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Two-Photon Spectra of Stiff Stilbenes: A Contribution to the Assignment of the Low Lying Electronically Excited States of the Stilbene System

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The one- and two-photon spectra of trans-stilbene are reinvestigated and compared to the spectra of two stilbene derivatives in which rotation around the vinyl-phenyl bonds is prevented by methylene or ethano bridges. The spectra are compared to recent theoretical results that did not agree with some of the earlier assignments. The new experimental data lead to a consistent assignment of the low energy part of the singlet spectrum of trans-stilbene up to an excitation energy of about 50 000 cm^{-1}, which is in excellent agreement with the theoretical findings. Special consideration is given to the weaker of the first two allowed singlet transitions whose location has been under discussion for quite some time.

Introduction

In the field of spectroscopy stilbene (**1**) is certainly one of the most extensively investigated organic compounds. One of the reasons for the continuing interest in this molecule is its leading role in the investigation of photoinduced isomerizations, processes that are not only crucial for the understanding of many photochemical transformations and their solvent dependence but also for our own view of the external world as they form a key step in the visual process.[1−7] One concern among others was and still is the ordering of the low lying electronically excited states as this order is a cornerstone in the understanding of the photophysical and photochemical behavior of the molecule. Recently a breakthrough has been achieved by Molina, Merchán, and Roos[8] who succeeded in calculating the electronically excited singlet states of stilbene up to an energy of about 6 eV with high quality ab initio methods. The CASPT2 method[9−11] applied in this study yields results which in most cases are accurate up to 0.3 eV.[11−13]

Earlier, mostly semiempirical calculations had shown that stilbene is one of those molecules for which results depend strongly on the parametrization of the electron interaction in these methods.[14−18] Despite some general understanding that was achieved by combining the results of semiempirical calculations with the information obtained from spectroscopic investigations, the overall picture was not very conclusive. Even now, with the new theoretical results, there remain questions about how to combine these results with the available experimental information.

In the present contribution we supplement the findings of Molina et al. with some new experimental results on stilbene and two stilbene derivatives in which the rotation around the vinyl−phenyl bond is blocked by alicyclic rings.[19a] In addition to the long-known *trans*-1-(1-indanylidene)indane **2** we included *trans*-1-(1-benzocyclobutenylidene)benzocyclobutene **3**, a compound only recently synthesized by one of the authors[19b] (Scheme 1).

Materials and Methods

For this work, *trans*-**1** was purchased from Aldrich and used after recrystallization.

The compound *trans*-**2** was prepared from 1-indanone according to the procedure described in the literature.[20] The crude product was purified by chromatography on silica using *n*-hexane as eluent and further crystallization from methanol. The yellow product (needles) has a mp of 140−141 °C with an isomeric purity of about 99.9% shown by TLC. The product was completely characterized by spectroscopic properties.[19] All attempts to isolate the more polar cis isomer by this chromatographic method failed, because the cis isomer partly rearranges to the more stable trans product under these conditions on silica.[19b]

The compound *trans*-**3** was prepared from benzocyclobutenone[21] by treatment with low valent titanium species. Details can be found in ref 19b. The crude product, a 1:1 mixture of the isomers, was separated by preparative HPLC. The less polar trans isomer was crystallized from methanol yielding colorless crystals with a mp of 148−150 °C. The more polar cis isomer has a mp of 123−125 °C.

Absorption spectra were measured on a UV spectrometer (Perkin-Elmer 559). A commercially available low-temperature cell was used to measure spectra at liquid nitrogen temperature (≈77 K).

Fluorescence as well as one- and two-photon excitation spectra were obtained with essentially the same setup as described in ref 15. In contrast to the earlier measurements, an added low-temperature cell now allowed measurements down to 77 K. Excitation spectra were detected at the 0−0 transition or on the first intense vibronic peak of the fluorescence emission with bandwidths of several 100 cm^{-1}. One-photon excitation spectra were used to check if the observed fluorescence is due to the investigated compound.

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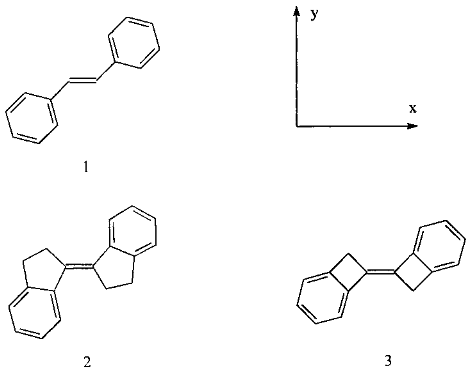
SCHEME 1: Structures and Coordinate System



All spectroscopic measurements were performed in 3-methylpentane (3MP) solutions, concentrations ranging between 10^{-3} and 10^{-5} mol/L. 3MP was purchased from Aldrich and purified according to literature procedures.

What is obtained in the two-photon measurements is the product of the two-photon cross-section $\delta(\nu)$ and the fluorescence quantum yield $\eta(\nu)$. Application of linearly and circularly polarized excitation light yields $\delta_{\uparrow\uparrow}\eta$ and $\delta_{\curvearrowright}\eta$, respectively. $\delta_{\uparrow\uparrow}$ and $\delta_{\curvearrowright}$ are the two independent quantities that can be obtained from two-photon measurements on isotropic samples in a one-color experiment.[22,23] The η independent ratio $\Omega = \delta_{\curvearrowright}/\delta_{\uparrow\uparrow}$ is known as the two-photon polarization parameter. Ω, which lies in the range between 0 and 3/2, is an excellent symmetry indicator.[22] Data points were taken in steps of 5 Å if not stated otherwise.

Prolonged irradiation of solutions of **2** and **3** leads to the appearance of cis products, which in contrast to **1**, absorb at lower energies than the corresponding trans forms (Table 1). Reconstruction of the spectrum of *cis*-**2** from the spectra of a photostationary mixture and of pure *trans*-**2**, both measured at liquid nitrogen temperature (LNT), leads to a result[19a] very similar to that obtained by Saltiel.[24] Application of the same procedure to **3** also resulted in a spectrum with well resolved vibrational peaks (Table 1). To avoid the influence of accumulating amounts of the cis forms, samples were repeatedly changed during optical measurements.

