stilbenes; Ogawa *et al.* (1995).[56]

The most pronounced effect of the nondynamic electron correlation on the ground-state geometry of planar TSB occurs for the ethylenic double bond. It increases 0.019 Å with respect to the corresponding HF result. The computed result at the CASSCF level (1.351 Å) is about 0.02 Å longer than the gas-phase electron diffraction value reported by Traetteberg *et al.*[9] and the X-ray data derived by Bouwstra *et al.*[54] Ogawa *et al.*[55,56] have recently analyzed the unusually short ethylene bond deduced from X-ray crystallographic studies on TSB, which shows a structure approximately of S_2 symmetry. They have concluded that the short $\mathrm{C_1{-}C_{1'}}$ distance is an artifact which originates from the large-amplitude torsional motion of the $\mathrm{C_1}$−phenyl bonds in crystals. The actual length of the ethylene bond in *trans*-stilbenes has been estimated by these authors to be within the range 1.35−1.36 Å.[56] Our result supports their conclusion. On the other hand, the gas-phase structure concluded by Traetteberg *et al.*[9] from electron diffraction experiments at 200 °C, C_2 symmetry with the $\mathrm{C_1}$-phenyl groups rotated about 30°, yields a ethylene bond which is definitely too short. As noted in Table 1 the bond distances of the benzene ring also increase, at most 0.01 Å, at the CASSCF level compared to the HF results. Agreement between the computed and the crystal data is noted for the bond angles.

Champagne *et al.*,[7] in a high-resolution frequency-domain study, have determined all three principal rotational constants for the lowest vibrational levels of the S_0 and S_1 states of TSB. The results demonstrate that TSB is a rigid, planar asymmetric top in the zero-point vibrational levels of both electronic states. The corresponding rotational constants along the three principal axes of inertia for ground-state TSB in the gas phase at the zero-point vibrational level are 2.611, 0.263, and 0.241 GHz,[7] in good agreement with earlier experimental results.[57] The computed values of the rotational constants for the optimized structure at the CASSCF level are 2.729, 0.261, and 0.238 GHz, respectively. They deviate from experiment by +4.5%, −0.8%, and −1.2%, respectively. These results are only slightly improved compared to the results obtained by using the optimized structure at the HF level. For this reason, the good results obtained also with the optimized structure obtained with the QCFF/PI method, and deviations for the rotational constants of only +1.8%, −0.5%, and −1.0%, respectively, are not particularly surprising.[7] The optimal QCFF/PI distance of the ethylene bond for ground-state planar TSB, which is predicted as the most stable conformer, has been computed to be 1.359 Å,[58] in agreement with the present estimate.

The structure resulted from the CASSCF, 12 MO's active with 10 active electrons; full geometry optimization of ground-state TSB has been used throughout in the spectroscopic study.

The bond distances at this level are expected to deviate by less than ±0.01 Å from the true gas-phase structure.

3.2. Vertical Excited States. In this section we present and discuss the results obtained for the excited states of TSB. With the C_2 axis chosen as the z axis and the molecule in the xy plane, the dipole-allowed $\pi\pi^*$ transitions belong to the irreducible representation B_u of the C_{2h} symmetry group. The computed transition moments involving these states will be oriented in the xy plane. For planar TSB, allowed two-photon $\pi\pi^*$ transitions correspond to final A_g states. Most of the available experimental data come from solution, where the ground state of stilbene might be somewhat twisted. As the result of the nonplanarity, two-photon transitions to final B states (symmetry point group C_2), which are related to the main bands in the one-photon spectrum, may gain some intensity. However, the correspondence between the electronic spectra in crystal and solution phases,[15,16] together with the available experimental information in gas phase,[7] indicate that a consistent interpretation of the electronic spectrum of TSB can be achieved from calculations on the planar structure. Nonplanarity is expected to have a minor influence on the computed properties, as has also been found in previous theoretical studies.[18]

The electronic states of stilbene may be qualitatively understood from a high-symmetry model, where two benzene molecules interact with ethylene. This topological model assumes an artificial D_{2h} symmetry, with a linear arrangement of the ethylene CC bond and the ethylene−phenyl bonds. From a combination of the electronic states of ethylene and the two phenyl groups, a corresponding number of valence excited states of A_g and B_u symmetry can be derived for planar TSB. For the qualitative description it will be assumed that the description of the low-lying excited states of stilbene involves only the highest occupied and the lowest unoccupied MO's of the system. The highest five occupied and lowest virtual MO's in TSB come from the corresponding linear combinations of the HOMO and LUMO of the two benzene moieties with the HOMO and LUMO of ethylene, respectively. The π molecular orbital diagram of TSB relative to the benzene molecules and ethylene is depicted in Figure 2, where a schematic representation of the canonical HF MO's is also shown.

