On the Origin of Nonvertical Triplet Excitation Transfer: The Relative Role of Double-Bond and Phenyl-Vinyl Torsions in the Stilbenes

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The results of theoretical calculations at the B3LYP-DFT level using the 6-31+G(d,p) basis set on the ground and triplet states of the stilbenes (*c*-**1**, *t*-**1**) and of 2,3-diphenylnorbornene (**2**) are described. They are not consistent with the premise that structural constraints require that the stilbene moiety of **2** assume a planar geometry in its relaxed triplet state. Pronounced pyramidalization at the olefinic carbon atoms gives a PhCCPh dihedral angle of 51.0° in ^{3}**2***. Furthermore, the dihedral angles of ^{3}**2*** that involve phenyl−vinyl torsions, 22.3 and 26.5°, do not attain the assumed value of 0°. Thus, it is likely that **2** was improperly used as a rigid model for *c*-**1**. The calculations predict that in **2** and in **1** torsional motion about the CC double bond affords the most stabilization in the triplet state. As suggested earlier, it is that motion and not phenyl−vinyl torsion that most facilitates nonvertical energy transfer to the stilbenes. A single energy minimum is found on the stilbene triplet energy surface, close to the postulated geometry of the "phantom" (perpendicular, ^{3}*p*-**1***) triplet.

Introduction

Nonvertical triplet excitation transfer (NVT) was postulated to explain unexpectedly large rate constants for endothermic triplet energy transfer to *cis*-stilbene (*c*-**1**).[1] The phenomenon is encountered generally with flexible acceptor molecules that have significantly different ground state and triplet state equilibrium geometries.[2] In such cases, vanishingly small Franck−Condon (F−C) factors prevent direct observation of the 0−0 band of the vibronic progression of the acceptor. The donor/acceptor encounter complex explores a range of different nuclear configurations as it seeks to minimize the energetic demands for the process. With *cis*-stilbene as the acceptor, it was reasoned that torsional displacement about the central double bond is the key vibration that accounts for activation energies for endothermic triplet excitation transfer that are much smaller than the deficit predicted on the basis of spectroscopically determined donor and acceptor triplet energies.[1,2] *trans*-Stilbene was initially considered a vertical triplet excitation acceptor,[1] but activation energies for the highly endothermic transfers from anthracene and 9,10-dichloroanthracene donors led to the conclusion that it functions as a NVT acceptor as well.[3] Accordingly, it was postulated that the stilbene triplet energy surface has a single potential energy minimum in the perpendicular geometry which is more shallow on the trans side.[3]

It was suggested at the outset that the much longer interaction of a donor/acceptor encounter as compared to light absorption in a photon/molecule interaction, may allow coupling of vibrational motions between the two systems and lead to a relaxation of F−C reqirements.[1] Others have argued that NVT involves no greater geometric distortions than expected for the corresponding spectroscopic transitions for which F−C factors, albeit small, are finite.[4−6] We have favored Liu's "hot band" mechanism,[7,8] which also draws analogy from spectroscopy.[3] NVT via this mechanism is the result of excitation transfer to acceptor molecules which are thermally excited along relevant vibrational coordinates, as expected from the Boltzman distribution law. The focus was originally on bonds that experience reversal of single/double bond order with excitation, as, for instance, the central bonds of the stilbenes[1] (double → single) or of the biphenyls[8a,b] (single → double), and, specifically, on torsional motions about these bonds that accommodate the major differences between S_0 and T_1 equilibrium geometries, i.e., "planar" → twisted in the stilbenes and twisted → planar in the biphenyls.

The view that C═C double bond torsion is the key ground-state motion that minimizes energetic demands for triplet excitation transfer to the stilbenes was challenged on the basis of observations showing that 2,3-diphenylnorbornene (**2**) functions as a nonvertical triplet energy acceptor in much the same way as *c*-**1**.[9−11] Because the chromophores of **2** and *c*-**1** are identical but for assumed severe restrictions of double-bond twisting in **2**, it was concluded that double-bond torsion in NVT to *c*-**1** is minimal. NVT to flexible and nonplanar acceptors was proposed to be primarily a consequence of single-bond (phenyl−vinyl torsion in *c*-**1** and **2**) in the ground-state acceptors. The relative importance of double-bond and phenyl−vinyl torsions for *c*-**1** as a triplet energy acceptor was evaluated with the use of **2** as a model and the premise that "phenyl−vinyl torsion is dominant in the relaxation of ^{3}**2***."[10a] The presumed inability of ^{3}**2*** to relax by twisting around the double bond led to the conclusion that "*some two-thirds of the relaxation of* ^{3}**1*** *is due to phenyl−vinyl torsion and about one-third to double-bond torsion*." Although it was recognized that relief of steric hindrance as ^{3}**2*** approaches small phenyl−vinyl dihedral angles might require torsional distortion or pyramidalization at the norbornene double bond, such motions were characterized as