Coordinate Systems and State Assignments. The coordinate system used in this paper is shown in Scheme 1. There is now overwhelming evidence that trans-stilbene in its zero vibrational level is planar in S_0 as well as in S_1.[25-28] However, the barrier to rotation around one of the vinyl–phenyl bonds is so low (825 cm^{-1} in S_o in the gas phase[29]) that there is nearly free rotation at room temperature.[30] This is in agreement with an angle of about 30° found by Traetteberg et al. from an electron diffraction study of *trans*-**1** in the gas phase.[31] In solution there will be a distribution of torsional angles Θ (compare Figure 5) that depends on the temperature and probably also on the viscosity of the solvent.[32]

To compare the electronic states of stilbenes with different geometries and therefore different symmetries it is convenient to relate to the topological symmetry of the planar π-system which is D_{2h}.[8,15,18] This not only has the advantage of easily relating excited states of trans and cis forms of the same species but it also allows monitoring of states that interchange their order either due to changes in molecular geometry or due to the uncertainties in the theoretical calculations.

The CASPT2 Results. Before we present and discuss our own findings we briefly summarize the theoretical results of Molina et al.[8] and compare them with the experimentally available information. Figure 1 shows the CASPT2 results in form of a line spectrum. Table 2 contains additional theoretical and experimental information. The calculated states are labeled with respect to point group C_{2h} and, in parentheses, with respect to the topological symmetry D_{2h}. The latter is easily derived from the leading configurations reported by Molina et al. Numbers in the order of increasing energy are used only in connection with the topological symmetry labels to avoid confusion in cases where the order is not the same in theory and experiment.

The three transitions with larger oscillator strength are in near perfect agreement with what is known experimentally as bands A, B, and C.[18] The 0–0 transition of band A is located at 32242 ± 3 cm^{-1} in the gas phase[33,34] and at 31100 cm^{-1} in an Ar matrix at 12 K.[18] In solvents, such as 3MP, which yield glasses at liquid nitrogen temperature, the 0–0 transition is at 30 700 ± 200 cm^{-1} and the Franck–Condon maximum, which relates most closely to the vertical transition, at 32 200 ± 200 cm^{-1}. At room temperature the FC maximum shifts to higher energies (ca 33 700 cm^{-1}) in nearly all solvents in accordance with the increased average deviation from planarity.

Because of the preferred short axis orientation there is no doubt that $^1B_u(3^1B_{2u})$ is the transition responsible for the main body of band B. The calculated angle with respect to the first allowed transition is 43° compared to an experimental average of about 50° (see ref 18 for details). $^1B_u(3^1B_{3u})$, which is assigned to band C, is again predicted to be preferentially long-axis polarized (9° with respect to $^1B_u(1^1B_{3u})$). Dicroitic measurements lead to an angle of (21 ± 8)° between the two transition moments.[18] The first Rydberg transition (1^1A_u) was found at 43 000 cm^{-1} in the CASPT2 result, slightly below the second stronger π–π* transition and much lower than the first ^1A_u transition predicted by CNDO/S (54 000 cm^{-1}).[18]

Earlier semiempirical calculations[13-18] led to the same assignment as far as the nature of the three intense transitions is concerned. The weak transitions, however, depended strongly on the parametrization[18] and varied to such an extent that there were always some questions on the validity of the assignment of bands B and C. A relatively weak ^1B_u transition was found in most of the semiempirical calculations between bands A and B, prompting discussion on the proper assignment of the spectrum. The CASPT2 results reveal that the energy of this transition has been underestimated considerably in the semiempirical calculations. CASPT2 puts it close to $^1B_u(3^1B_{2u})$, the intense transition responsible for the main body of band B. Because of the nearly equal orientation of the transitions ^1B_u-(2^1B_{2u}) and $^1B_u(3^1B_{2u})$ and another weak transition $^1B_u(2^1B_{3u})$ that is predicted to lie in this region, it will be difficult to detect the weak transitions experimentally even if they contribute somewhat to band B.

The ^1A_g states that result from the CASPT2 calculation do not agree with our earlier assignment of the two-photon excitation spectrum.[15] On the basis of the results of semiempirical calculations, we had placed the second excited ^1A_g close to the first one leading to a large gap between the third and the fourth ^1A_g state. In light of the CASPT2 results, such an assignment is no longer acceptable. We come back to this point when we discuss our new experimental results.

One problem that remains is the relative order of the first two ^1B_u transitions in trans-stilbene. The CASPT2 calculations predicted a weak transition $^1B_u(1^1B_{2u})$, that lies vertically 2400 and adiabatically 1500 cm^{-1} in front of the strong $^1B_u(1^1B_{3u})$. This weak transition results primarily from a combination of local phenyl excitations (L_b^-). Molina et al. argue that $^1B_u(1^1B_{2u})$

TABLE 1: Peak Positions Measured in 3MP (in 1000 cm^{-1})

		A		a					B	
		0−0	0−1	0−0	0−1	A′	b	c	0−0	0−1
trans-1	RT[a]		32.7							44.0
	LNT[b]	30.7	32.2	31.7	33.2		38.4	40.9	42.15	43.55
trans-2	RT	29.6	31.1			34.6			40.8	42.15
	LNT	29.4	30.95	31.5		34.5	40.4	41.8	40.7	42.05
cis-2	LNT	28.4	30.0						39.8	41.2
trans-3	RT	31.0	32.5			35.8			41.95	43.25
	LNT	30.7	32.2	33.9	35.3	35.6	≈40	≈41.5	41.65	43.0
cis-3	LNT	29.9							40.75	

[a] RT: room temperature. [b] LNT: Liquid nitrogen temperature.