The canonical MO's and the corresponding orbital energies for planar TSB have been obtained from a HF calculation using the ANO-type C[3s2p1d]/H[2s] valence basis set at the optimal CASSCF geometry used in the spectral study. The x axis has been taken in the direction of the ethylene bond, the long axis of the system in symmetry D_{2h} (the z axis is perpendicular to the plane of the molecule). This leads to an unconventional labeling of the HOMO and LUMO of ethylene, b_{1u} and b_{3g}, respectively. The HOMO(e_{1g}) of the benzene molecule spans $b_{2g} + b_{3g}$ and the LUMO(e_{2u}) spans $a_u + b_{1u}$ in the point group D_{2h}. The occupied MO's of the supersystem formed by two benzene molecules result in the symmetries b_{1u}, b_{2g}, b_{3g}, and a_u of the D_{2h} point group. They are built as plus and minus combinations of the two individual degenerate MO's of the noninteracting benzene(1) and benzene(2) molecules: $b_{2g}(1) + b_{2g}(2)$, $b_{2g}(1) - b_{2g}(2)$, $b_{3g}(1) + b_{3g}(2)$, and $b_{3g}(1) - b_{3g}(2)$, respectively. The so-derived MO's of b_{1u} symmetry of the supersystem can subsequently interact with the HOMO(b_{1u}) of ethylene. A similar analysis can be applied to the virtual MO's (see Figure 2). This scheme will be used in connection with the discussion of the computed electronic states at the CASSCF and the CASPT2 levels. The computed excitation energies and oscillator strengths are compiled in Table 2, where they are also related to the observed bands. The assignments will be discussed in detail below. In order to get further insight into the nature of the excited states, Table 3 lists the main contributions to the corresponding CASSCF wave functions. The total number of configurations involved is 84 792 and 85 092 for states of B_u and A_g symmetry, respectively.

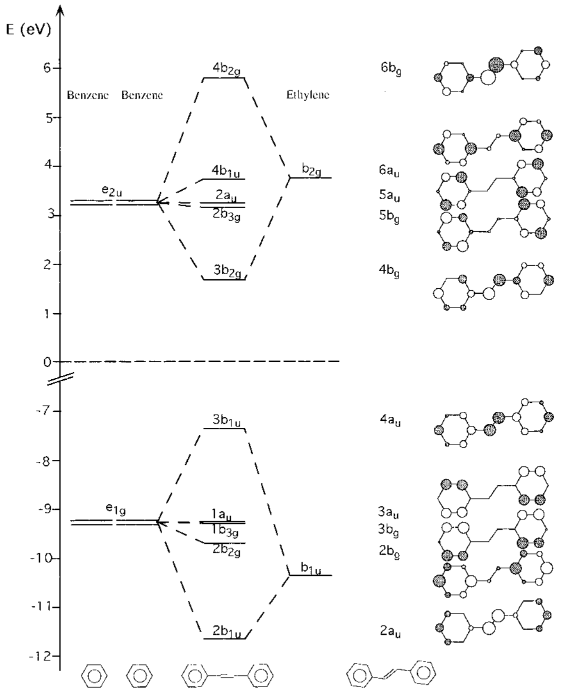

Figure 2. Schematic diagram showing the highest five occupied and lowest five unoccupied π molecular orbital distribution of *trans*-stilbene, relative to two benzene moieties and ethylene, in the topological D_{2h} point group and in the C_{2h} symmetry of the system. The canonical MO's using the ANO-type C[3s2p1d]/H[2s] basis set are displayed on the right. Orbital energies correspond to the canonical MO's of planar (C_{2h} symmetry) *trans*-stilbene. The optimized CASSCF geometry was employed.

3.2.1. The Singlet B_u States. We present in this section the results for the singlet B_u states and compare them to the observed one-photon spectra[15,16,18] and the experimentally derived information about the polarization of the corresponding transitions.[16,18−20]

The most intense feature of the spectrum is computed at 4.07 eV. It corresponds to the transition to the 2^1B_u state with a calculated oscillator strength of 0.7. The excited state is described mainly by the one-electron promotion from the HOMO($4a_u$) into the LUMO($4b_g$). This configuration has a weight of 71% in the CASSCF wave function. In accordance with the nature of the $4a_u$ and $4b_g$ MO's in the topological symmetry ($3b_{1u}$ and $3b_{2g}$, see Figure 2), the transition is of the B_{3u}-like type and is found to be polarized along the long axis of the TSB molecule, in agreement with experimental evidence.[18−20] The transition moment is oriented parallel to the a inertial axis within 2°, which agrees with the experimental estimate of ±13° in the gas phase.[7] In the same energy range, a weak transition is also present. It involves the lowest singlet excited state, the 1^1B_u state, which is placed at 3.77 eV with an oscillator strength of 0.04. The difference between the CASPT2 and CASSCF results for the excitation energy of the first transition, 1.7 eV, is slightly smaller than for the strongest transition, 2.0 eV. This difference gives a measure of the importance of dynamic correlation contributions to the excitation energy, which are usually larger for ionic states.[37] It can be related to the larger ionic character of the 2^1B_u state compared to the 1^1B_u state, in agreement with previous theoretical descriptions at the PPP (full CI) level.[59] The 1^1B_u state has a pronounced multiconfigurational character (*cf.* Table 3). It is

