J. Phys. Chem. A **2000,** *104,* 11443−11450

Direct Photoisomerization of the 1,6-Diphenyl-1,3,5-hexatrienes. Medium Effect on Triplet and Singlet Contributions

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Received: July 1, 2000; In Final Form: September 8, 2000

Quantum yields for the interconversion of the *all-trans-*, *cis*,*trans*,*trans*- and *trans*,*cis*,*trans*-1,6-diphenyl-1,3,5-hexatrienes (DPH) in methylcyclohexane (MCH) or acetonitrile (AN) following 366 nm excitation show these processes to be relatively inefficient. Their dependence on the concentration of the DPH reveals significant participation of triplet states in the overall process. Despite very low intersystem crossing quantum yields (0.029 and 0.010 in MCH and AN, respectively) singlet and triplet contributions in the photoisomerization of *all-trans*-1,6-diphenyl-1,3,5-hexatriene are roughly equal in MCH, and, for the trans,cis,trans isomer, in AN. However, in AN the cis,trans,trans isomer forms nearly exclusively by a singlet pathway from the other two isomers. The cis,cis,trans isomer, a very minor component in photostationary states, appears to form primarily from the cis,trans,trans isomer whose excited singlet state also gives another isomer, tentatively identified as *ctc*-DPH. The major radiationless channel of the excited singlet state of each DPH isomer is direct decay to the original ground state. Barriers to torsional relaxation of the planar lowest DPH excited singlet states (2^1A_g and 1^1B_u) must be significantly higher than previously supposed. Photoisomerization quantum yields of *all-trans*-DPH in the presence of fumaronitrile (FN) are also separated into singlet and triplet contributions. Fumaronitrile quenches DPH fluorescence and singlet contributions to the photoisomerization equally, but enhances DPH triplet formation and the triplet contribution to the photoisomerization. Radical cations of DPH form in AN but do not participate in isomer interconversion.

Introduction

all-trans-1,6-Diphenyl-1,3,5-hexatriene (*ttt*-DPH) is the first member of the α,*ω*-diphenylpolyene vinylogous family whose lowest excited singlet state is the forbidden doubly excited 2^1A_g state.[1−3] It has attracted a great deal of interest as a model for the longer polyenes. Single photon excitation of *ttt*-DPH initially gives the 1^1B_u state which couples vibronically with the nearby 2^1A_g state to give mixed states that exist in thermal equilibrium.[4] The lowest excited state, which is mainly 2^1A_g in character, is populated from the higher, mainly 1^1B_u state, in the femtosecond time scale.[5,6] Extremely fast $1^1B_u \leftrightarrows 2^1A_g$ equilibration renders both these states viable intermediates for trans → cis photoisomerization. However, the focus has been on the 2^1A_g state[7−9] based on Birks' extension of the Orlandi and Siebrand (OS) photoisomerization mechanism for the stilbenes[10] to the higher members of the α,*ω*-diphenylpolyene family.[11] In the OS mechanism, the 2^1A_g state of stilbene is postulated to have its energy minimum at the perpendicular geometry, $^1p^*$, and torsional relaxation from the excited state of either isomer to this global minimum is assumed to experience no energy barrier.[10,12] The barrier in the $^1t^* \rightarrow {}^1p^*$ direction is assigned to the crossing of the 1^1B_u and 2^1A_g states along the twisting coordinate. Because in DPH the 2^1A_g state is lower in energy than the 1^1B_u state, no such barrier can be relied upon to account for enormously longer fluorescence lifetimes relative to *trans*-stilbene. The required barrier was postulated to originate because of geometry-dependent mixing between the 1^1B_u and 2^1A_g states of DPH. Optimum mixing and maximum stabilization of the lowest excited singlet at the planar geometry and diminished mixing and lesser stabilization with departure from planarity supposedly create a barrier along the torsional coordinate.[11] Small barrier heights were estimated from the temperature dependencies of fluorescence quantum yields and lifetimes on the basis of the assumption that torsional motion leading to photoisomerization is the only process competing with fluorescence.[11] Weaknesses in this mechanism were presented in a recent review,[3] and it was shown to be incorrect in a preliminary report of our results.[13] Low photoisomerization quantum yields obtained on direct excitation of the DPH isomers[13] invalidated Birks' assumption that fluorescence and photoisomerization are complementary processes that fully account for the decay of the S_1 state of *ttt*-DPH.