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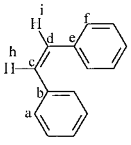
TABLE 1: Comparison of Experimental and Theoretical Energy Differences[a]

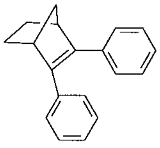
compound	quantity	exp	theor	ref[b]
1[c]	$T_1 \leftarrow S_0$, ^1c-**1**	56 ± 1	55.7	10, 16, 17
	$T_1 \leftarrow S_0$, ^1t-**1**	49 ± 1	49.1	17−19
	$E_T - {}^3p$-**1***	46.6 ± 1.5	45.7	17
	E_{rel}, ^3c-**1*** → ^3p-**1***	14.5 ± 3	15.0	
	$E_c - E_t$, S_0	4.6 ± 0.1	5.0	20
2	$T_1 \leftarrow S_0$	56 ± 1[d]	53.6	10a
	$E_T - {}^3p$-**2***	46.9 ± 0.8	46.1	10a
	E_{rel}, ^{3}**2*** → ^3p-**2***	9 ± 2	7.5	
3	$T_1 \rightarrow S_0$	57.2 ± 1.3	58.2	10a
	$E_T - {}^3p$-**3***	56.0 ± 0.5	56.4	10a
	E_{rel}, ^{3}**3*** → ^3p-**3***	1.2 ± 2	1.8	10a

[a] All energies in kcal/mol. [b] References are for experimental values. Theoretical spectroscopic transitions are "vertical", i.e., θ_1, θ_2, θ_3, and θ_4 for the triplet sate are fixed to ground-state values. [c] Except for the first entry, which is relative to the *c*-**1** ground-state energy, −540.720 946 au, all other values are relative to *t*-**1** in S_0, −540.728 888 au. [d] Assumed the same as that for *c*-**1**.[10a]

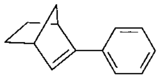
small and slight.[10a] The conclusion that "*there is thus no necessity to invoke double-bond torsion to any significant extent to explain NVT to 1*" contradicts the original explanation for the phenomenon.[10a]



c-**1**



2



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We present results from theoretical calculations that are inconsistent with (i) the assumed relative importance of double-bond and phenyl−vinyl motions in the relaxation of ^{3}**2*** and (ii) the conclusion that phenyl−vinyl torsion is the key coordinate in the functioning of *c*-**1** as a NVT acceptor.

Computational Details

Calculations were performed with the Gaussian 98 program package.[12] The Becke three-parameter hybrid functional,[13a,14a] in combination with the Lee, Yang, and Parr correlation functional,[13b] denoted B3LYP,[14b] was employed in these density functional theory (DFT) calculations. Geometry optimizations[15] were performed with the 6-31+G(d,p) basis set.[12] Stationary points on S_0 and T_1 potential energy surfaces were further characterized with calculations of vibrational frequencies. No scaling factors were used for zero-point energy corrections or for any other calculated thermochemical values. Calculated bond lengths and bond angles are given in angstroms and degrees, respectively.

Results and Discussion

Calculated energies at the B3LYP-DFT level using the 6-31+G(d,p) basis set for the ground and lowest triplet states are shown, together with experimental values, in Table 1 (see last column for references). Except as noted, stilbene energies are given relative to the energy of the ground-state global minimum at the *trans*-stilbene geometry taken as zero. Geometries for all energy minima on the S_0 and T_1 surfaces were fully optimized, Table 2, and were stable minima as no imaginary frequencies were found. Dihedral angles involving C═C double bond torsion were fixed and other geometric coordinates were optimized in calculating the energy along hypothetical cis → trans reaction coordinates in S_0 and T_1. Analogous calculations were performed for 2-phenylnorbornene, **3**, as a test for the calculations and because its energetics on triplet excitation were considered in the earlier study.

TABLE 2: Geometry of Energy Minima in S_0 and T_1 of Stilbene[a]

	^{1}t-**1**[b]	^1c-**1**	^3p-**1***	^{1}**2**	^{3}**2***
			Dihedral Angles		
θ_1	179.72	6.97	90.25	8.34	50.98
θ_2	178.13	4.81	83.68	1.54	12.80
θ_3	−4.72	30.62	0.47	30.32	26.51
θ_4	175.09	30.62	0.47	46.28	22.28
			Bond Lengths, Å		
C_b-C_c	1.466	1.475	1.418	1.476	1.413
C_c-C_d	1.348	1.349	1.467	1.361	1.503