TABLE 2: Calculated Vertical Excitation Energies and Oscillator Strengths for *trans*-Stilbene

state	CASSCF, eV	CASPT2, eV	osc str		experimental data	
					ΔE, eV	osc str[c]
singlet states						
1^1B_u	5.42	3.77	0.038	band A	3.98,[a] 4.22,[b] ≈4.0,[c]	0.74
2^1B_u	6.05	4.07	0.723		3.71(0−0),[d] 4.00(0−0)[e]	
2^1A_g	5.41	4.13	forbidden		∼4.1[f]	
3^1A_g	5.92	4.95	forbidden		5.02[f]	
4^1A_g	7.41	5.30	forbidden		∼5.3[f] (shoulder)	
1^1A_u(3s)	5.54	5.33	0.001			
3^1B_u	7.96	5.42	0.371	band B	5.43[b], ∼5.4[c]	0.29
4^1B_u	7.76	5.42	0.117			
5^1B_u	7.18	5.46	0.019			
$1^1B_g(3p_x,3p_y)$	5.73	5.53	forbidden			
$2^1B_g(3p_x,3p_y)$	5.94	5.69	forbidden			
6^1B_u	8.36	5.95	0.524	band C	6.15[b]	0.41
lowest triplet state						
1^3B_u	3.02	2.56			2.21,[a] 2.13,[b], 2.15[i]	

[a] One-photon absorption spectrum in benzene at room temperature; Suzuki (1960).[15] [b] One-photon absorption spectrum in *n*-heptane at room temperature; Suzuki (1960).[15] [c] In 3-methylpentane at room temperature; Hohlneicher and Dick (1984)[18] and Gudipati *et al*. (1995).[19] [d] 0−0 line resolved in dibenzyl crystals at 20 K; Dyck and McClure (1962).[16] [e] 0−0 transition observed in molecular beams; Champagne *et al*. (1990).[7] [f] Two-photon absorption spectrum in ethanol at room temperature; Hohlneicher and Dick (1984).[18] [g] From $S_0 \rightarrow T_1$ oxygen-perturbed absorption; Ni *et al*. (1989).[24] [h] Phosphorescence origin; Ikeyama and Azumi (1994).[25] [i] Origin band in $S_0 \rightarrow T_1$ absorption; Ikeyama and Azumi (1994).[25]

TABLE 3: Principal Configurations and Weights, Number and Weights of Singly, Doubly, and Triply Excited Configurations with Coefficients Larger than 0.05 of the Ground and Singlet Valence Excited States of *trans*-Stilbene

state	principal configurations	weight			
		%	S	D	T
1^1A_g	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^2$	81	2 (1%)	18 (8%)	
1^1B_u	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^1(5b_g)^1$	26	10 (74%)	10 (6%)	
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^1(4a_u)^2(4b_g)^1$	24			
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^1(4b_g)^1$	7			
2^1B_u	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^1(4b_g)^1$	71	9 (82%)	4 (3%)	3 (1%)
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^1(4a_u)^2(4b_g)^1$	6			
2^1A_g	$(2a_u)^2(2b_g)^2(3b_g)^1(3a_u)^2(4a_u)^2(4b_g)^1$	28	9 (71%)	14 (8%)	
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^1(5a_u)^1$	16			
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^1(4a_u)^2(6a_u)^1$	10			
	$(2a_u)^2(2b_g)^1(3b_g)^2(3a_u)^2(4a_u)^2(5b_g)^1$	8			
3^1A_g	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^0(4b_g)^2$	28	6 (39%)	21 (43%)	1 (1%)
	$(2a_u)^2(2b_g)^1(3b_g)^2(3a_u)^2(4a_u)^2(4b_g)^1$	17			
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^1(6a_u)^1$	13			
	$(2a_u)^2(2b_g)^2(3b_g)^1(3a_u)^2(4a_u)^2(4b_g)^1$	5			
4^1A_g	$(2a_u)^2(2b_g)^1(3b_g)^2(3a_u)^2(4a_u)^2(4b_g)^1$	32	12 (74%)	9 (7%)	3 (1%)
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^1(6a_u)^1$	28			
3^1B_u	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^1(4a_u)^2(4b_g)^1$	34	10 (66%)	13 (13%)	
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^1(5b_g)^1$	10			
	$(2a_u)^2(2b_g)^1(3b_g)^2(3a_u)^2(4a_u)^2(5a_u)^1$	6			
4^1B_u	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^1(5b_g)^1$	30	11 (60%)	16 (19%)	
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^0(4b_g)^1(5a_u)^1$	9			
	$(2a_u)^1(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^2(5b_g)^1$	6			
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^1(4a_u)^2(4b_g)^1$	6			
5^1B_u	$(2a_u)^1(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^2(4b_g)^1$	26	7 (42%)	24 (40%)	
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^0(4b_g)^1(6a_u)^1$	12			
	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^2(4a_u)^1(6b_g)^1$	12			
	$(2a_u)^2(2b_g)^2(3b_g)^1(3a_u)^2(4a_u)^1(4b_g)^2$	9			
	$(2a_u)^2(2b_g)^1(3b_g)^2(3a_u)^2(4a_u)^1(4b_g)^2$	8			
6^1B_u	$(2a_u)^2(2b_g)^2(3b_g)^2(3a_u)^1(4a_u)^2(5b_g)^1$	33	14 (75%)	12 (6%)	2 (1%)
	$(2a_u)^2(2b_g)^2(3b_g)^1(3a_u)^2(4a_u)^2(5a_u)^1$	17			
	$(2a_u)^2(2b_g)^1(3b_g)^2(3a_u)^2(4a_u)^2(5a_u)^1$	10			

described mainly by the singly excited configurations HOMO → LUMO + 1 and HOMO − 1 → LUMO, with weights in the CASSCF wave function of 26% and 24%. This structure of the CASSCF wave function can be rationalized in terms of the orbital energies differences of the MO's implied. Both are very similar, about 11 eV. Thus, the HOMO → LUMO + 1 and HOMO − 1 → LUMO configuration are quasi-degenerate, and, since they also interact, "minus" and "plus" linear combinations are formed. The former is pushed down and has a low oscillator strength, whereas the latter is moved up to a higher energy and carries most of the intensity. In contrast to some earlier studies, we find the minus state to be the first excited state. The relative ordering of the two lowest ^1B_u states depends on the parametrization employed in the semiempirical studies. The "minus" character is in accordance with the low intensity of the transition. In spite of the perpendicular direction predicted from the symmetry of the major one-electron configurations involved, the "minus" nature of the state, as well as its marked multiconfigurational character, yields a computed transition moment oriented mainly in the direction of the long axis. As shown in Figure 3, the direction of the polarization for the first transition is found within 7° of the strongest transition.

