

Biindanylidenes: Role of Central Bond Torsion in Nonvertical Triplet Excitation Transfer to the Stilbenes

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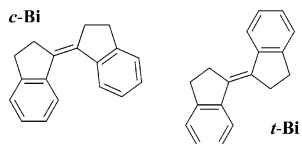
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Nonvertical triplet excitation transfer (NVET) is recognized as a general phenomenon involving molecules with markedly different ground and triplet state equilibrium geometries. It was first proposed to account for larger than expected triplet energy transfer rate constants from energy-deficient donors to *cis*-stilbene (**c-St**).¹ Of several views concerning the mechanism of NVET, consensus points to Liu's hot-band mechanism.² Energy requirements for the transfer are reduced by population of ground-state vibrational modes of the acceptor that provide access to geometries that destabilize the ground state (S_0) while stabilizing the triplet state (T_1).³ The proposal that double bond torsion is involved in NVET to **c-St** was based on expected destabilization along $^1c \rightarrow ^1p$ (*cis* to perpendicular in S_0) and stabilization along $^3c^* \rightarrow ^3p^*$ (in T_1) coordinates.¹ At first, *trans*-stilbene was classified as a vertical triplet excitation acceptor,¹ but activation parameters for triplet energy transfer from anthracene (**A**) and 9,10-dichloroanthracene led to the conclusion that it, also, is a NVET acceptor.³ A single potential energy minimum at the perpendicular geometry, more shallow on the *trans* side, was postulated on the T_1 surface.³

Torsions about essential single bonds facilitate NVET when they diminish the energy gap between ground and triplet excited-state surfaces as in biphenyls,^{2b} in octatetraene,⁴ and in oximes.⁵ Because **c-St** and 2,3-diphenylindane behave similarly as triplet energy acceptors, phenyl–vinyl instead of central bond torsion was proposed as the main reaction coordinate (RC) in NVET to **c-St**.^{6–8} However, theory is inconsistent with the idea that the norbornene skeleton precludes torsional displacement of the phenyl rings about the double bond in T_1 and does not support a primary role for single bond torsions in NVET to **c-St**.⁹

Our evaluation of the contribution of single bond torsions in NVET to the stilbenes has centered on the *stiff*-stilbenes, *cis*- and *trans*-biindanylidene (**c-Bi** and **t-Bi**), as acceptors. **t-Bi**, synthesized



(70–80%) from 1-indanone (Aldrich) by McMurry coupling,¹⁰ was chromatographed on silica gel followed by recrystallization from hexane, and its identity was confirmed by spectroscopy (NMR, UV–vis)¹¹ and by X-ray crystallography.¹² Irradiation of a 10^{-2} M N_2 -outgassed benzene solution of **t-Bi** at 313 nm equilibrated the isomers (ca 65% **c-Bi**), and **c-Bi**, isolated by chromatography on pyridine-deactivated alumina, was purified by multiple recrystallizations from hexane.¹¹ Exposure of the isomers (>99.5% pure, GC) to room light was avoided.

Anthracene was purified via the photodimer.¹⁴ Toluene (Fisher reagent), washed in turn with H_2SO_4 , aqueous K_2CO_3 and deionized

Table 1. Arrhenius Parameters for Energy Transfer from $^3A^*$ ^a

| | trans isomer | | cis isomer | |
|------------------------|--------------|----------------|-------------|----------------|
| | log A | E_a^\ddagger | log A | E_a^\ddagger |
| St ^b | 9.66 ± 0.30 | 6.03 ± 0.30 | 8.80 ± 0.13 | 4.74 ± 0.20 |
| Bi | 9.72 ± 0.50 | 3.63 ± 0.15 | 8.96 ± 0.55 | 3.07 ± 0.16 |

^a Energies in kcal/mol. ^b From ref 3.

