LETTERS

Additional Evidence for Planarity in Isolated *trans*-Stilbene: A Study of α-Deuterio-*trans*-stilbene

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The geometry of the isolated *trans*-stilbene molecule has been investigated through the study of a close analogue, α-deuterio-*trans*-stilbene, in which the inversion symmetry is broken. Both the jet-cooled fluorescence excitation and dispersed fluorescence spectra show no observable intensity down to 0.02% of the origin in the fundamentals of two low-frequency vibrational modes which should become allowed if the molecule were nonplanar. However, we do observe at least one new transition in the first 400 cm^{-1} which is present due to symmetry lowering as a result of the isotopic substitution. We conclude that both isolated α-deuterio-*trans*-stilbene and *trans*-stilbene itself are planar in both their ground and first excited singlet states.

Introduction

The geometry of *trans*-stilbene in the gas phase has been the subject of several previous studies.[1-6] The floppiness of the phenyl rings about the ethylenic carbon–phenyl bonds makes it difficult to predict the geometry of the isolated molecule with certainty. In the crystal the molecule takes on a C_i geometry with a small tilt of the phenyl rings out of the plane.[1] In the gas phase, the electron diffraction studies of Traetteburg et al.[2] pointed to a C_2 geometry for the molecule. Baskin et al.[3] have obtained results viewing the pure rotational coherence effects on polarized picosecond fluorescence decays which are most consistent with a molecule with inversion symmetry. Myers et al.[4] argue for a C_{2h}

or C_i geometry based on the absence of certain bands in the absorption spectrum.

Recent spectroscopic studies[5,6] of the S_0–S_1 fluorescence excitation and dispersed fluorescence spectra near the origin in a supersonic jet have provided stronger evidence for the molecule's geometry. The analysis of Suzuki et al.[5] indicated the existence of an inversion center in the molecule. The extension of this work

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(1) Dyck, R. H.; McClure, D. S. *J. Chem. Phys.* **1962**, *36*, 2326.
(2) Traetteberg, M.; Fransten, E. B.; Mijlhoff, F. C.; Hoekstra, A. *J. Mol. Struct.* **1975**, *26*, 57.
(3) Baskin, J. S.; Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1987**, *86*, 2483.
(4) Myers, A. B.; Trulson, M. O.; Mathies, R. A. *J. Chem. Phys.* **1985**, *83*, 5000.
(5) Suzuki, T.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1986**, *90*, 6431.
(6) Spangler, L. H.; van Zee, R.; Zwier, T. S. *J. Phys. Chem.* **1987**, *91*, 2782.

by our group combined with additional information from *p*-methyl-*trans*-stilbene[6] has led us to the conclusion that the isolated molecule is planar (i.e., C_{2h}). A short summary of that work is given below.

The complete assignment of the low-frequency region of the excitation and dispersed fluorescence spectra of *trans*-stilbene involves only three modes: ν_{25}(C_e–C_e–Ph in-plane bend), ν_{36}(C_e–Ph out-of-plane bend), and ν_{37}(C_e–Ph out-of-plane torsion). The out-of-plane bend and torsion are seen throughout the spectrum only as even overtones and combination bands. In particular, a careful search for the 37_0^1 transition was unsuccessful and placed a strict bound on its intensity of 0.1% of the origin intensity. If the molecule were C_2 symmetry, the ν_{36} and ν_{37} fundamentals would be allowed. Thus on this basis alone the molecule is either C_{2h} or C_i symmetry.

In order to distinguish between these two possibilities we took fluorescence excitation and dispersed fluorescence spectra of a close analogue of *trans*-stilbene; namely, *p*-methyl-*trans*-stilbene. This molecule was chosen because the methyl group is a small perturbation on the electronic structure so that the molecule will likely have the same geometry as *trans*-stilbene itself. At the same time, the presence of the methyl group does remove the inversion symmetry of the molecule. The ν_{36} and ν_{37} modes which are A_u in C_{2h} become A'' in C_s. Thus if *p*-methyl-*trans*-stilbene is planar we expect once again to see only even overtones and combinations involving these modes while if it is nonplanar the fundamentals will be allowed. LIF excitation and dispersed fluorescence spectra of *p*-methyl-*trans*-stilbene allowed us to readily identify the 37_0^2 transition, but the 37_0^1 fundamental is not observed to within 1% of the origin intensity. Hence we conclude that both *p*-methyl-*trans*-stilbene and, by analogy, *trans*-stilbene itself, are planar.

While these studies provide strong evidence for *trans*-stilbene's planarity, the results are not completely unambiguous. First, methyl substitution significantly complicates the low-energy region of the spectrum by introducing internal rotation structure.[7] Such structure is interesting in its own right but interferes with a complete vibrational assignment and with the search for fundamental transitions. Second, though one would not expect methyl group substitution in the para position to change the geometry of the molecule, such a geometry change could conceivably occur. Third, methyl substitution in the para position may be too weak a perturbation on the molecule to induce much intensity in the fundamentals even if they are allowed. The stringent limits we place on the absence of the fundamentals argue against this. However, the methyl group's effect may be muted by para substitution which places it far from the ethylenic moiety which is the primary carrier of the π–π^* transition.