The computed transitions to the 1^1B_u and 2^1B_u states can be related to the low-energy part of the observed one-photon

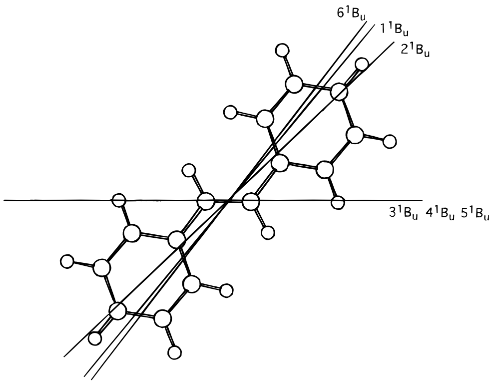

Figure 3. Computed transition moment directions at the CASSI level for the singlet−singlet spectrum of *trans*-stilbene.

absorption spectra. The lowest energy band, the A band, is the most intense, with the maximum located at 3.98 eV in benzene solution, at 4.22 eV in *n*-heptane and ethanol, and approximately at 4.0 eV in 3-methylpentane.[15,17,18] The 0−0 line has been resolved in dibenzyl crystals at 3.17 eV.[16] A slightly higher energy of the band origin has been observed in the gas phase, at 4.00 eV in the fluorescence excitation spectrum in the collision-free environment of a molecular beam.[7] Over the whole range of the A band, the degree of polarization has been found to be nearly constant, mainly in the direction of the long molecular axis. This conclusion has been reached by using different techniques; from experiments in crystals,[16] in polyethylene matrix,[20] in solution,[18] and for the isolated system in an argon matrix.[19] Still, the possibility of multiple additional electronic transitions appearing in the A band with low intensities has been suggested. In particular, a relatively weak electronic transition, hidden under the strong A band, placed on the high-energy side of this band and with a perpendicular polarization, has been predicted for TSB.[21] We find, however, no evidence for such an electronic transition in this energy region, but vibronically allowed excitations cannot be excluded. The high-energy side of the A band in the one-photon absorption overlaps with the most intense part of the two-photon absorption spectra (see ref 18). One electronic transition, with an energy of 4.13 eV, is found between the strongest one-photon electronic transition, at 4.07 eV, and the most intense two-photon feature at 4.95 eV (*cf.* Table 2). Therefore, the features observed at the tail of the A band, which is also the low-energy region of the most intense two-photon band, are probably due to vibronic coupling. Anyway, the present results are in accordance with a progressive change of polarization observed along the A band.[19,20]

The prediction of a weak transition 1^1B_u below the fully allowed HOMO → LUMO excitation computed as the 2^1B_u state (hereafter named as ^1B_u(HL)) is in apparent disagreement with experimental evidence. If one makes the usual assumption that the strong absorption at the lowest energy and the fluorescent emission arise from the same excited level, there is quite good mirror image symmetry between absorption and emission spectra, as well as the expected fluorescence lifetime at low excess energy (see, e.g., refs 2, 6, and 27). The medium-induced red spectral shift (0.29 eV) of the electronic origin in the dibenzyl crystal[16] relative to the isolated molecule[7] is also consistent with a strongly allowed transition. In order to get more insight into the relative state ordering, geometry optimization for the the lowest state of B_u symmetry was carried out at the CASSCF(12MO's/10e) level by using the VZP basis set. The structure of the 1^1B_u state is planar (C_{2h} symmetry). The ethylene bond length in the excited state (1.420 Å) increases, while the single C_1-C_2 bond distance (1.379 Å) decreases with respect to the ground state. The remaining bond distances[60] are longer in the excited state. The effect is particularly pronounced for the C_2-C_3 bond distance.

The nature of the CASSCF wave function of the relaxed ^1B_u state is similar to that of the lowest vertical ^1B_u state (see Table 3). At the CASPT2 level (LS = 0.3 au) the 0−0 transition energy is computed to be 3.59 eV, employing the same of ANO-type basis set as for the vertical spectrum. Attempts to optimize the geometry for the second root of B_u symmetry have failed due to convergence problems. (Geometry optimizations are restricted to a given root; no state average is implemented in the available gradient codes.) In order to estimate the electronic origin of the ^1B_u(HL) state, the geometry of the lowest ^1B_u state was employed. One would expect similar changes in the equilibrium geometry for both states, which might be related to the convergence problems of the CASSCF procedure for the upper root. The transition for ^1B_u(HL) at the equilibrium geometry of the lowest ^1B_u state is computed to be 3.78 eV. The ^1B_u(HL) state obtained from the CASSCF state average (equally weighted) of the two lowest roots (same ANO-type basis set as for the vertical spectrum) has a contribution of 75% for the HOMO → LUMO configuration. A red-shift of 0.18 and 0.29 eV from the band maxima are then predicted for the 1^1B_u and 2^1B_u states, respectively. At this geometry they are thus separated by only 0.19 eV.