[a] θ_1 = bcde, θ_2 = hcdi, θ_3 = idef, and θ_4 = abch. [b] The most recent X-ray crystal structure for ^1t-**1** found θ (abcd) = 5.3° and 1.33 and 1.47 Å for C_c-C_d and C_b-C_c, respectively.[21,22]

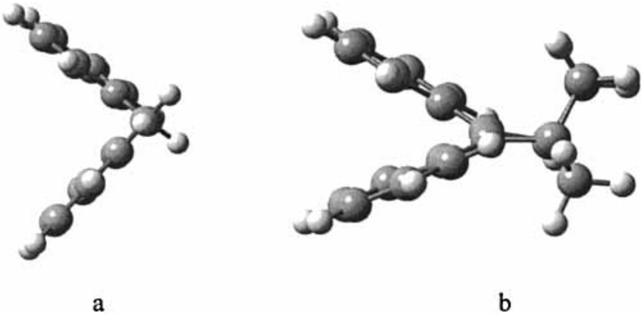

Figure 1. Calculated structures for the global energy minima of the triplet states of (a) **1** and (b) **2**.

The predicted geometries for the ground states of *cis*- and *trans*-stilbene are consistent with results from a comprehensive theoretical study that has compared calculations at various levels of theory with experimental findings.[22] Experimental and theoretical triplet energies and values for the energy difference between *cis*- and *trans*-stilbene in the ground state are in remarkable agreement. This conclusion is consistent with the good agreement obtained between theoretical calculations and experiment on the S_0 and T_1 surfaces of the 2,4-hexadiene isomers.[23] Confidence in our approach is provided by a recent critical comparison of the application of different theoretical approaches to the calculation of the triplet potential energy surfaces of 1,3-butadiene and 1,3,5-hexatriene in which it was concluded that energies and geometries obtained by DFT methods are in good agreement with those predicted by CASSCF, CASPT2, and spin-projected UMP4(SDTQ) calculations and with experiment.[24]

In accord with experiment, the predicted stabilization on relaxation of ^{3}**2***, 7.5 kcal/mol, is half the value for ^3c-**1***, 15.0 kcal/mol. It is on the structural origins of these relaxation energies that the calculations differ markedly from the recent proposal, Table 2. What is striking is the optimum geometry of ^{3}**2*** in which the PhCCPh dihedral angle is predicted to be 51.0° in strong disagreement with the assumption that the structural constraints of the norbornene framework require that angle to be close to 0°. Nor do the dihedral angles in ^{3}**2*** that involve phenyl−vinyl torsions, 22.3 and 26.5°, attain the assumed values of 0°. Similarly, pyramidalization of the olefinic carbons plays a key role in determining the relaxed triplet structure of norbornene.[25] The expectation that conjugation might relieve electron−electron repulsion, assumed to be responsible for pyramidalization, and thus lead to increased tendency to planarity[25] is not borne out in ^{3}**2***. Views of the calculated