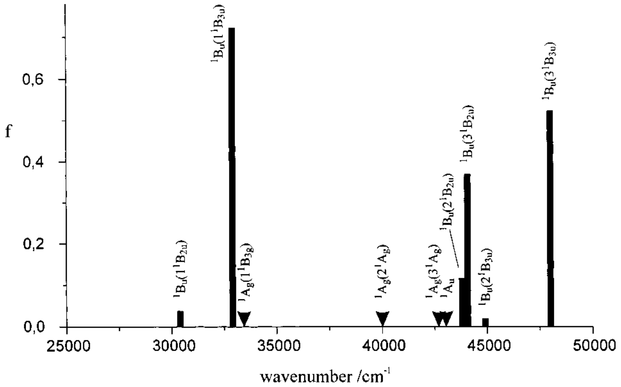


Figure 1. Vertical excitation energies and oscillator strengths (f) as found in the CASPT2 calculation of ref 8. The labels are explained in the preceding section.

TABLE 2: CASPT2 Results from Reference 8

C_{2h}	D_{2h}	E_{vert}/1000 cm^{-1}	E_{ad}/1000 cm^{-1}	f_{theor}	∠ to x	f_{exp}[a]
^1B_u	1^1B_{2u}	30.4	29.0	0.038	50°	
^1B_u	1^1B_{3u}	32.9	30.5	0.723	43°	0.74
^1A_g	1^1B_{3g}	33.3				
^1A_g	2^1A_g	40.0				
^1A_g	3^1A_g	42.8				
^1A_u		43.0		0.001	per	
^1B_u	2^1B_{2u}	43.8		0.117	0°	0.29
^1B_u	3^1B_{2u}	43.8		0.371	0°	
^1B_u	2^1B_{3u}	44.9		0.019	0°	
^1B_u	3^1B_{3u}	48.0		0.524	52°	0.41

[a] From ref 18.

may indeed be the lowest singlet state and not yet be discovered. They refer to the low lying ^1A_g states of polyenes that have been overlooked for such a long time. However, these ^1A_g states have finally been discovered from the incompatibility of fluorescence and absorption spectra (Stokes shift, structure, fluorescence decay time).[35] Such an incompatibility does not occur in trans-stilbene. The observed fluorescence is clearly related to band A and no additional fluorescence has been detected thus far. High-resolution gas-phase experiments,[25,27,33,34] as well as matrix isolation studies,[36] did not show indications of a second electronically excited state below or directly above the 0−0 transition of band A.

If $^1B_u(1^1B_{3u})$ is the lowest excited singlet state S_1 in trans-stilbene, $^1B_u(1^1B_{2u})$ must be located somewhere on the high energy side of the onset of band A. The existence of an additional transition in the region of band A is, however, not a new concept. It was first suggested in 1973 by Bernstein that a second transition may be hidden under the high energy flank of band A.[37] Somewhat later Yogev and Margulis provided further evidence for such a transition in 4,4′-dimethyl trans-stilbene.[38] The onset of this transition was estimated to lie not more than 1000 cm^{-1} higher than the onset of the intense long axis polarized one. The continuing difficulties with the assignment of this state resulted in part from the fact that most semiempirical calculations predicted $^1B_u(1^1B_{2u})$ to be preferentially short-axis polarized. Because there is no clear indication of a short-axis polarized transition in the linear dichroism spectra of **1** and **2**,[15,18,39,40] it was argued that if this transition is really underlying band A it must be too weak to influence the observed polarization. The new calculations of Molina et al. confirm a result found earlier from semiempirical studies:[18] As soon as the first two ^1B_u transitions come close together they start to mix and the weak $^1B_u(1^1B_{2u})$ borrows some intensity from the strong $^1B_u(1^1B_{3u})$, but with this borrowed intensity it also acquires the long-axis polarization of the latter. The lack of pronounced short-axis polarization is therefore not in disagreement with the location of $^1B_u(1^1B_{2u})$ in the region of band A.

Results and Discussion

Figure 2 shows the newly measured two-photon absorption spectrum of **1** (lower panel) together with the spectrum measured earlier at room temperature in ethanol[15] (upper panel). The new spectrum shows the same general structure as the older one with two distinct differences: A broad band around 35 500 cm^{-1} and a peak at 39 300 cm^{-1} are missing in the new spectrum. We believe that these two bands have been due to photoproducts in the older measurements. It is well known that under irradiation *trans*-**1** forms dihydrophenanthrene in addition to *cis*-**1**. Special care was taken in the new measurements to prevent the accumulation of photoproducts by changing the sample after short periods of light exposure.

The absence of the broad band around 35 500 cm^{-1} in the newly measured two-photon spectrum reveals three members of a progression with a spacing of 1550 cm^{-1}. The maxima at 31 700, 33 200, 38 400, and 40 900 cm^{-1} are shifted by 100 to 200 cm^{-1} to higher energies compared to the old spectrum. This is quite different from the 400 to 500 cm^{-1} low energy shift (measured at the 0−1 transition) that we observed for bands A and B in the one-photon spectrum when we went from room temperature to liquid nitrogen temperature (Figure 2 and Table 1). This shift is very similar for ethanol and 3MP. The different shift of band A and the structure we termed *a* is a clear indication that these two bands result from different transitions. If *a* were due to vibronically induced two-photon activity connected to band A, it had to shift in the same way as the one-photon allowed part of A. That we are dealing with two different transitions is further confirmed by the fact that the vibrational structure of band *a* does not become much sharper when we go from RT to LNT, a sharp contrast to the vibronic structure of band A. This behavior is in line with the assignment of band *a* to $^1A_g(1^1B_{3g})$. This transition corresponds mainly to the in-phase combination of the two local ^1L_b transitions ($^1L_b{}^+$)[15] and is therefore less affected by twists of the phenyl rings than the first strong ^1B_u transition. Because of the localized nature