Investigations of the triplet-sensitized photoisomerization of the DPH isomers have led to a thorough understanding of the behavior of DPH triplets,[14,15] which is used in this paper to separate photoisomerization quantum yields following direct excitation into triplet and singlet contributions. Decay without photoisomerization is shown to be the dominant S_1 radiationless deactivation channel in *ttt*-, *ctt*-, and *tct*-DPH.

Experimental Section

Materials. Fumaronitrile, FN, (Aldrich, reagent) was recrystallized twice from benzene. All other materials were as previously described.[14]

Irradiation Procedure. Irradiations were carried out in a Moses merry-go-round apparatus[16] immersed in a thermostated water bath. Temperature was controlled by a heating coil connected to a thermoregulator (Polyscience Corporation). A Hanovia medium-pressure Hg lamp (200 W, Ace Glass, Inc.) and Corning CS 7−37 and 0−52 filters were used for excitation at 366 nm. The benzophenone-sensitized photoisomerization of *trans*-stilbene was used for actinometry, $\phi_{t\rightarrow c} = 0.55$.[17,18]

10.1021/jp002359f CCC: $19.00

Solutions, 3.0 mL, were pipetted into Pyrex ampules, 13 nm o.d., degassed, and flame-sealed at a constriction as has been described. Sample preparation, degassing and analysis were performed under nearly complete darkness (red light).

Analytical Procedures. Actinometer solutions were analyzed by GLC and DPH solutions by HPLC ($\lambda_{\mathrm{mon}} = 350$ nm) as previously described.[14]

Fluorescence Measurements. Fluorescence spectra of acetonitrile solutions were measured with a Hitachi/Perkin-Elmer MPF-2A fluorescence spectrophotometer as previously described.[19] Fluorescence spectra of methylcyclohexane solutions were measured with a Hitachi F 4500 spectrophotometer. Temperature control was provided by a Neslab RTE−4DD circulating bath connected to a block surrounding the sample cell. Temperatures were measured with an Omega Engineering model 199 RTD digital thermometer.

Results

Photostationary States. Degassed samples of *ttt*-DPH, 1.06×10^{-3} M, in MCH irradiated at 366 nm for different time intervals at 21.1 °C attain the photostationary state of 2.5% *ctt*-DPH, 7.2% *tct*-DPH, 0.22% *cct*-DPH and 90.1% *ttt*-DPH after ∼130 min and maintain it for the duration of the experiment, 220 min, Figure 1 in ref 13. The [ctt]/[tct] ratio is constant at 0.34 ± 0.01 throughout the experiment, but the [cct]/[tct] ratio increases with time consistent with contribution from a sequential two-photon excitation pathway for *cct*-DPH formation. The photostationary fractions of the two major cis isomers at 20 °C decrease slightly as the initial DPH concentration is increased in the 2.74×10^{-4} to 1.37×10^{-3} M range: 3.05% to 2.45% for ctt, and 7.41% to 6.40% for tct. The photostationary state for 5.6×10^{-4} M DPH in degassed AN irradiated at 366 nm is 36.4% ctt, 5.0% cct, 10.2% tct, and 48.4% ttt. Increasing the DPH concentration to 1.06×10^{-3} M leads to a photostationary state of 23.9% ctt, 2.0% cct, 10.6% tct, and 63.5% ttt at 20 °C.