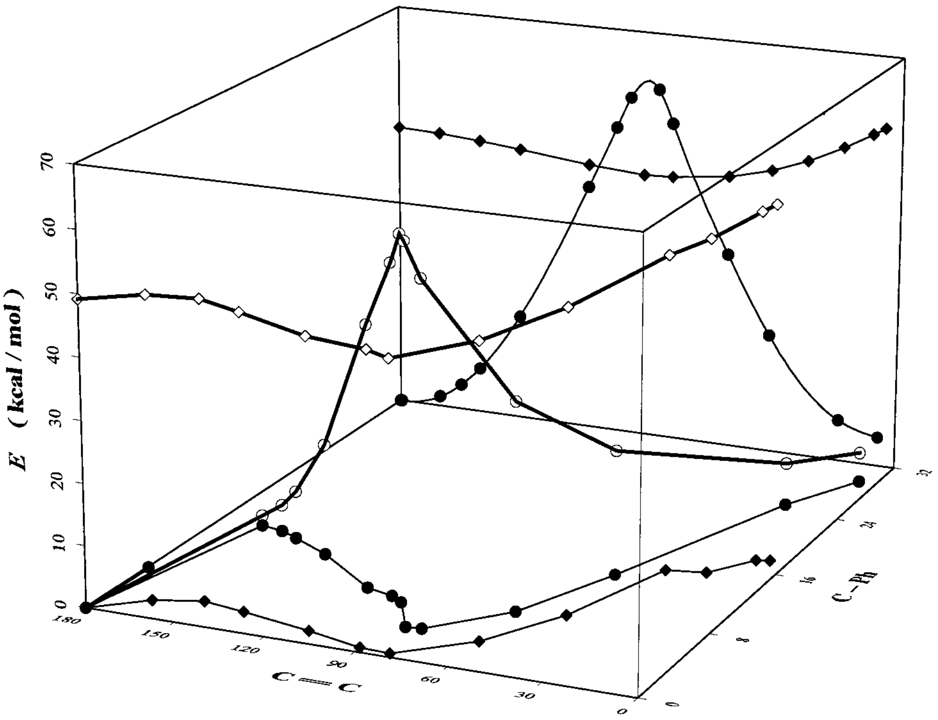

Figure 2. Calculated potential energy curves for twisting about the central bond in S_0(○) and T_1(◇) of stilbene. Except for the global minima at *c*-**1** and *t*-**1** in S_0 and at ^{3}p in T_1 for which geometries are fully optimized, $\theta_1 = \theta_2$ is fixed. Open and closed symbols distinguish points plotted in three dimensions from those that are projected on coordinate planes. Projections (solid symbols) on the $E = 0$ kcal/mol plane show the variation in $(\theta_3 + \theta_4)/2$ as a function of θ_1. Projections on a $(\theta_3 + \theta_4)/2$ = constant plane give curves in good agreement with those of previous proposals.[3b,10,15,18]

structures of ^{3}*p*-**1*** and ^{3}**2*** in which the relative positions of the two phenyl groups are clearly evident are shown in Figure 1. By fixing C═C torsional angles to their S_0 values and allowing all other coordinates, including phenyl−vinyl torsional angles, to assume optimum values, we find that no more than 3.4 of the 7.5 kcal/mol and 2.7 of the 15.0 kcal/mol stabilization energies in ^{3}**2*** and ^{3}*c*-**1***, respectively, can be attributed to phenyl−vinyl torsional motion. On the basis of these values alone, we could paraphrase the earlier paper to state that some $^3/_4$ of the relaxation energy of ^{3}*c*-**1*** is due to double bond torsion and about $^1/_4$ to phenyl−vinyl torsion. However, this is clearly an oversimplification, as other vibrational motions may also play significant roles. One must not overlook, for instance, the reversal in double/single bond character (and lengths) that accompanies these $S_0 \rightarrow T_1$ transitions.[26]

Figure 2, which is analogous to Figure 1 in ref 10a, shows the predicted coupling between double bond and phenyl−vinyl torsions as one moves along the chosen trajectories on the stilbene S_0 and T_1 energy surfaces. It is inconsistent with the assumption that departure of phenyl−vinyl torsional angles from zero occurs only to alleviate steric hindrance as cis geometries are approached; the usual depiction of stilbene cis−trans isomerization as a mutual rotation of two planar benzyl moieties is not strictly accurate. By predicting a single minimum close to the postulated geometry of the "phantom" (perpendicular, ^{3}*p*-**1***) triplet (postulated: $\theta_1 = \theta_2 = 90°$, $\theta_3 = \theta_4 = 0°$; calculated: $\theta_1 = 90.25°$, $\theta_2 = 83.65°$, $\theta_3 = \theta_4 = 0.47°$, Figure 1), the calculations support the conclusion that *trans*-stilbene (*t*-**1**) is a NVT acceptor. Because θ_3 and θ_4 are 0° and 0.47° for ^{3}*t*-**1*** and ^{3}*p*-**1***, respectively, the ∼3 kcal/mol of stabilization has very little to do with phenyl−vinyl torsion and must be due in large part to double bond torsion. The ground state potential energy curve is not expected to represent the minimum energy path for cis−trans interconversion. Imposition of $\theta_1 = \theta_2$ on the calculations in Figure 2 may be responsible for the ∼12 kcal/mol overestimation of the barrier for cis−trans isomerization in S_0.[27] Lower energy pathways probably have $\theta_1 \neq \theta_2$ and allow some pyramidalization at the central carbon atoms.

Calculated expectation values of the total spin operator, $\langle \hat{S}^2 \rangle$, prior to spin annihilation are 2.0589, 2.0504, and 2.0302 for the global energy minima of the stilbene triplet and the triplets of **2** and **3**, respectively, and become 2.0021, 2.0016, and 2.0005 on application of the spin annihilation procedure incorporated in the UB3LYP calculations, sufficiently close to the expected $\langle \hat{S}^2 \rangle = 2$ for pure triplets.

In conclusion, the calculations support the initial proposal that assigned to double bond torsion the key role in enabling NVT to the stilbenes. We emphasize, however, that, as multidimensional surfaces are involved, many other vibrations will also contribute as the donor/acceptor pair attains the optimum path for NVT.

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Supporting Information Available: Tables S1−S4 give calculated total energies and geometric coordinates for stationary point structures on the S_0 and T_1 surfaces of 1 and the T_1 surface of 2. Table S5 gives the total energy and geometric coordinaties for ^{1}*p*-1, the perpendicular ground state of 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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