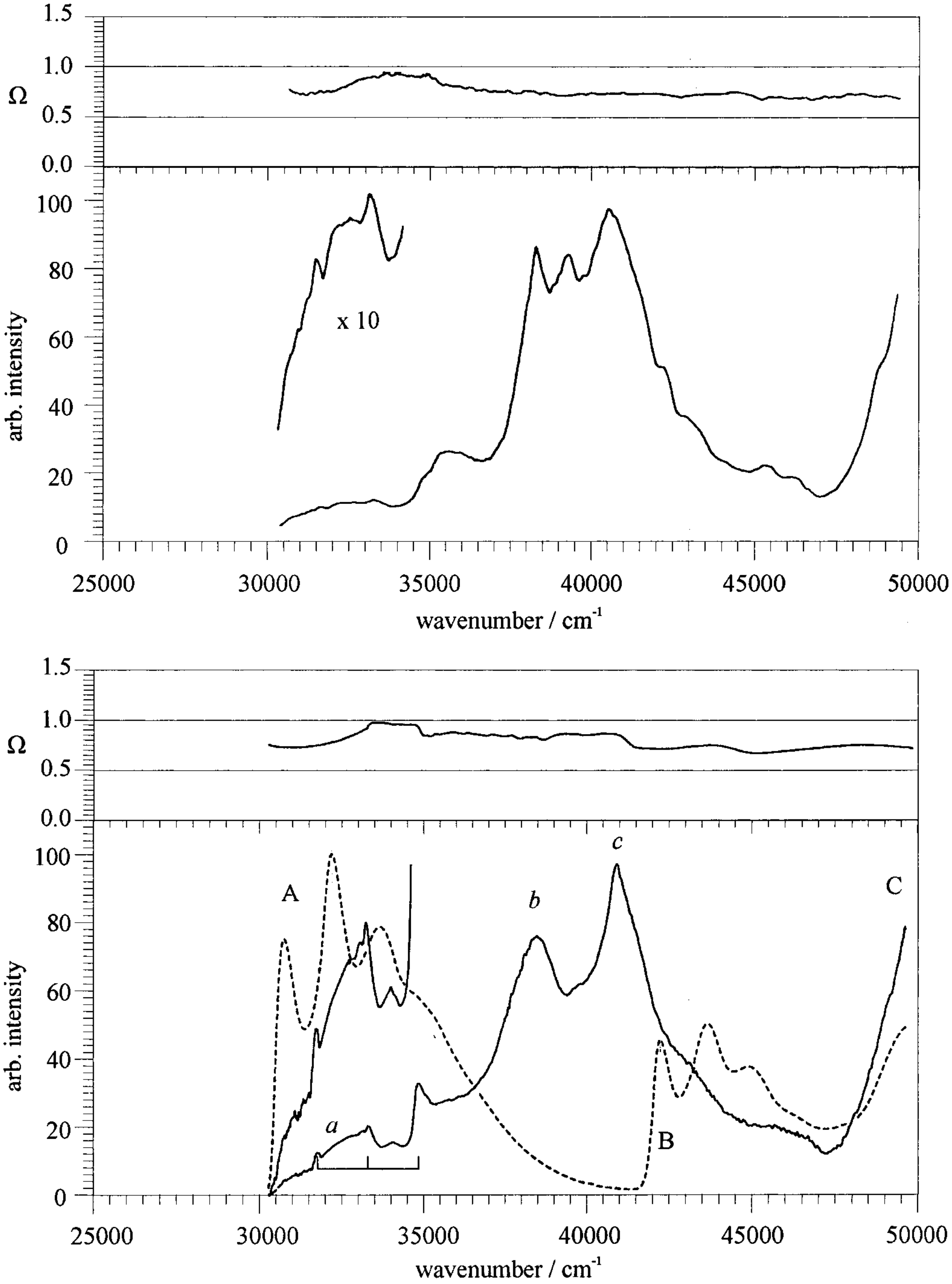


Figure 2. Two-photon excitation spectrum $\delta_{\uparrow\uparrow}\eta$ and two-photon polarization parameter Ω for *trans*-**1**. Upper panel: in ethanol at room temperature (from ref 15). Lower panel: in 3MP at liquid nitrogen temperature (≈77 K). The one-photon absorption spectrum is shown by the dashed curve.

of $^1A_g(1^1B_{3g})$, the progression forming mode in band *a* is most likely a ring breathing mode and not the stretching mode of the central double bond that dominates the vibrational structure of band A.

What must be assigned as vibrationally induced is the weak two-photon activity in front of band *a*. It could result from vibronic coupling between $^1B_u(1^1B_{3u})$ and the nearby $^1A_g(1^1B_{3g})$, but there is also a possibility that the yet unidentified $^1B_u(1^1B_{2u})$ transition contributes to this activity. In 3MP the distance between the 0−0 transitions of $^1B_u(1^1B_{3u})$ and $^1A_g(1^1B_{3g})$ is only 900 cm^{-1}. In the free molecule the two transitions are expected to be even closer together because of the larger solvent shift of the one-photon allowed transitions.[41] For the 0−0 transition of band A, this shift is 1500 cm^{-1} for 3MP at 77 K and 600 cm^{-1} for an argon matrix at 12 K.[18]

With the CASPT2 results at hand the further assignment of the two-photon spectrum is now obvious: band *b* corresponds to $^1A_g(2^1A_g)$ and band *c* to $^1A_g(3^1A_g)$. Semiempirical calculations predicted moderate two-photon activities and Ω values around 0.75 for these two transitions.[15] With this new assignment the distances between the three lowest ^1A_g transitions and their location with respect to the two low lying intense ^1B_u transitions are now in close agreement with the CASPT2 results.