Quantum Yields. Conversions, f_{xxt}, to photoisomers, where x is either c or t, were corrected for back reaction and for the presence of the isomer as an impurity, $f^{\mathrm{o}}_{\mathrm{xxt}}$, by the use of

$$f^{\mathrm{cor}}_{\mathrm{xxt}} = f^{\mathrm{e}}_{\mathrm{xxt}} \ln \frac{f^{\mathrm{e}}_{\mathrm{xxt}} - f^{\mathrm{o}}_{\mathrm{xxt}}}{f^{\mathrm{e}}_{\mathrm{xxt}} - f_{\mathrm{xxt}}} \tag{1}$$

where $f^{\mathrm{cor}}_{\mathrm{xxt}}$ and $f^{\mathrm{e}}_{\mathrm{xxt}}$ are the corrected and photostationary state conversions, respectively.[20,21] Because photostationary states are not available under all conditions employed for the quantum yield measurements, conversions were kept relatively small in order to minimize the magnitude and error of back reaction corrections. Quantum yields measured as a function of [DPH] in MCH for the three isomers are listed in Table 1. The elution time of *cct*-DPH is too close to that of *ctt*-DPH, and it appears as a shoulder on the tail of the *ctt*-DPH peak. The fact that this shoulder is readily observable when starting from *ctt*-DPH, despite the huge size of the ctt peak, shows that there is a significant ctt → cct reaction channel. Starting from *ttt*-DPH and *tct*-DPH, conversions to *cct*-DPH were too small for accurate evaluation. The cutting and weighing procedure of enlarged Xerox copies of HPLC traces[22] gave estimates of [cct]/[ctt] ratios of ≤0.08 starting from *ttt*-DPH in MCH and ≤0.22 starting from *tct*-DPH in MCH or AN. A new, well-resolved peak whose elution time is 0.91 ± 0.01 that of *ctt*-DPH is observed only for *ctt*-DPH as the starting isomer. This peak, tentatively assigned to *ctc*-DPH, is comparable in size to that of the *tct*-DPH product. The quantum yield of this product was estimated based on the ctc/tct area ratio, by neglecting any differences in correction factors and in ϵ_{350} values. Photoisomerization quantum yields in AN are given in Table 2. The effect of additives on photoisomerization quantum yields starting from *ttt*-DPH was evaluated in AN. No effect was found for diethylamine, lithium chloride, and lithium perchlorate concentrations up to 0.015, 0.0012, and 0.11 M, respectively. Significant effects were observed in the presence of FN in both MCH and AN, Tables 3 and 4, respectively.

TABLE 1: Quantum Yields for the Photoisomerization of DPH Isomers in MCH, 20.0 °C[a]

10^3[DPH], M	ϕ_{ctt}	ϕ_{tct}	ϕ_{ttt}	ϕ_{ctc}[b]
ttt-DPH[c]				
0.306	0.0035	0.013_5		
0.355	0.0039	0.014_9		
0.575	0.0042	0.015_4		
0.795	0.0046	0.017_4		
1.35	0.0059	0.020_6		
ctt-DPH[d]				
0.401		0.010	0.14	0.0069
0.802		0.012	0.20	0.013
1.20		0.015	0.27	0.020
tct-DPH[e]				
0.433	0.0042		0.20	
0.865	0.0052		0.27	
1.30	0.0073		0.43	

[a] PSS fractions were assumed to be independent of [DPH]. [b] Estimated values, see text. [c] $f^{\mathrm{o}}_{\mathrm{ctt}} = f^{\mathrm{o}}_{\mathrm{tct}} = 0$; conversions were $f_{\mathrm{ctt}} \leq 0.008$, $f_{\mathrm{tct}} \leq 0.03$. [d] Values of $f^{\mathrm{o}}_{\mathrm{tct}}$ and $f^{\mathrm{o}}_{\mathrm{ttt}}$ were 0.0004 and 0.0018, respectively; conversions were $f_{\mathrm{ctt}} \leq 0.008$, $f_{\mathrm{tct}} \leq 0.03$. [e] Values of $f^{\mathrm{o}}_{\mathrm{ctt}}$ and $f^{\mathrm{o}}_{\mathrm{ttt}}$ were 0.0017 and 0.0022, respectively; conversions were $f_{\mathrm{ctt}} \leq 0.0015$, $f_{\mathrm{ttt}} \leq 0.07$.

