Communications to the Editor

Conformer-Specific Adiabatic Cis → Trans Photoisomerization of *cis*-1-(2-Naphthyl)-2-phenylethene. A Striking Application of the NEER Principle

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The fluorescence spectrum of *cis*-1-(2-naphthyl)-2-phenylethene (*c*-NPE) was first reported by Hammond et al. for the hexane solution.[1] The spectrum was highly unusual for a *cis*-1,2-diarylethylene in that it exhibited a well-resolved vibronic structure similar to that of the trans isomer (*t*-NPE). Soon thereafter, the fluorescence spectrum of *c*-NPE in a hydrocarbon glass at −170 °C was shown to have the expected broad structureless appearance.[2a] Since furthermore, the quantum yield of this *c*-NPE emission, ϕ_f^c, was shown to diminish sharply as the temperature was raised,[2b,c] it was concluded that the room temperature emission[1] attributed to *c*-NPE was actually that of the trans isomer.[2] *t*-NPE contamination of the *c*-NPE samples employed in the initial study was suspected.[2] We show here that both of these early studies are correct, in large part, and that the emission observed from ambient *c*-NPE solutions is nearly exclusively due to adiabatic formation of ^1t-NPE$_B$*, the excited singlet state of the more extended conformer of the trans isomer, Scheme 1.

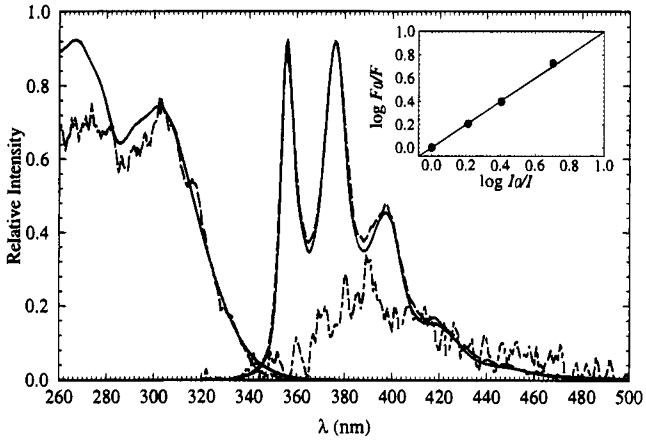
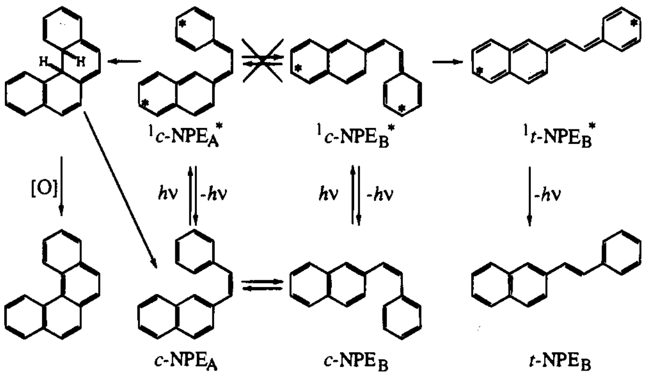


Figure 1. Absorption (ϵ_{max} = 1.57 × 10^4 M^{-1} cm^{-1} at 302 nm) and fluorescence spectra of *c*-NPE in MCH (−) and fluorescence excitation spectrum of *c*-NPE and contributions of ^1t-NPE$_B$* and ^1c-NPE* (×10) emissions in *c*-NPE fluorescence (− − −). All fluorescence spectra are corrected for nonlinearity in instrumental response. Inset: logarithmic plot of relative *c*-NPE fluorescence area vs relative incident excitation intensity.

Scheme 1



c-NPE, synthesized as previously described,[1] was purified by repeated chromatography on alumina to >99.9% purity (0.039% *t*-NPE remained, GLC). Fluorescence measurements were carried out at 30.0 °C in methylcyclohexane (MCH) using a flow cell system as described for *cis*-stilbene.[3] Since a very small number of fluorescence and/or fluorescence excitation spectra were measured for each 250 mL solution, there was negligible emission due to build-up of *t*-NPE photoproduct. Such build-up hampered studies in static cells. Fluorescence and fluorescence excitation spectra for Ar-outgassed solutions are compared with the fluorescence spectrum of *t*-NPE$_B$[4] and the absorption spectrum of *c*-NPE, respectively, in Figure 1. The agreement between the two sets of spectra, though not exact, is excellent. That the emission from *c*-NPE solutions cannot be due to *t*-NPE impurity is unequivocally established by (i) better resolved vibrational structure than for *t*-NPE fluorescence spectra because the latter include contributions of the broader *t*-NPE$_A$ fluorescence,[4] (ii) agreement between *c*-NPE absorption and fluorescence excitation spectra (since ^1c-NPE$_A$* does not undergo adiabatic cis → trans isomerization, exact agreement was not expected), (iii) linear dependence of fluorescence intensity on incident excitation intensity (inset, Figure 1), and (iv) the effect of O_2 on spectral shape and intensity (see below).