In *trans*-1-(1-indanylidene)indane **2** the bands A and B are shifted to lower energies with respect to **1** by 1300 and 1400 cm^{-1}, respectively (Figure 3). A freshly prepared 3MP solution measured at LNT did not show a shoulder at the onset of band A. Such a shoulder was observed by Vogel et al.[42] (see also ref 32) and attributed to the formation of association complexes. We observe such a shoulder only after irradiation and attribute

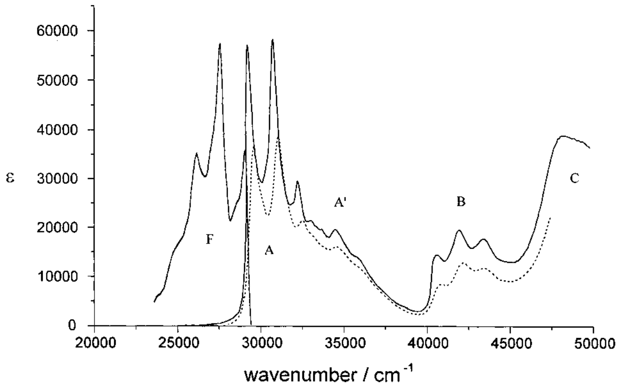


Figure 3. Absorption and fluorescence (F) spectra from a 3-methylpentane (3MP) solution of *trans*-**2**. Dashed line: room temperature; full line: ≈77 K. The intensity of the low-temperature absorption spectrum is not corrected for the volume contraction of the solvent. The fluorescence intensity is in arbitrary units and not corrected for instrumental response.

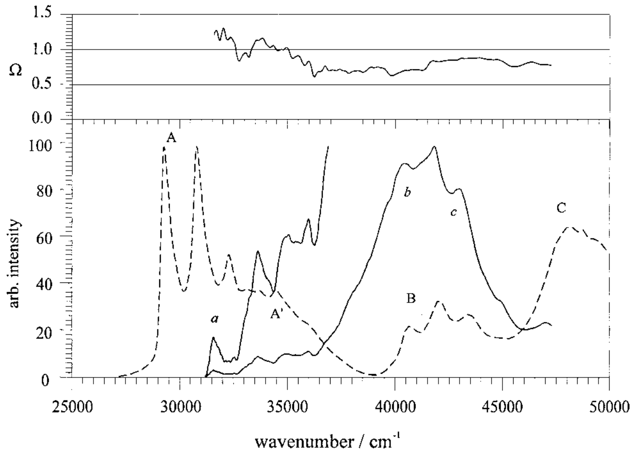


Figure 4. Two-photon excitation spectrum $\delta_{\uparrow\uparrow}\eta$ and two-photon polarization parameter Ω for *trans*-**2** measured in 3MP at ≈77 K. The one-photon absorption spectrum is shown by the dashed curve.

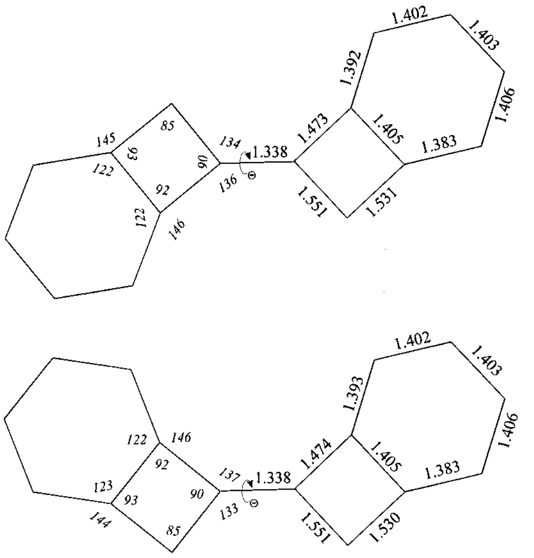


Figure 5. Selected bond lengths in Å and bond angles in degree as obtained from a DFT calculation with Becke3 exchange[44] and Lee-Yang-Parr correlation[45] potential. Basis set: 6-31G*.

it to the apperance of *cis*-**2** as discussed in section 2. A low energy shift of bands A and B is predicted by CNDO/S and INDO/S calculations if the π systems of both molecules are assumed to be planar. Therefore, this shift cannot be taken as an indication for a nonplanar π system in **1** (compare the discussion in ref 32). The spectral shift and the increase in vibrational fine structure between RT and LNT is much smaller than in **1** in accordance with the strongly hindered twist around the vinyl−phenyl bonds. The shift is of the order of 300 cm^{-1} for all discernible maxima, except the one at 34 600 cm^{-1} that does not move by more than 150 cm^{-1} (Table 1). Together with the fact that this maximum does not fit into the progression observed for band A this is a strong indication that this maximum does not belong to band A and results instead from a separate transition. For this reason we put a separate label (A′) to this structure.

The fluorescence is clearly related to band A. First of all, the estimated radiative lifetime of 1.6 ns [4] is in disagreement with a weak electronic transition. Second, as already discernible from the low resolution spectra of Figure 3, the frequencies of the progression forming modes 7a$_g$ and 8a$_g$, which strongly involve the stretching of the central double bond,[43] are reduced in S$_1$ by about 60 cm^{-1} compared to S$_0$. If the fluorescence were related to $^1B_u(1^1B_{2u})$ we should not observe such a reduction because of the local phenyl character of that excitation.

The two-photon excitation spectrum of **2**, measured in 3MP at LNT, is shown in Figure 4 together with the one-photon absorption spectrum. As in the case of **1**, the two-photon spectrum consists of a weak band (*a*) at the onset followed by a stronger one between 38 000 and 44 000 cm^{-1}. Unlike **1**, we did not observe any detectable two-photon activity prior to the onset of band *a*. The vibrational fine structure of band *a* is more complex than in **1**. It leads to modulations in Ω beginning with values larger than one. It is interesting to note that compared to **1**, band *a* does not shift toward lower energies. The location of the 0−0 transition of band *a* is nearly the same in **1** and **2** (Table 1), leading to a larger energetic separation between the onsets of bands A and *a*. Because we assign band *a* to a transition strongly localized in the phenyl rings, this lack of shift is not surprising: The 0−0-transitions of toluene and *o*-xylene differ by only 300 cm^{-1}.

The bands that we assigned to $^1A_g(2^1A_g)$ and $^1A_g(3^1A_g)$ in **1** are shifted toward higher energies in **2** so that they are strongly overlapping with the one-photon allowed band B. From the comparison of all three investigated compounds we assign the maxima at 40 300 cm^{-1} (*b*) and 41 700 cm^{-1} (*c*) to the vertical transitions to $^1A_g(2^1A_g)$ and $^1A_g(3^1A_g)$, respectively. However, because of the strong overlap with band B, it is possible that some of the two-photon activity in this region is due to vibronic coupling.