TABLE 2: Quantum Yields for the Photoisomerization of DPH Isomers in AN, 20.0 °C[a]

10^3[DPH], M	ϕ_{ctt}	ϕ_{tct}	ϕ_{ttt}	ϕ_{ctc}[b]
ttt-DPH[c]				
1.00	0.056	0.035		
ctt-DPH[d]				
0.387		0.017	0.26	0.0066
0.451		0.017	0.26	0.0077
0.580		0.020	0.33	0.0098
0.773		0.022	0.36	0.0126
1.20		0.032	0.59	0.033
tct-DPH[e]				
0.417	0.034		0.16	
0.487	0.034		0.14	
0.626	0.034		0.19	
0.835	0.033		0.20	
1.30	0.031		0.29	

[a] PSS fractions were assumed to be independent of [DPH]. [b] Estimated values, see text. [c] $f^{\mathrm{o}}_{\mathrm{ctt}} = f^{\mathrm{o}}_{\mathrm{tct}} = 0$; conversions were $f_{\mathrm{ctt}} = 0.036$ and $f_{\mathrm{tct}} = 0.022$. [d] f^{o} values as in Table 1; conversions were $f_{\mathrm{tct}} \leq 0.007$ and $f_{\mathrm{ttt}} \leq 0.092$. [e] f^{o} values as in Table 1; conversions were $f_{\mathrm{ctt}} \leq 0.0014$ and $f_{\mathrm{ttt}} \leq 0.055$.

Fluorescence Quenching. The quenching of *ttt*-DPH fluorescence by FN was determined in degassed and air-saturated AN solutions at ambient temperature (20−22 °C) and in MCH solutions at 22 °C. Stern−Volmer (SV) plots of $\phi^{\mathrm{o}}_{\mathrm{f}}/\phi_{\mathrm{f}}$ where $\phi^{\mathrm{o}}_{\mathrm{f}}$ is the fluorescence quantum yield of the degassed 1.00×10^{-3} M DPH in AN solution, vs [FN] (concentrations up to 0.015 M were employed) are parallel with slopes $K_{\mathrm{sv}} = 88.5 \pm 2.4$ and 87.9 ± 3.4 M^{-1} in the presence and absence of air, respectively. The corresponding intercepts are 1.36 ± 0.02 and 0.987 ± 0.029. Analogous plots for the quenching of 9.2×10^{-7} and 5.0×10^{-6} M DPH by FN (concentrations up to 0.0044 M were

TABLE 3: FN Effect on the Photoisomerization of *ttt*-DPH in MCH, 20.0 °C[a]

10^3[FN],M	10^3[DPH],M	ϕ_{ctt}	ϕ_{tct}
7.6[b]	0.400	0.0034	0.013_8
	0.800	0.0042	0.016_7
	1.20	0.0047	0.019_1
	1.60	0.0061	0.024_1
	2.00	0.0072	0.028_9
1.0	1.21[c]	0.0056	0.022_2
2.0		0.0049	0.018_9
3.0		0.0051	0.019_7
4.0		0.0058	0.020_5
5.0		0.0052	0.021_0

[a] Irradiation at 366 nm; all conversions corrected for back reaction neglecting possible concentration effects on PSS. [b] Conversions were $f_{ctt} \leq 0.0062$ and $f_{tct} \leq 0.024$. [c] Conversions were $f_{ctt} \leq 0.004$ and $f_{tct} \leq 0.014$ for a saturated FN solution in MCH.

TABLE 4: FN Effect on the Photoisomerization of *ttt*-DPH in AN, 20.0 °C[a]

10^3[FN], M	ϕ_{ctt}	ϕ_{tct}
0.00	0.056	0.035
3.03	0.043	0.034
6.05	0.032	0.032
9.08	0.032	0.032
12.1	0.029	0.029
15.1	0.026	0.028

[a] [*ttt*-DPH] = 1.00×10^{-3} M; conversions were $f_{ctt} \leq 0.036$ and $f_{tct} \leq 0.022$ and were back reaction corrected by neglecting any effect of [FN] on the PSS.