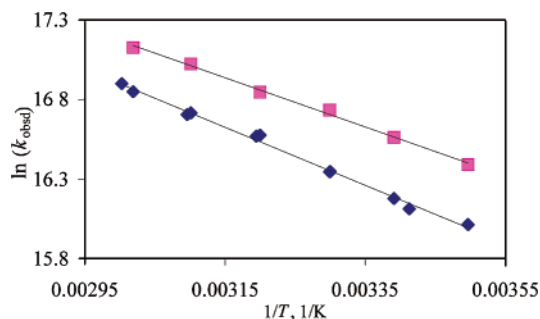


Figure 1. Arrhenius plots for energy transfer rate constants from $^3A^*$ to **c-Bi** (■) and **t-Bi** (◆).

water, was distilled over sodium. The crystal structure of **t-Bi** shows it to be planar (see Supporting Information, SI).^{12,13a,b}

Laser flash spectroscopy was as previously described,¹⁵ except that Kiton Red dye in a Moletron L 251 laser cell (0.80 cm optical path), excited with second harmonic 532 nm pulses from the Nd:YAG laser, produced 586.3 nm pulses, which, mixed with 1064 nm pulses generated the desired 378 nm pulses. Samples (4 mL aliquots, $[A] = 5.00 \times 10^{-5}$ M, $[c-Bi] = 2.0\text{--}8.0 \times 10^{-4}$ M and $[t-Bi] = 2.0\text{--}10.0 \times 10^{-4}$ M at 21.7 °C) were degassed in 13 mm o.d. ampules provided with 1.0 cm quartz sidearm cells using freeze–pump–thaw cycles, as needed to achieve $\leq 5 \times 10^{-6}$ Torr; the ampules were flame-sealed at a constriction (for further details see SI). Activation parameters in Table 1 are from the Arrhenius plots of energy transfer rate constants (from plots of $^3A^*$ first-order decay rate constants¹⁶ vs density-corrected $[c-Bi]$ and $[t-Bi]$), Figure 1.

Comparison of activation parameters for **Bi** and **St** isomers provides strong evidence that the excitation transfer processes remain nonvertical despite strongly inhibited phenyl–vinyl torsion in **c-** and **t-Bi**. The near identity of the small A factors of the respective isomers is significant. Their magnitude reflects similar attenuations by Franck–Condon overlap factors, which decrease as vibrational quantum numbers corresponding to the transition state (TS) increase. Our results are consistent with central bond torsion as the key RC for NVET to the stilbenes.

Calculations using Gaussian 98¹⁷ provide structural and energetic insights. Stationary point geometries in S_0 and T_1 were optimized¹⁸ using the ONIOM model¹⁹ (the C_8H_6 inner layer consists of the central C=C with immediately attached CH_2 and C=CH moieties) implemented in Gaussian with the B3LYP exchange–correlation functional²⁰ and 6-31G(d) and 6-311+G(d,p) basis sets. Vibrational

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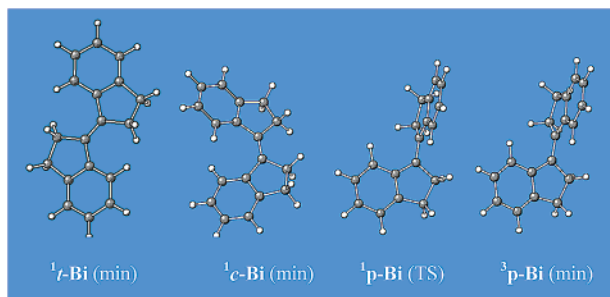


Figure 2. Stationary point geometries on the **Bi** S_0 and T_1 surfaces, including TS for ${}^1c\text{-Bi} \rightarrow {}^1t\text{-Bi}$ isomerization.