Finally we turn to the newly available 1-(1-benzocyclobutenylidene)benzocyclobutene (**3**). Figure 5 shows the result of ab initio (DFT/B3LYP/6-31G*[44,45]) geometry optimizations for the trans and cis forms. The carbon skeleton is predicted to be planar in both cases. The strain of the four-membered rings leads to C−C−C bond angles of up to 146° but this is only of minor importance to the π system. The overall structure of the electronic spectrum of *trans*-**3** (Figure 6) is indeed similar to what we observe for **1** and **2**. Bands A and B are shifted to higher energies compared to **2** so that the 0−0 transition of band A coincides with that of **1** in the LNT spectra (Table 2). The 0−0 transition of band B lies 400 cm^{-1} lower than in **1**. The structure A′ is more pronounced than in **2** and shifted by 1100 cm^{-1} to higher energies. The corresponding shift of the 0−0 transition of band A is only 1000 cm^{-1}. This, together with the different shift of A and A′ between RT and LNT (see Table 2), provides further evidence that A′ results from a separate electronic transition. It is interesting to note that the narrowing

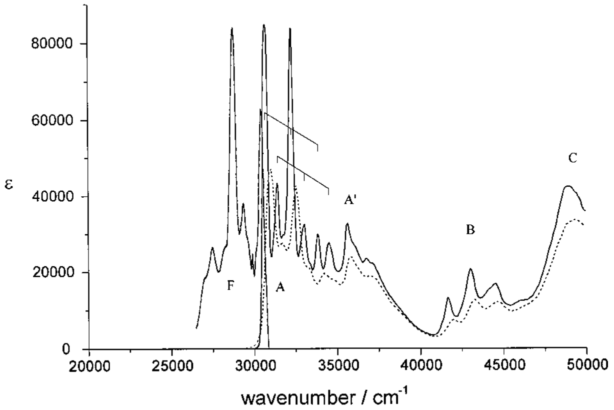


Figure 6. Absorption and fluorescence (F) spectra from a 3MP solution of *trans*-**3**. Dashed line: room temperature. Full line: ≈77 K. See caption to Figure 3 for details.

between RT and LNT is more pronounced in **3** than in **2**. This is most likely due to the remaining conformational mobility of the five-membered rings in **2**. The barrier to inversion between the two possible envelope forms of each ring is so low that the inversion is not frozen at LNT.

Band A exhibits two well resolved vibrational progressions that cover a more complex vibrational fine structure as we know from high-resolution measurements.[43] Therefore, it is not surprising that the mirror symmetry between absorption and emission is far from being perfect. The comparison of emission and absorption is further complicated because our sample of *trans*-**3** contained a small amount of *cis*-**3** that could be identified in the above-mentioned high-resolution measurements. As *cis*-**3** absorbs at longer wavelengths than *trans*-**3**, energy transfer can lead to a non-negligible amount of cis fluorescence even when the cis isomer is not detectable in absorption. However, the two dominating maxima in the fluorescence band clearly belong to the trans form. In accordance with the assignment of band A to $^1B_u(1^1B_{3u})$ we again observe an increase of the distance between the main vibronic bands of about 60 cm^{-1} when we compare fluorescence and absorption.

The two-photon excitation spectrum is shown in Figure 7. The spectrum is noisier than those of **1** and **2** because we had to work with more dilute solutions. However, the overall structure is the same as in **1** and **2**. Bands *b* and *c* appear at similar energies as in **2**, leading to a somewhat better separation from band B. The 0−0 transition of band *a* is shifted by 2500 cm^{-1} toward higher energies compared to **1** and **2**. This shift further increases the separation between the onsets of bands A and *a*. As in the case of **2**, we did not find any detectable two-photon activity below the onset of band *a*. Vibronic coupling that makes the $^1B_u(1^1B_{3u})$ transition partially two-photon allowed appears to be suppressed by the increased energetic separation from band *a* and perhaps the rigidity of **2** and **3**.

Conclusions

The combined spectroscopic information that is obtained from the one- and two-photon absorption spectra of trans-stilbene **1** and two of its sterically confined derivatives (**2** and **3**) provides a solid experimental basis for a consistent description of the low lying electronically excited states of the trans-stilbene system up to an energy of about 50 000 cm^{-1}. With the exception of $^1B_u(1^1B_{2u})$, the experimental results agree in detail with the recent theoretical findings of Molina et al.[8] $^1B_u(1^1B_{2u})$ was found as the lowest excited singlet state in the CASPT2 calculation, but there is no experimental evidence for a weak transition at energies lower than the onset of band A whose assignment to $^1B_u(1^1B_{3u})$ is unquestioned. There is, on the other hand, a clear indication for a weak to medium intense transition (A′) that starts somewhere between 1000 and 5000 cm^{-1} above the onset of band A. We assign A′ to $^1B_u(1^1B_{2u})$. The alternative assignment to $^1B_u(2^1B_{2u})$, a weak to medium intense transition predicted between $^1B_u(1^1B_{3u})$ and $^1B_u(3^1B_{2u})$ by many semiempirical calculations, is not feasible in the light of the CASPT2 results. It would mean that, different from all other low lying singlet states, this state is predicted by more than one eV too high, about three times the error margin experienced in earlier applications of the CASPT2 method.[11]

For the rest of the low lying excited singlet states the assignment is straightforward. Band C results from the transition