The apparent discrepancy between theory and experiment as regards the lowest ^1B_u state is not easy to resolve. The vertical separation of the two lowest states is computed to be 0.3 eV. Adiabatically, it is considerably smaller, maybe even negative. Such small energy differences cannot be resolved with the present computational technique, which has an inherent error of about the same size. Due to the different nature of the states, the environment could also affect their relative ordering. It is also highly probable that the two states are strongly coupled vibronically, which further complicates the interpretation of the experiment.

The lowest B_u state, here obtained in vacuum, might be connected to the low-intensity transition suggested at the high-energy side of the A band in solvent.[21] Another possibility is that the weak transition predicted in the present work has not yet been experimentally detected in gas phase. Examples of the existence of two fluorescent singlet excited states, related to the two lowest singlet excited states in the absorption spectra with weak and strong intensity, are known. An illustrative molecular system was *all-trans*-1,8-diphenyloctatetraene, which was studied in the classic paper of Hudson and Kohler (1973).[61] A similar situation has been demonstrated more recently for *all-trans*-retinal. Tahara and Hamaguchi[62] have revealed, based on a time-resolved fluorescence study, the presence of two components for *all-trans*-retinal. According to these authors, the photoexcitation first produces the optically allowed S_2 state, which relaxes to the optically forbidden S_1 state within 1 ps. The fast and slow fluorescence components have been assigned to the S_2 and S_1 states, respectively. CASPT2 studies of electronic spectra have been performed on octatetraene,[42] retinal, and related systems.[63] The results give support to the previously mentioned experimental spectral features. Similarly, the present results suggest a dual fluorescence for TSB. Determination of the long-lived fluorescence component in TSB might be hampered by the rapid trans → cis photoisomerization process and by strong vibronic coupling. It is also possible, as will be discussed below, that the presence of two low-lying excited states of B_u symmetry might have a great impact on the understanding of the earliest step of the photoadiabatic isomerization reaction. A long-lived fluorescence component has not been revealed in TSB in spite of numerous studies. *cis*-Stilbene, however, presents fluorescence with a relative long lifetime (see discussion in ref 27). Connected to this problem might also be the findings reported in the adiabatic $^1c^* \rightarrow {}^1t^*$ conversion.[64] Subtraction of the pure-component spectra of *trans*- and *cis*-stilbene from the experimental emission spectra gives a residual curve containing a small peak at ≈3.87 eV.[64] On the other hand, spectral features on the low-energy side of the 0−0 transition are present,[65] which are usually attributed to sequence or to hot bands.[66] In addition, while TSB in a single crystal of dibenzyl at 20 K shows an absorption spectrum completely polarized along the long axis of the stilbene molecule, the fluorescence spectrum is not highly polarized.[16] All these hints point to the complexity of the problem. Further theoretical and experimental studies are required to fully clarify the importance of the two low-lying singlet B_u states of TSB, as well as their impact on the photophysical properties and photoisomerization characteristics.

The so-called B band in the one-photon absorption spectrum has a medium relative intensity, with the strongest peak centered at 5.43 eV in *n*-heptane and in ethanol at room temperature and around 5.4−5.5 eV in 3-methylpentane at 77 K.[15,18] The calculations yield three states, 3^1B_u, 4^1B_u, and 5^1B_u in this energy region (*cf*. Table 2). The most intense state is 3^1B_u at 5.42 eV. It is nearly degenerate with both the 4^1B_u and the 5^1B_u states. The CASSCF wave function for the 3^1B_u state is dominated by the “plus” linear combination of the singly excited configurations HOMO → LUMO + 1 and HOMO − 1 → LUMO, which have weights of 10% and 34%, respectively. The $1^1A_g \rightarrow 3^1B_u$ transition is relatively strong, with a computed oscillator strength of 0.4, in accordance with the “plus” character of the final state. For this state, which has a topological B_{2u}-like symmetry, the transition moment is expected to have a sizable component along the short molecular axis. The computed transition moment also makes an angle of 46° with the moment of the strongest transition (see Figure 3). This result is in agreement with experimental evidence: 45° found in ethanol,[18] 50°(±4) in stretched polyethylene films,[20] and 65°(±10) in argon matrix.[19] The transition moments involving the 4^1B_u and the 5^1B_u states have similar orientations (around 46°), in agreement with the experimental fact that band B has been found to be fairly homogeneously polarized. The mixed polarization of the transitions to the 4^1B_u and the 5^1B_u states can be rationalized by the mixed character of the main configurations describing the CASSCF wave function, translated into the topological B_{3u}- and B_{2u}-like symmetries. The CASSCF wave functions of the 4^1B_u and the 5^1B_u states involve deeper occupied and higher virtual π MO’s. The 5^1B_u state has a more complex multiconfigurational character with nearly the same contribution of singly and doubly excited configurations with a total weight of 42% and 40% (considering only configurations with coefficients larger than 0.05), respectively.