In this Letter we report LIF excitation and dispersed fluorescence spectra of α-deuterio-*trans*-stilbene
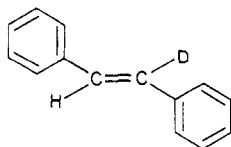
We will see that deuterium substitution in the α position produces virtually no perturbation on the frequencies of the 25, 36, and 37 normal modes. It will leave the geometry completely unperturbed while breaking the symmetry strongly enough to allow other modes to appear in the spectrum. The 36_0^1 and 37_0^1 fundamentals are still not observed even at a level 4000 times smaller than that of the origin. As a result, we conclude that the isolated *trans*-stilbene molecule is planar.

Experimental Section

The experimental apparatus and conditions are virtually identical to that previously described. The α-deuterio-*trans*-stilbene sample is heated to 110 °C, entrained in 3 atm helium,
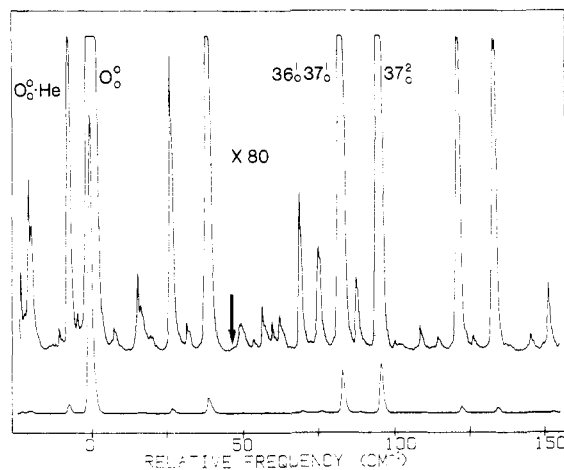
(7) Bosma, W. B.; van Zee, R.; Zwier, T. S.; Spangler, L. H., to be published.

Figure 1. Fluorescence excitation spectrum of the first 150 cm^{-1} of the S_0–S_1 transition in α-deuterio-*trans*-stilbene. The upper trace is a similar scan at 80 times higher sensitivity. The arrow in the figure points to the expected position of the 37_0^1 transition.

and expanded through a pulsed valve with 500 μm diameter pinhole into the vacuum chamber. The cold molecules so produced are crossed 1 cm downstream with the doubled output of an excimer pumped dye laser which is attenuated and defocused to avoid saturation. Either total fluorescence is collected as a function of laser wavelength or the emission from a given feature is dispersed with a $^3/_4$-m monochromator to provide 7-cm^{-1} resolution dispersed fluorescence spectra.

α-Deuterio-*trans*-stilbene was prepared by using a modified Wittig synthesis in which benzyl chloride is reacted with triethyl phosphite to produce an ylide which subsequently reacts with C_6H_5CDO (Cambridge Isotope Labs) to produce exclusively α-deuterio-*trans*-stilbene.[8] NMR spectra confirmed our successful synthesis and the isotopic purity of the sample. The purity of the sample is further substantiated from the LIF excitation spectrum which shows the sample to be >99% α-deuterio-*trans*-stilbene.

Results and Discussion

Figure 1 shows a portion of the fluorescence excitation spectrum of α-deuterio-*trans*-stilbene. Apart from a small shift of the spectrum 6 cm^{-1} to the blue of its position in *trans*-stilbene, the first 200 cm^{-1} of the spectrum is indistinguishable from that of *trans*-stilbene (see Figure 1 of ref 6). The small isotope shift to the blue is enough to allow us to look carefully for *trans*-stilbene impurity in the sample, which is not observed. The isotope shift of the origin is due to zero point energy shifts between ground and excited states produced by deuteration. The shift is smaller but in the same direction as the +37-cm^{-1} shift between C_6H_6 and C_6H_5D.[9]

The 36_0^2, $36_0^1 37_0^1$, and 37_0^2 transitions are trivially assigned from the spectrum. More importantly, we can view the spectrum at greatly increased sensitivity in order to search for the 37_0^1 transition. The expected position of the transition is known with great certainty because higher overtone transitions show the 37 mode to be very harmonic in the excited state. The upper trace of Figure 1 is magnified from the lower trace by a factor of 80. The arrow marks the expected position of 37_0^1 which we do not observe even at 0.02% of the origin intensity (0.2% of 37_0^2)!

Dispersed fluorescence spectra give a similar result. The spectra of the low-frequency transitions are identical with those of *trans*-stilbene. When the emission from the origin is dispersed we do not observe the 37_1^0 transition to within about 1% of the origin intensity.