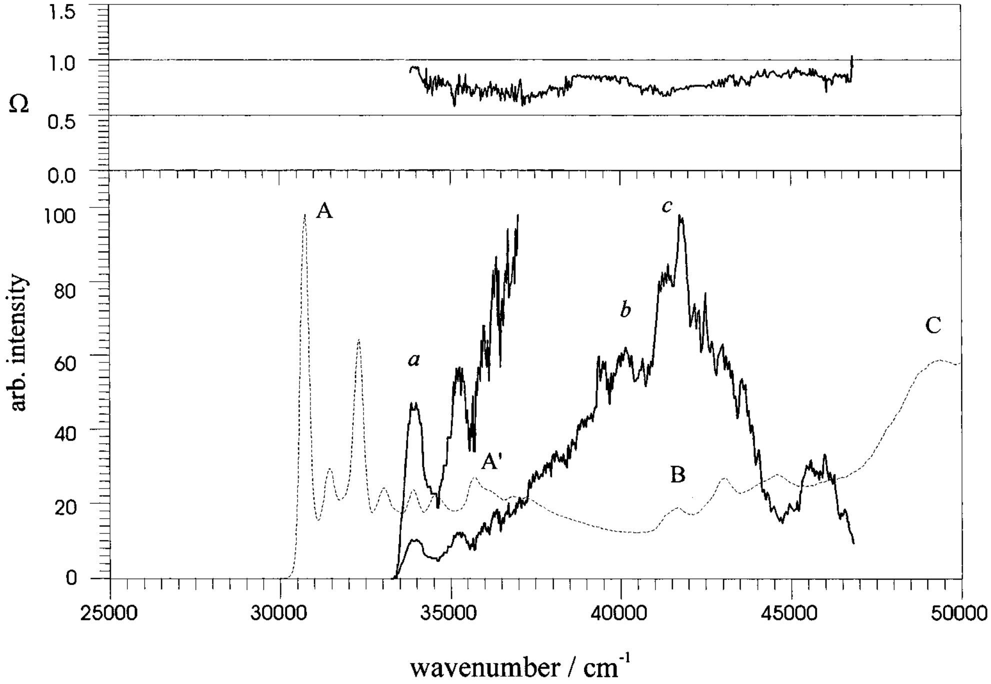


Figure 7. Two-photon excitation spectrum $\delta_{\uparrow\uparrow\eta}$ and two-photon polarization parameter Ω for *trans*-**3** measured in 3MP at ≈77 K. Dashed line: one-photon absorption at room temperature.

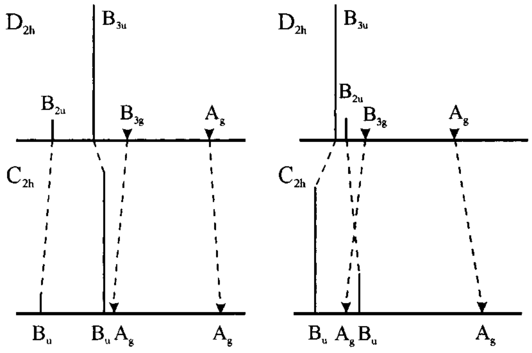


Figure 8. Possible interaction schemes. See text for details.

to $^1B_u(3^1B_{3u})$. The main body of band B is related to the more intense and more short-axis polarized of the transitions to $^1B_u(2^1B_{2u})$ and $^1B_u(3^1B_{2u})$. The exact order of these two states, which are predicted to be nearly degenerate in the CASPT2 result, cannot be determined from the available experiments. The first excited ^1A_g state ($^1A_g(1^1B_{3g})$) lies only 1000 (in **1**) to 3000 cm^{-1} (in **3**) higher than $^1B_u(1^1B_{3u})$. It will be interesting to see if the different separation between these two states in **1** and **3** is reproduced by the CASPT2 method. The second and the third excited ^1A_g states are located around 40 000 cm^{-1}. The separation between the three lowest excited ^1A_g states, as well as their location with respect to the states $^1B_u(1^1B_{3u})$ and $^1B_u(3^1B_{2u})$, is in excellent agreement with the theoretical results.

Although the incorrectly predicted order of the first two ^1B_u states still falls into the 0.3 to 0.4 eV margin that is claimed for well-designed CASPT2 calculations, it is tempting to discuss possible reasons for this failure. One explanation comes from the specific character of $^1B_u(1^1B_{2u})$. In the topological symmetry D_{2h}, this state results mostly from the out-of-phase combination of the ^1L_b states of the two phenyl rings ($^1L_b^-$). The corresponding in-phase combination ($^1L_b^+$) leads to the lowest ^1A_g state. In D_{2h} these states belong to the irreducible representations B_{2u} and B_{3g}, which means they cannot interact with B_{3u} and A_g singlet states. Deviation from the topological D_{2h} symmetry causes 1^1B_{3g} to mix with the ^1A_g states and 1^1B_{2u} with the $^1B_{3u}$ states. As there is no doubt that $^1A_g(2^1A_g)$ is located above $^1A_g(1^1B_{3g})$, this interaction can only stabilize the latter (see Figure 8). For $^1B_u(1^1B_{2u})$ the situation is more complicated. If 1^1B_{2u} lies below 1^1B_{3u} in the D_{2h} model, the mixing increases the stabilization of $^1B_u(1^1B_{2u})$ (Figure 8, left). This is what appears to happen in the CASPT2 calculation. If, however, 1^1B_{2u} lies only slightly above 1^1B_{3u} in the parent D_{2h} system (Figure 8, right), the interaction increases the separation of the two states with the likely consequence that $^1B_u(1^1B_{2u})$ or $^1L_b^-$ is now at higher energies than $^1A_g(1^1B_{3g})$ or $^1L_b^+$. This is exactly what we observe in **2** and **3** where the band labeled A′ is located 2000 to 3000 cm^{-1} above the onset of the first band (*a*) in the two-photon spectrum. It may well be that it needs only minor changes in the geometry to reverse the order of the first two ^1B_u states in the CASPT2 result.

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References and Notes

(1) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.

(2) Meier, H. *Angew. Chem.* **1992**, *104*, 1425; *Int. Ed. Engl.* **1992,** *31*, 1399.

(3) Arai, T.; Tokumaru, K. *Chem. Rev.* **1993**, *93*, 23.