The 6^1B_u state is placed at 5.95 eV. It is described mainly by the HOMO − 1 → LUMO + 1 configuration with a weight in the CASSCF wave function of 33%. In addition, it also has nonnegligible contributions of configurations characterized by excitations from deeper MO’s to higher virtual MO’s (*cf*. Table 3). The state has a singly excited character; the total contribution of one-electron excited configurations has a weight of 75% in the CASSCF wave function. The computed intensity for the $1^1A_g \rightarrow 6^1B_u$ transition is 0.5. The corresponding transition moment is, within about 9°, oriented in the direction of the long axis (see Figure 3), which is consistent with the B_{3u}-like topological nature (see Figure 2) of the leading configurations in the multiconfigurational wave function. The results are in agreement with experiment. The maximum of the C band is in the one-photon absorption spectrum located at 6.15 eV in *n*-heptane[15] and at about the same energy in ethanol at room temperature.[15,18] The relative angle with respect to the strongest transition, determined at the maximum of band C, at 6.35 eV in the fluorescence−excitation spectrum in argon matrix at 15 K, is 21°(±8).[19]

The energy difference between the CASSCF and CASPT2 results is largest for the 6^1B_u and the 3^1B_u states. This dynamic correlation effect decreases the excitation energies by about 2.5 eV. The strong correlation effects may explain the difficulties experienced in earlier, semiempirical, attempts to assign the B band. These methods also usually predict C as the most intense band, in disagreement with experiment (for a compilation of semiempirical results on the electronic spectrum of TSB, see, *e.g.*, refs 18, 19, 26, 58, and 59).

3.2.2. The Singlet A_g States. Three optically forbidden states of ^1A_g symmetry have been found at 4.13, 4.95, and 5.30 eV. The CASSCF wave functions of the 2^1A_g and 4^1A_g states are dominated by singly excited configurations, with total weights of 71% and 74%, respectively. The 3^1A_g state is, however, predominantly doubly excited. The $(\mathrm{HOMO})^2 \rightarrow (\mathrm{LUMO})^2$ configuration has the largest weight, 28%, and the total weight of the doubly excited configuration functions is 43% (*cf*. Table 3). The 3^1A_g state, computed at 4.95 eV, clearly corresponds to the intense two-photon absorption band observed around 5 eV.[18,22,23] The present result confirms previous theoretical locations of the 3^1A_g state (see, *e.g.*, refs 18, 33, and 59), the controversial state, which is believed to play a fundamental role in the trans−cis photoisomerization process of stilbene.

In the two-photon absorption spectrum of TSB in ethanol at 77 K reported by Hohlneicher and Dick,[18] two additional bands below 5 eV are also found, with the most intense peaks located at ≈4.1 and ≈4.4 eV. Here, only one electronic excited state of ^1A_g symmetry has been found in this region, 2^1A_g at 4.13 eV. This results seems to suggest that one of the observed bands in the two-photon spectrum might be due to vibronic coupling. A similar situation has been found in biphenyl,[45] where no electronic two-photon states were found below the strongest two-photon transition. The $1^1A_g \rightarrow 2^1A_g$ transition for TSB, vertically computed at 4.13 eV, can be assigned tentatively as the maximum of the lowest band observed in the two-photon spectrum. It holds, assuming a similar deviation from experiment as for the $1^1A_g \rightarrow 3^1A_g$ transition. Accordingly, the second two-photon band centered around 4.4 eV, which is situated at the high-energy side of the band A of the one-photon spectrum, must be caused by vibronic coupling. This reasoning connects nicely with the above discussion on the experimental evidence of a transition of weak intensity on the high-energy side of band A in the one-photon absorption spectrum. It would not be unlikely that both, one-photon and two-photon observed phenomena in the same energy range, were closely related. The suggestion is somewhat speculative, however, since the data obtained here only tells us that there is one electronic state of A_g symmetry in the energy range 4.0−4.5 eV. The 4^1A_g computed at 5.30 eV can be related to a shoulder observed in the strongest band of the two-photon spectrum.[18]

3.2.3. The Low-Lying Singlet Rydberg States. As far as we know, there is no experimental information about Rydberg states of stilbene. In order to determine the energy range in which these states could be observed, the low-lying Rydberg transitions have been computed. The CASPT2 method places the 1^1A_u-($4a_u \rightarrow 3s$) state at 5.33 eV. The computed intensity is low, 0.001. That is, the 3s Rydberg state is situated in the energy region between the main band of the two-photon spectrum and the B band of the one-photon spectrum. The dipole-forbidden 1^1B_g and 2^1B_g 3p Rydberg states are found between the B and C one-photon bands, with excitation energies of 5.53 and 5.69 eV, respectively. For all the three Rydberg states, dynamic correlation accounted for by the CASPT2 method have a minor influence, at most 0.25 eV, on the computed excitation energies. The CASSCF wave function of the Rydberg states is described mainly by the singly excited configuration from the HOMO to the corresponding Rydberg orbital.

3.2.4. The Lowest Triplet State. The lowest triplet state is 1^3B_u with a computed vertical excitation energy of 2.56 eV. The 1^3B_u state is described mainly by the single excited configuration HOMO → LUMO, which has a weight of 76% in the CASSCF wave function. The singlet−triplet splitting is 1.51 eV, which is smaller than the singlet−triplet gap in the lowest triplet state of benzene, 1^3B_{1u}, computed to be 2.21 eV,[38] reflecting the larger delocalization of the HOMO and LUMO orbitals in stilbene.