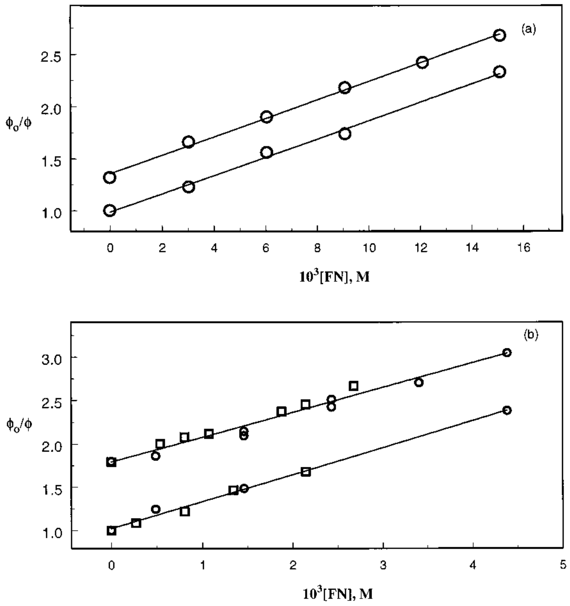


Figure 1. Quenching of *ttt*-DPH fluorescence by FN in degassed and air-saturated AN (a) and MCH (b). In each panel the upper line is in the presence of air. In (b) the circles and squares are for *ttt*-DPH 5.0×10^{-6} and 9.2×10^{-7} M, respectively.

employed) in MCH solutions are again parallel with slopes $K_{SV} = 286 \pm 14$ and 312 ± 11 M^{-1} and intercepts 1.794 ± 0.03 and 1.02 ± 0.02 in air-saturated and degassed solutions, respectively. SV plots are shown in Figure 1.

Discussion

Fluorescence quantum yields and lifetimes of the highly fluorescent *all-trans*-1,6-diphenyl-1,3,5-hexatriene (*ttt*-DPH) exhibit strong medium sensitivity.[23] It is not surprising, therefore, that *ttt*-DPH has long been considered an ideal fluorescence probe for microenvironment.[7,23−27] Torsional relaxation leading to photoisomerization has usually been assumed to be the sole radiationless decay process competing with fluorescence[7,11] and the expectation that such a large intramolecular motion should be sensitive to medium fluidity has been a central theme in the interpretation of observed medium effects. Often ignored has been the effect of medium polarizability on the $2^1A_g-1^1B_u$ energy gap that controls the extent of mixing between these two states and, consequently, the magnitude of the radiative decay rate constant that strongly influences both the fluorescence quantum yield and lifetime. Here we provide the missing photoisomerization quantum yields and their medium dependence that are essential for the evaluation of the degree to which torsional relaxation contributes to the radiationless deactivation of the singlet excited state(s) of *ttt*-DPH. It is shown below that the Birks extension of the OS mechanism for stilbene photoisomerization[10] to DPH and higher members of the diphenylpolyene family[11] fails this experimental test.

The All-Trans Isomer. We consider first photoisomerization in trans → cis directions starting from *ttt*-DPH. The quantum yields for terminal, ϕ_{ctt}, and central ϕ_{tct}, bond isomerization in Tables 1 and 2 are somewhat smaller than the values in our preliminary report. The discrepancy, due in part to large conversions with unreliable back reaction corrections and to the higher temperature employed in the early experiments, does not affect the conclusions. The quantum yields are much smaller than expected on the basis of the assumption that deviations of *ttt*-DPH fluorescence quantum yields from unity ($\phi_f = 0.65$ and 0.15 in MCH and AN, respectively at 25 and 23 °C, respectively)[23] are due entirely to torsional relaxation along trans → cis photoisomerization coordinates.[7,11,23] If the major radiationless decay processes involved formation of twisted intermediates, ^{1}ptt* and ^{1}tpt*, whose decay gave cis and trans ground-state double bonds with nearly equal probability, then $(\phi_{ctt} + \phi_{tct}) = 0.18$ and 0.42 would be expected in MCH and AN, respectively. The experimental values give $(\phi_{ctt} + \phi_{tct}) = 0.018$ and 0.091 in MCH and AN, respectively, and, due to triplet involvement, these sums would be even smaller at lower *ttt*-DPH concentrations.