One final point remains. In order for our new data to be conclusive with regard to the *trans*-stilbene geometry we must

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(9) (a) Garforth, F. M.; Ingold, C. K.; Poole, H. G. *J. Chem. Soc.* **1948**, 508. (b) Nieman, G. C.; Tinti, D. S. *J. Chem. Phys.* **1967**, *46*, 1932.
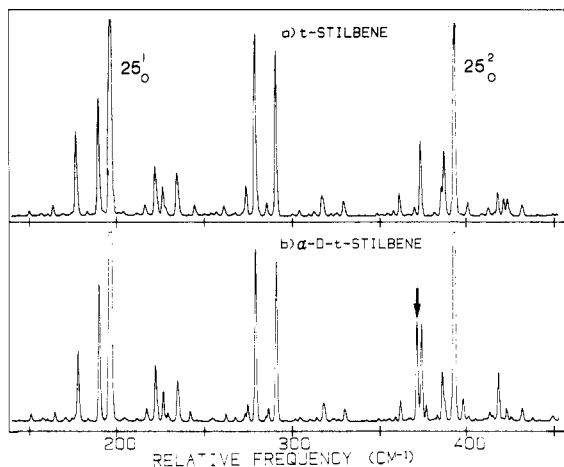
Figure 2. A comparison of the fluorescence excitation spectrum of (a) *trans*-stilbene and (b) α-deuterio-*trans*-stilbene in the region 150–450 cm^{-1} above the origin. The arrow in (b) marks a new transition which grows in upon deuterium substitution.

be confident that the deuterium substitution is a strong enough perturbation to induce new transitions in the spectrum which are allowed in C_s but not in C_{2h}. Figure 2 shows one of the clearest examples of such a transition. There we show the region between 25_0^1 and 25_0^2 in *trans*-stilbene and α-deuterio-*trans*-stilbene. The spectra have been shifted slightly relative to one another so that they overlap properly. Note the near-identical appearance of most of the spectrum. However, the transition marked by the arrow in Figure 2b (372 cm^{-1} above the origin) is a strong peak which is not observed in *trans*-stilbene. There is ample evidence that this band is the fundamental of a new vibration, hereafter called X_0^1, which has become allowed by deuterium substitution. First, the new vibration is seen in combination with $\nu_{25}(25_0^1X_0^1)$, ν_{36}-$(36_0^1 37_0^1 X_0^1)$, and $\nu_{37}(37_0^2 X_0^1)$. Second, its intensity is such that the band cannot be simply assigned to a slightly shifted band in the *trans*-stilbene spectrum. Third, the dispersed fluorescence scan of the X_0^1 transition shown in Figure 3 confirms our assignment. While the spectrum is complicated, it has as its largest peak a transition 390 cm^{-1} from the origin, likely corresponding to one quantum of excitation of the new mode in the ground state (X_1^1). Then the transition at 590 cm^{-1} would be $25_1^0 X_1^1$ and at 790 cm^{-1} $25_2^0 X_1^1$. Another strong transition in the dispersed spectrum of Figure 3 is 114 cm^{-1} above the ground-state origin, the 36_2^0 transition. Its presence indicates that the new mode is strongly coupled to ν_{36}, the C_e–Ph out-of-plane bend, as well. Finally, the dispersed fluorescence spectrum of Figure 3 looks very similar to that of a new transition which appears in the *p*-methyl-
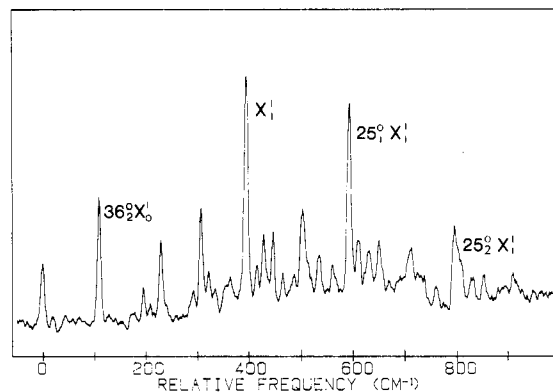

Figure 3. Dispersed fluorescence spectrum of the transition marked with an arrow in Figure 2. The tentative assignment of several transitions is given in the figure.

trans-stilbene spectrum at 190 cm^{-1}. Thus the transition is present in both *p*-methyl- and α-deuterio-*trans*-stilbene, both of which lack the inversion symmetry of *trans*-stilbene. The presence of this strong transition in α-deuterio-*trans*-stilbene and its absence in *trans*-stilbene points to the transition being a new one which is allowed by virtue of its A′ symmetry in C_s but is not allowed in C_{2h} where it is of B_u symmetry.

It is difficult to unambiguously assign this transition based on the present data. Unfortunately, the frequency of this transition does not correspond well with any of the B_u modes calculated by Warshel.[10] However, in distinguishing C_{2h} from C_i geometries, it is only the B_u modes whose intensity will be affected by the loss of inversion symmetry. Hence the new transition is most likely one of the three B_u modes Warshel calculates with frequency below 600 cm^{-1}.

The presence of this new transition leads us to believe that α-deuterium substitution is a strong enough perturbation so that if the molecule were not C_s we would see the 36_0^1 and 37_0^1 transitions. Yet we have not seen these transitions even down to a level 4000 times smaller than the origin intensity. As a result, our earlier conclusion[6] on the *trans*-stilbene geometry remains a good one: the isolated *trans*-stilbene molecule is planar in both its ground and first excited singlet states.

(10) Warshel, A. *J. Chem. Phys.* **1975**, *62*, 214.