Scrutiny of the fluorescence spectra in Figure 1 reveals a slight deviation that becomes progressively more pronounced as Ar-outgassing is replaced first by air and then by O_2. Arbitrary subtraction of the fluorescence spectrum of *t*-NPE$_B$ from the emission spectra of *c*-NPE solutions gives less structured difference spectra with further exaggerated deviation from the *t*-NPE$_B$ fluorescence spectrum. Principal component analysis with self-modeling (PCA-SM) treatment[4] of a matrix consisting of the *c*-NPE emission spectra, the difference spectra, and the spectrum of *t*-NPE$_B$[4] reveals a two-component system whose two pure component combination coefficient limits are defined by the combination coefficients of the *t*-NPE$_B$ fluorescence spectrum and by the known Stern−Volmer constant[4b] for O_2 quenching in MCH of ^1t-NPE$_B$*, $K_{SV}{}^{t\text{-}B}$ = 780 ± 20 M^{-1}. The new component is a noisy, structureless emission, $\lambda_{max} \simeq$ 390 nm (Figure 1), consistent with an unknown combination of the fluorescence spectra of ^1c-NPE$_A$* and ^1c-NPE$_B$*. The contribution of this emission for Ar-, air-, and O_2-saturated solutions increases from 3.7 to 5.9 to 21.9% in that order, reflecting its short lifetime. Measured against quinine bisulfate as fluorescence standard,[5] the fluorescence quantum yield of

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[4] (a) Saltiel, J.; Sears, D. F., Jr.; Choi, J.-O.; Sun, Y.-P.; Eaker, D. W. *J. Phys. Chem.* **1994**, *98*, 35−46. (b) Adjustments for deviations from unity of Stern−Volmer plots in ref 4a have led to small changes in the Stern−Volmer constants that were reported earlier.

[5] Meech, S. R.; Phillips, D. *J. Photochem.* **1983**, *23*, 193−217.

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c-NPE in O_2-free MCH was decomposed to $\phi_f^{t\text{-B}} = (1.86 \pm 0.05) \times 10^{-2}$ and $\phi_f^c = (5.2 \pm 1.1) \times 10^{-4}$ (spectra and quantum yields are corrected for the small fluorescence contribution of the *t*-NPE impurity). Since at least some of the incident light is absorbed by *c*-NPE_A (see Scheme 1), we estimate that no less than 2% of ^1c-$\text{NPE}_B{}^*$ undergoes adiabatic isomerization to ^1t-$\text{NPE}_B{}^*$, whose fluorescence quantum yield is known to be 0.76.[4] Though not as efficient as adiabatic cis → trans photoisomerization on the lowest singlet excited state surface of more complex olefins,[6-8] substitution of the 2-naphthyl group for a phenyl group in stilbene leads to at least a 10-fold enhancement in the adiabatic photoisomerization pathway for *one of the conformers only*. Whether this reflects more favorable energetics for the adiabatic pathway or a longer lifetime at a roughly perpendicular geometry, $^1p^*$, remains to be established. The increase in the ^1c-$\text{NPE}_B{}^* \rightarrow {}^1t$-$\text{NPE}_B{}^*$ adiabatic pathway is all the more remarkable when one considers that estimated activation energies[4,9] for radiationless decay of ^1t-$\text{NPE}_B{}^*$ are significantly higher than those for the same process in stilbene.[10] Values of $E_{tp}{}^B = 10.4$ and ~7 kcal/mol have been based on the temperature dependencies of fluorescence lifetimes[9] and fluorescence quantum yields,[2c,4] respectively, and a somewhat smaller value was based on the temperature dependence of trans → cis quantum yields.[2c,4] Of course, the barrier that would be experienced in the $^1p^* \rightarrow {}^1t^*$ direction, assuming that the twisted geometry represents a minimum on NPE_B's lowest excited singlet state surface, would depend on the still unknown relative energies of $^1p^*$ and $^1t^*$. These findings suggest that the adiabatic cis → trans photoisomerization pathway, first suggested by Olson,[11] may be more common than is generally assumed. For instance, the similar features in the fluorescence spectra of *cis*- and *trans*-1,2-di(1-naphthyl)ethene in 3-methylpentane[12] were also suggested to indicate the presence of the trans isomer as an impurity in cis samples.[2] In light of the present results, we shall investigate the possibility of adiabatic $^1c^* \rightarrow {}^1t^*$ photoisomerization in that system as well.

Our ϕ_f^c value is consistent with Fischer's values for hydrocarbon media at much lower temperatures, for which the adiabatic isomerization is completely suppressed.[2] An excellent Arrhenius plot is obtained by assuming a limiting $\phi_{f0}{}^c = 0.67$ at very low temperature. It gives $A = (3.32 \pm 0.32) \times 10^{13}$ s^{-1} and $E_a = 2.86 \pm 0.02$ kcal/mol as activation parameters, suggesting that the torsional relaxation of ^1c-NPE* experiences mainly the solvent's barrier to viscous flow.[3c] A rough estimate of $\tau_f = 4 \pm 1$ ps for ^1c-NPE* under our conditions can be based on our ϕ_f^c value, in agreement with the insensitivity of this fluorescence to $[O_2]$.

A relatively high efficiency of the known, conformer-specific photocyclization of ^1c-$\text{NPE}_A{}^*$ [13] probably accounts for the absence of cis → trans adiabatic photoisomerization in that conformer. The sharp drop in cis → trans photoisomerization quantum yields when *c*-NPE is excited at the red edge of its absorption spectrum[1,2,14] without diminution in dihydrophenanthrene formation[14] suggests that ^1c-$\text{NPE}_A{}^*$, selectively formed by excitation at longer wavelengths, undergoes only photocyclization. Previous results of photocyclization studies[13] and those from this study are summarized in Scheme 1. They provide a striking example of the application of Havinga's nonequilibration of excited rotamers (NEER) principle.[15]

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