The involvement of triplets in the photoisomerization had been discounted primarily because measured *ttt*-DPH intersystem crossing quantum yields, ϕ_{is}, are very small in solvents devoid of heavy atoms at ambient temperature.[28−32] Relevant to the present work are the values of $\phi_{is} = 0.029$ and 0.010 in cyclohexane[30] and in AN,[32] respectively, which, although small, are not negligible relative to the overall photoisomerization quantum yields in Tables 1 and 2. Assuming that ϕ_{is} in MCH is the same as ϕ_{is} in cyclohexane, these intersystem crossing quantum yields allow calculation of triplet contributions to the photoisomerization quantum yields.

The DPH triplet was designated as ^{3}eet* in degassed MCH and AN solutions because it exists as an equilibrium mixture of isomeric ^{3}ttt*, ^{3}tct*, ^{3}ctt*, and ^{3}cct* triplets.[14,22] Transient observations have established that at infinite dilution the lifetime of ^{3}eet* is 38.7 ± 1.0 and 65.4 ± 0.2 μs in MCH and AN, respectively.[14] As the DPH concentration is increased, self-quenching (the τ's drop to 30.6 and 59.2 μs at [*ttt*-DPH] = 1×10^{-3} M)[14] occurs in competition with much more efficient triplet excitation transfer steps between the isomeric DPH triplets and the ground state of the starting DPH. The latter events are chain carrying steps for quantum chain photoisomerization. Neglecting the minor *cct*-DPH formation, the simplest mechanism for the photoisomerization of *ttt*-DPH that includes the known behavior of the triplets[14] is shown below

$$^1\text{ttt} \xrightarrow{h\nu} {}^1\text{ttt}^* \tag{2}$$

$$^1\text{ttt}^* \xrightarrow{k_f} {}^1\text{ttt} + h\nu \tag{3}$$

$$^1\text{ttt}^* \xrightarrow{k_{nr}} {}^1\text{ttt} \tag{4}$$

$$^1\text{ttt}^* \xrightarrow{k_{is}} {}^3\text{eet}^* \tag{5}$$

$$^1\text{ttt}^* \xrightarrow{k_1} {}^1\text{ptt}^* \tag{6}$$

$$^1\text{ttt}^* \xrightarrow{k_3} {}^1\text{tpt}^* \tag{7}$$

$$^1\text{ptt}^* \xrightarrow{k_{d1}} \alpha'\,{}^1\text{ctt} + (1 - \alpha')\,{}^1\text{ttt} \tag{8}$$

$$^1\text{tpt}^* \xrightarrow{k_{d2}} \beta'\,{}^1\text{tct} + (1 - \beta')\,{}^1\text{ttt} \tag{9}$$

$$^1\text{eet}^* \xrightarrow{k_d} \alpha\,{}^1\text{ctt} + \beta\,{}^1\text{tct} + (1 - \alpha - \beta)\,{}^1\text{ttt} \tag{10}$$

$$^3\text{eet}^* + {}^1\text{ttt} \xrightarrow{k_{ttt}} \gamma\,{}^1\text{ctt} + \delta\,{}^1\text{tct} + (\gamma_{en} + \delta_{en})\,{}^3\text{eet}^* + [2(1 - \gamma - \delta) + \gamma_q + \delta_q]\,{}^1\text{ttt} \tag{11}$$

where α′ and β' are decay fractions leading to the cis isomer from the twisted intermediates and rate constants and decay fractions describing the decay of the equilibrated triplets were determined in our earlier work.[14,22] The quantitative analysis of *ttt*-DPH fluorescence has established the absence of adiabatic pathways from ^{1}ttt* to excited cis singlet states, ^{1}xxt*.[33]