(4) Rettig, W.; Majenz, W.; Herter, R.; Letard, J.-F.; Lapouyade, R. *Pure Appl. Chem.* **1993**, *65*, 1699.

(5) Gröner, H. H.; Kuhn, *J. Adv. Photochem.* **1995**, *19*, 1.

(6) Whitten, D. G. *Acc. Chem. Res.* **1995**, *26*, 502.

(7) Majima, T.; Tojo, S.; Ishida, A.; Takamuku, S. *J. Phys. Chem.* **1996**, *100*, 13615.

(8) Molina, V.; Merchán, M.; Roos, B. O. *J. Phys. Chem.* A **1997**, *101*, 3478.

(9) Anderson, K.; Malmquist, P.-A.; Roos, B. O.; Sadlej, A. J. K.; Wolinski, J. *J. Chem. Phys.* **1990**, *94*, 5483.

(10) Anderson, K.; Malmqvist, P.-A.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(11) Roos, B. O.; Fülscher, M. P.; Malmqvist, P.-A.; Merchán, M.; Serrano-Andrés, L. *Theoretical Studies of Electronic Spectra of Organic Molecules* in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995.

(12) Roos, B. O.; Anderson, K. *Chem. Phys. Lett.* **1995**, *245*, 215.

(13) Beck, M. E.; Rebentisch, R.; Hohlneicher, G.; Fülscher, M. P.; Serrano-Andrés, L.; Roos, B. O. *J. Chem. Phys.* **1997**, *107*, 9464.

(14) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; John Wiley and Sons: New York, London, 1962.

(15) Hohlneicher, G.; Dick, B. *J. Photochem.* **1984**, *27*, 215.

(16) Galvao, D. S.; Soos, Z. G.; Ramasesha, S.; Etemad, S. *J. Chem. Phys.* **1993**, *98*, 3016.

(17) Soos, Z. G.; Ramasesha, S.; Galvao, D. S.; Etemad, S. *Phys. Rev.* **1993**, *B47*, 1742.

(18) Gudipati, M. S.; Maus, M.; Daverkausen, J.; Hohlneicher, G. *Chem. Phys.* **1995**, *192*, 37 and references therein.

(19) (a) Wrzal, R. *Spektroskopische und Theoretische Untersuchungen an Stilben und sterisch gehinderten Homologen*, Dissertationsschrift Universität zu Köln, 1993. (b) Frank, R. *Synthese und Eigenschaften von sterisch definierten Stilben Derivaten*, Dissertationsschrift Technische Universität München, 1994.

(20) Lenoir, D.; Lemmen, P. *Chem. Ber.* **1984**, *117*, 2300.

(21) Schiess, P.; Heitzmann, M. *Angew. Chem.* **1977**, *89*, 485; *Int. Ed. Engl.* **1977**, *16*, 469. See also: *Org. Synth.* **1995,** *72*, 116.

(22) Monson, P. R.; McClain, N. M. *J. Chem. Phys.* **1970**, *53*, 29. Monson, P. R.; McClain, N. M. *J. Chem. Phys.* **1972,** *56*, 4817.

(23) Dick, B.; Gonska, H.; Hohlneicher, G. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 746.

(24) Saltiel, J.; Sun, Y.-P. In *Photochromism: Molecules and Systems*; Dürr, H., Bouos-Laurent H., Eds.; Elsevier: Amsterdam, 1990; p 64.

(25) Spangler, L. H.; van Zee, R.; Zwier, T. M. *J. Phys. Chem.* **1987**, *91*, 2782.

(26) Spangler, L. H.; van Zee, R.; Blankespoor, C.; Zwier, T. M. *J. Phys. Chem.* **1987**, *91*, 6077.

(27) Champagne, B. B.; Pfanstiel, J. P.; Plusquellic, D. F.; Pratt, D. W.; van Herpen, W. M.; Meerts, W. L. *J. Phys. Chem.* **1990**, *94*, 6.

(28) Felker, P. M.; Zewail, A. H. In *Femtosecond Chemistry*; Manz, J., Woeste, L., Eds.; VCH: Weinheim, Germany, 1995; Vol. 1, p 193.

(29) Chiang, W.-Y.; Laane, J. *J. Chem. Phys.* **1994**, *100*, 8755.

(30) Lhost, O.; Brédas, J. L. *J. Chem. Phys.* **1992**, *96*, 5279.

(31) Traetteberg, M.; Frantsen, E. B.; Mijlhoff, F. C.; Hoekstra, A. J. *J. Mol. Struct. (THEOCHEM)* **1975**, *26*, 57.

(32) Ogawa, K.; Suzuki, H.; Futakami, M. *J. Chem. Soc., Perkin Trans. 2* **1988**, *39*.

(33) Amirav, A.; Jortner, J. *Chem. Phys. Lett.* **1982**, *95*, 266.

(34) Syage, J. A.; Lambert, W. R.; Felker, P. M.; Zewail, A. H.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1982**, *88*, 266.

(35) Hudson, B. S.; Kohler, B. E. *J. Chem. Phys.* **1973**, *59*, 4984.

(36) Weber, M., Masters Thesis, Cologne, 1995.

(37) Bernstein, J. *Spectrochim. Acta* **1973**, *29A*, 147.

(38) Yogev, A.; Margulies, L. *Israel J. Chem.* **1977**, *16*, 258.

(39) Dyck, R. H.; McClure, D. S. *J. Chem. Phys.* **1962**, *36*, 2326.

(40) Uznanski, P.; Kryszewski, M.; Thulstrup, E. W. *Spectrochim. Acta* **1990**, *46A*, 23.

(41) Liptay, W. *Z. Naturforsh.***1965**, *20A*, 1441.

(42) Vogel, J.; Schneider, S.; Dörr, F.; Lemmen, P.; Lenoir, D. *Chem. Phys.* **1984**, *90*, 387.

(43) Hohlneicher, G.; Kautz, I.; Tillmanns, B.; Lenoir, D.; Frank, R. *J. Mol. Struct. (THEOCHEM)* **1995**, *348*, 191.

(44) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(45) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.