Table 2. Calculated Energy and Geometry Parameters

| | ONIOM energy, a.u. | $E_{\text{rel.}}$ kcal/mol | $\langle S^2 \rangle$ | CC=CC, deg | C=C, Å |
|---------------------|-----------------------|-------------------------------|-----------------------|---------------|-----------|
| ${}^1t\text{-Bi}$ | -695.65137 | 0.00 | 0.00 | -178.41 | 1.354 |
| ${}^1c\text{-Bi}$ | -695.64649 | 3.06 | 0.00 | 9.01 | 1.352 |
| ${}^1p\text{-Bi}^a$ | -695.58592 | 41.07 | 1.07 | 93.09 | 1.458 |
| ${}^3p\text{-Bi}$ | -695.58528 | 41.48 | 2.06 | 87.62 | 1.459 |

^a Characterized by a single imaginary frequency at 134.7i cm^{-1} .

frequencies identify stationary points as either minima or TS structures (first-order saddle point). Results are shown in Figure 2 and Table 2. ${}^3p\text{-Bi}$ is the only stationary minimum found on T_1 . TSs for ${}^3p\text{-Bi}$ interconversions were found at 49.7 (planar trans) and 56.3 kcal/mol (nearly planar cis, see SI).

Calculated and X-ray ${}^1c\text{-Bi}^{13c}$ structures agree: 165.6 and 164° (average) phenyl–vinyl and -9.0 and -5° (average) central bond dihedral angles (DAs), respectively. Fixing the phenyl–vinyl DAs at 180° and optimizing all other geometric parameters leads to a DA of 23.8° at the central bond at 1.3 kcal/mol above the predicted gas phase ${}^1c\text{-Bi}$ energy minimum. Due to severe *o*-H repulsion, torsional distortion of the phenyl–vinyl DA toward planarity can be achieved only if compensated by opposing distortion at the central bond. Phenyl–vinyl and central bond torsions are strongly coupled, but it is the latter that is primarily responsible for the decrease in the S_0 – T_1 energy gap. Calculated and X-ray ${}^1t\text{-Bi}^{12,13a,b}$ structures deviate mainly in the phenyl–vinyl DA: 167.6 vs 179.8°, respectively. Optimization after fixing the phenyl–vinyl DAs at 180° results in a planar structure, essentially identical with the X-ray structure, 0.5 kcal/mol above the global energy minimum. The global minimum is predicted to be very shallow with respect to torsional phenyl–vinyl displacement toward planarity in the gas phase, and distortion along that coordinate contributes little to the decrease in the S_0 – T_1 energy gap. ${}^1p\text{-Bi}$ and ${}^3p\text{-Bi}$ geometries and energies are nearly identical, consistent with experimental observations on the stilbenes.⁹ The high TS energy for stilbene isomerization in S_0 was due to the use of spin-restricted B3LYP for the biradical. UB3LYP predicts 45.3 kcal/mol for ${}^1p\text{-St}$, very close to the energy of ${}^3p\text{-St}$.⁹ Calculated stabilizations for twisting from planar TSs to the global energy minimum at ${}^3p\text{-Bi}$ are 8.2 and 14.8 kcal/mol from the trans and cis sides, respectively. The prediction that ${}^3p\text{-Bi}$ lies in a deeper energy well than does ${}^3p\text{-St}^9$ justifies neglect of back energy transfer from ${}^3p\text{-Bi}$ to **A** in the encounter complex because excursions from ${}^3p\text{-Bi}$ toward ${}^3t\text{-Bi}(\text{TS})$ geometries are more endoergic than in **St**. Smaller azulene effects on trans/cis stationary state ratios for isomerization of ${}^3\text{Bi}$ than of ${}^3\text{St}$ (slope/intercept ratios for azulene plots in benzene are 120 and 41 M^{-1} for **St**^{1b,21} and **Bi**, respectively)²² support this prediction.

We again emphasize⁹ that while experiment and theory support the initial proposal that double bond torsion is the key reaction coordinate enabling NVET to the stilbenes, as multidimensional surfaces are involved, other vibrations, including bond stretching,¹⁵ will also contribute.

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Supporting Information Available: Details on kinetics measurements; coordinates and total energies of optimized structures (minima and TSs on S_0 and T_1) using ONIOM. X-ray/ONIOM structures; tables of X-ray data for **t-Bi** consisting of crystallographic parameters, positional parameters, bond distances, bond angles, and torsional angles (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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