Quantum yields for *ctt*- and *tct*-DPH formation from *ttt*-DPH are given by

$$\phi_{ctt} = \alpha' k_1 \tau_S^o + \frac{\phi_{is}^o(\alpha + \gamma k_{ttt}\tau_T^o[^1\text{ttt}])}{1 + (1 - \gamma_{en} - \delta_{en})k_{ttt}\tau_T^o[^1\text{ttt}]} \tag{12}$$

$$\phi_{tct} = \beta' k_3 \tau_S^o + \frac{\phi_{is}^o(\beta + \delta k_{ttt}\tau_T^o[^1\text{ttt}])}{1 + (1 - \gamma_{en} - \delta_{en})k_{ttt}\tau_T^o[^1\text{ttt}]} \tag{13}$$

which are derived by applying the steady-state approximation to all excited species. In eqs 12 and 13, $\tau_S^o = (k_f + k_{nr} + k_{is} + k_1 + k_3)^{-1}$ is the singlet lifetime of *ttt*-DPH and $\tau_T^o = k_d^{-1}$ is the lifetime of the equilibrated triplet. The first terms on the right-hand side of the equal signs in eqs 12 and 13 are singlet contributions, ϕ_{xxt}^S, and the second terms are triplet contributions, ϕ_{xxt}^T, to overall quantum yields. The values of ϕ_{ctt}^T and ϕ_{tct}^T were calculated with the use of the known ϕ_{is} values (see above) and the previously determined parameters for DPH triplets in MCH and AN,[13] Table 5. Subtraction of these values from the experimental quantum yields gives the singlet contributions, ϕ_{ctt}^S and ϕ_{tct}^S which are also listed in Table 5. The results in MCH reveal that the dependence of the observed quantum yields on [*ttt*-DPH] is due entirely to the quantum chain component of the triplet contribution to the overall process. The singlet contributions are sensibly concentration independent. The average values give $\phi_{ctt}^S = 0.0028 \pm 0.0002$ and $\phi_{tct}^S = 0.0098 \pm 0.0003$ in MCH. Assuming $\alpha' = \beta' = 0.5$ these quantum yields account for only 7.2% of the radiationless decay of ^{1}ttt*. Equation 4 is by far the major radiationless decay process of *ttt*-DPH in MCH, $\phi_{nr} = 0.30$. Dividing this quantum yield by the fluorescence lifetime[23] gives $k_{nr} = 2.2 \times 10^7$ s^{-1}, an unusually large value when one considers that rate constants for $S_1 \rightarrow S_0$ radiationless decay in polynuclear aromatic hydrocarbons with comparable or smaller $S_1{-}S_0$ energy gaps are immeasurably small relative to competing radiative and intersystem crossing rate constants.[34] Siebrand's energy-gap law predicts $k_{nr} = 1.2 \times 10^6$ s^{-1} for a polynuclear aromatic hydrocarbon with the same $S_1{-}S_0$ energy gap as DPH.[35] It appears that in DPH the radiationless decay process is facilitated by the flexibility of the polyene chain.

TABLE 5: Singlet and Triplet Contributions to the Photoisomerization of *ttt*-DPH in MCH and AN, 366 Nm, 20 °C

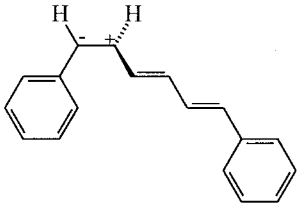
10^3[*ttt*−DPH],M	$10^2\phi_{ctt}^{T\ a}$	$10^2\phi_{ctt}^{S\ b}$	$10^2\phi_{tct}^{T\ a}$	$10^2\phi_{tct}^{S\ b}$
		MCH		
0.306	0.09_8	0.25	0.39_6	0.95
0.355	0.10_7	0.28	0.43_7	1.05
0.575	0.14_8	0.27	0.60_8	0.93
0.795	0.18_5	0.28	0.76_3	0.98
1.35	0.26_3	0.33	1.09	0.97
		Ave: 0.28(2)[c]		Ave: 0.98(3)[c]
		AN		
1.00	0.10_6	5.5	0.59_3	2.9_3

[a] Calculated from the second term on the right-hand side of eqs 12 and 13 with $\phi_{is}^o = 0.029$ in MCH[30] and 0.01 in AN.[31,32] [b] Calculated by subtraction of ϕ_{xxt}^T values from experimental quantum yields. [c] Value in parentheses is the uncertainty in the last significant figure.