A similar singlet−triplet splitting has been found for the lowest triplet state, 1^3B_u, of planar biphenyl, 1.53 eV.[45] In a simple molecular orbital model, the difference between the singlet and triplet states associated with a given configuration can be related to the magnitude of the exchange integral of the MO's involved. This suggests that the values for the exchange integral of the HOMO−LUMO pair are similar for the biphenyl and the *trans*-stilbene systems. The ethylene moiety interacting with the two benzene molecules has a pushing-down and pushing-up effect on the resulting LUMO and HOMO, respectively. As a result the lowest triplet of TSB is placed about 0.5 eV below the lowest triplet state of planar biphenyl, which has been found at 3.10 eV (experimental value 3.0 eV).[45]

Oxygen-perturbed $S_0 \rightarrow T_1$ absorption spectra have placed the lowest triplet state of TSB at 2.21 eV. Ni *et al.*[24] assigned the spectroscopic energy reported to the planar TSB triplet in which only relaxation of the ethylene stretch in T_1 was assumed to occur. Their value is slightly above the 0−0 energy observed in emission, 2.13 eV, and absorption, 2.15 eV.[25] The energy obtained at the CASPT2 level is somewhat larger, since it corresponds to a vertical transition. Usually, vertical excitation energies for singlet−triplet transitions of organic compounds are particularly accurate at the CASPT2 level (within ±0.1 eV),[36,37] which suggests that the stretching of the ethylene bond represents, compared to the value of Ni *et al.*, a relaxation energy about 0.1−0.2 eV. The remaining energy difference with respect to the 0−0 values being probably due to a further relaxation of the geometry of the lowest triplet state. This also means that the triplet potential energy surface is rather flat in the region between the vertical trans and the perpendicular geometry. Further insight into the nature of the T_1 state can be found in the comprehensive study performed by Langkilde *et al.*[26]

3.3. Implications of the trans−cis Photoisomerization Process of Stilbene in the Singlet Manifold. Let us assume that the twist about the ethylene double bond, with a rotational angle θ, can be considered as the main reaction coordinate in the trans−cis photoisomerization process of stilbene. It is also a reasonable assumption to expect that the potential energy curves of stilbene with respect to the torsion angle would maintain certain similarities with that of ethylene. Discarding the possible complications due to the presence of Rydberg states, the following trends are present in ethylene (see, *e.g.*, ref 67). With increasing torsion about the double bond, the S_0 surface rises steeply, reaching a maximum at the perpendicular conformation, the dimethylene system. The T_1, S_1, and S_2 surfaces show minima for $\theta = 90°$. In a simple two-electron two-orbital model, the ground state, N, and the doubly excited, Z, states become degenerate at 90° and they can further interact. The minus combination results in the diradical ^1D state, which is pushed down in energy, and the plus combination gives rise to the zwitterionic $^1Z(+)$ state, which is energetically pushed up. The ^1D state of dimethylene correlates with ground-state ethylene, N. The corresponding diradical triplet state ^3D at 90° originates from the T state of the parent molecule. The $^1Z(-)$ and the $^1Z(+)$ states of dimethylene are related to the singly excited, V, and doubly excited, Z, states of ethylene, respectively.

Similar trends have been found for stilbene. The barrier on the S_0 surface for the trans → cis isomerization has, for example, been estimated to 49 kcal/mol.[3] On the other hand, the present study confirms the presence of a state with a large doubly excited character, the 3^1A_g state vertically placed at 5 eV, responsible for the main band in the two-photon absorption spectrum. This state can be related to the Z state of ethylene. A minimum at 90° is therefore expected on the corresponding surface. The perpendicular state that derives from the Z-like state is the so-called "phantom state".[68] It is unlikely that the small barrier of 3.3 ± 0.2 kcal/mol[28] on the S_1 surface, as proposed by Orlandi and Siebrand,[31] is due to a crossing between the curves of a low-lying singlet state of B_u-like type and the Z-like state, since the latter is vertically computed to be about 1 eV above the former in the trans isomer. Such a crossing, if occurring, would take place at twisted angles close to 90°, yielding a larger barrier. The original scheme of Orlandi and Siebrand[31] has been modified by Hohlneicher and Dick,[18] such that a number of additional avoiding crossings are introduced to lead eventually to the twisted perpendicular state.

There is, however, an alternative rationalization, apparently easier, for the small barrier in the trans−cis isomerization pathway along the S_1 surface. It involves the V-like state of TSB. The most plausible candidate for the V-like state of TSB is the 2^1B_u state, described mainly by the singly excited HOMO → LUMO configuration. The low-lying 1^1B_u and 2^1B_u states are computed to be within 0.3 eV of each other (*cf.* Table 2). Through configurational mixing, the adiabatic curves corresponding to these states should exhibit an avoided crossing at a small relative rotation angle with respect to the trans conformation, resulting in a minimum on the S_1 surface at the perpendicular conformation. It may be assumed that the 1^1B_u has an ascendent trend from the trans conformation, whereas the initial trend for the 2^1B_u state would be, according to its V-like character, descendent. This seems to be a natural explanation for the origin and nature of the barrier in the photoadiabatic isomerization reaction in the S_1 surface. The 2^1A_g state is computed slightly above the 2^1B_u state. Except for the V-like and Z-like (and T-like) states of TSB, the remaining states are expected to rise in energy with the twisting due to the local nature of the excitation to the benzene rings. Loss of interaction (conjugation) between the phenyl groups caused by the rotation is the origin of the ascendent trend in these states. An adiabatic crossing between 2^1A_g and 3^1A_g states should appear subsequently with the twisting. The relative positions, at the perpendicular conformation, of the V-like and Z-like derived states of 1,2-diphenyldimethylene can only be obtained by actual calculations, and any further analysis must await such results. Preliminary calculations employing small basis sets are in qualitative agreement with this point of view. On the other hand, the above rationalization might be easily oversimplified, since the optimal reaction path on S_1 almost certainly preserves no symmetry elements.

The semiempirical theoretical studies reported by Olbrich[69] and by Troe and Weitzel[70] have shown that the *trans* to the perpendicular conformation can be reached in an adiabatic manner on the S_1 surface. On the other hand, Rettig *et al.*[71] have concluded from semiempirical calculations on stilbene and stilbenoid donor−acceptor dye systems, that for substituted stilbenes the order of the ground and the excited state may be reversed in the perpendicular configuration, such that the zwitterionic state becomes the ground state.

In order to further clarify the static aspects of the reaction, in particular the role of the 3^1A_g state on the trans↔cis photoisomerization process of stilbene in the singlet manifold, additional theoretical studies are required. For this purpose, the present investigation at the CASSCF/CASPT2 level will be extended to characterize the low-lying excited states of *cis*-stilbene, as well as to determine crucial parts of the corresponding potential energy surfaces for the isomerization process.

4. Summary and Conclusions

We have presented results from a theoretical study of the electronic spectrum of *trans*-stilbene, which represents the first fully correlated *ab initio* investigation of the system. The study has been performed with multiconfigurational second-order perturbation theory, the CASPT2 method, which is by now a well-established method for accurate calculations of electronic spectra of organic compounds. It was not possible, for technical reasons, to include in the active space all the 14 valence π-orbitals. The reduction to 12 orbitals (leaving two of them in the virtual space) led to intruder state problems. A level-shift technique was used to reduce the effect of the intruders on the excitation energies for the valence singlet excited states.

The geometry of the ground state was optimized at the CASSCF level of theory. The results show that the length of the ethylene double bond has been underestimated in the experimental X-ray determination of the geometry. Similar results have earlier been obtained for other organic molecules. It is a well-known artifact of the X-ray technique to produce too short bond lengths between double-bonded carbon atoms.

There is agreement between calculated excitation energies and observed band maxima, calculated and observed relative intensities. Also the computed nature and polarization properties of the transitions agree with available experimental data.

The three lowest singlet states have been found within an energy range of 0.4 eV. The first and third states, 1^1B_u and 2^1A_g, originate from the lowest 1^1B_{2u} state of benzene of covalent nature. The 2^1B_u state is described mainly by the one-electron promotion HOMO → LUMO. Interesting is that the 2^1B_u state, which can be considered as the analogue to the ionic V-like state of ethylene, somewhat mixed with the second excited state of benzene (1^1B_{1u}) is not the lowest singlet excited state of *trans*-stilbene. A similar pattern was found in an earlier study of the electronic spectrum of biphenyl.[44] Three electronic transitions have been found in the energy range 5.4−5.5 eV. They correspond to the second observed band of the one-photon spectrum. Only one electronic transition has been, however, obtained in the third band; it is the transition to the 6^1B_u state, which has been calculated at 6 eV. On the other hand, the results clearly confirm that the $1^1A_g \rightarrow 3^1A_g$ transition at 5 eV is responsible for the main band of the two-photon absorption spectrum. The controversial 3^1A_g state has a pronounced doubly excited character and is the analogue in stilbene at the Z-like state of ethylene. The lowest singlet Rydberg states have also been computed. They play a minor role in the understanding of the low-energy part of the spectrum. The lowest triplet state of *trans*-stilbene, 1^3B_u, is analogous to the covalent T state of ethylene.

Previous theoretical descriptions of the electronic spectrum of *trans*-stilbene obtained with semiempirical methods have been shown to be highly dependent on the scheme employed. The general similarity between the present results and the the PPP-(full CI) results[59] is, however, striking. In particular, the lowest singlet excited state 1^1B_u at 3.97 eV was found to have covalent character and the 3^1A_g at 4.80 eV appeared as a doubly excited state. Characterization of the third one-photon absorption band failed, however, at the PPP level.[59] For sake of comparison, the CNDO/S results deviate as much as 1 eV from the CASPT2 results (see, *e.g.*, ref 18).

Implications of the present results for the trans → cis photoisomerization process have been briefly discussed. Arguments are given in favor an adiabatic photoreaction on the S_1 surface, in which the observed small barrier could be understood on the basis of an adiabatic crossing by configurational mixing between the two lowest 1^1B_u and 2^1B_u states. The generally accepted picture, where the doubly excited A_g-like state plays an important role in the process, might not be correct. Some of the earlier semiempirical studies have arrived to the same conclusion. However, the present vertical excitation energies do not give enough insight for more extensive conclusions regarding the isomerization process. A parallel study of the cis conformer of stilbene, together with the corresponding potential energy curves along the twisting coordinate, is under way and will hopefully clarify the most critical static aspects of the photoisomerization of stilbene, which is the prototype for this important class of unimolecular reactions.

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