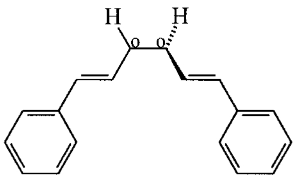
The presence of small amounts of *cct*-DPH in photostationary states obtained upon direct excitation of *ttt*-DPH in either MCH or AN, raises the possibility of its formation directly from *ttt*-DPH via two bond photoisomerization events in the potential energy surface of either the lowest excited singlet state or the triplet state or in both of these states. This has been shown to occur to a small extent in the triplet state[22] and one can imagine sequences starting from ^{1}ttt* (possibilities include: $^1\text{ttt}^* \rightarrow {}^1\text{ptt}^* \rightarrow {}^1\text{ppt}^*$ and $^1\text{ttt}^* \rightarrow {}^1\text{tpt}^* \rightarrow {}^1\text{ppt}^*$). However, starting from *ttt*-DPH, cct/ctt and cct/tct ratios increase as a function of time as the photostationary states in MCH and AN are established, consistent with *ctt*- and/or *tct*-DPH as the primary precursor(s) of *cct*-DPH.[13] In this work we roughly estimate that, starting from *ttt*-DPH, initial ϕ_{cct} values are ≤ 0.0003 in MCH. Since at least 15 to 25% of this limiting value can be attributed to photoisomerization via the equilibrated triplet state,[14,22] we conclude that two bond photoisomerization yielding *cct*-DPH directly from ^{1}ttt* is, at best, a highly inefficient process.

Dissection of the quantum yields into triplet and singlet components shows that, on changing the solvent from MCH to AN, terminal bond photoisomerization in the excited singlet state is enhanced much more than previously estimated.[13] The 20-fold increase in the value of ϕ_{ctt}^S can be compared with a relatively modest 3-fold increase in the value of ϕ_{tct}^S. Differential medium effects on the transition state for terminal vs central bond torsional relaxation are consistent with the proposed zwitterionic electronic distribution for ^{1}ptt* and diradicaloid character for ^{1}tpt*.[13] Charge separation in ^{1}ptt* is favored by the more polar solvent. Enhancement of the photoisomerization channel notwithstanding, it still accounts for only 20% of radiationless decay of ^{1}ttt* in AN at ∼20 °C, again assuming $\alpha' = \beta' = 0.5$.[36] In this solvent also, direct radiationless decay to ^{1}ttt is the major radiationless decay path, $\phi_{nr} = 0.66$.[36]

Formation of the tct isomer is favored in both solvents in the triplet state[13] and it may be tempting to conclude that this is because twisting about the central bond gives the more stable biradical.[22,37] This conclusion would be incorrect, however, because ^{3}ptt* and ^{3}tpt* are transition states and not intermediates



^{1}ptt*



^{1}tpt*

on the triplet energy surface.[14,22] Twisting about either terminal or central bond is not rate determining with respect to ^{3}ttt* photoisomerization. The product distribution reflects the equilibrium distribution of the isomeric triplet states. The formation of ^{1}tct is favored over that of ^{1}ctt because [^{3}tct*] > [^{3}ctt*] in both solvents.[14,22]

The Cis Isomers. Starting from the two cis isomers, the major photoproduct in both solvents is *ttt*-DPH, Tables 1 and 2. Formation of *cct*-DPH, the other shared one bond isomerization product, appears to be a significant process starting from *ctt*-DPH, but is a minor process starting from *tct*-DPH. Ironically, estimation of *cct*-DPH yields by HPLC, although relatively easy for tct samples in which the ctt peak is small, is precluded in ctt samples where the cct peak is overwhelmed by the large peak of the starting material.

We turn now to the DPH isomer that forms only upon direct excitation of *ctt*-DPH and must, therefore, involve a reaction path on the singlet excited state surface. The early elution time of this product suggests that it is identical to *cis*-IV, a minor DPH isomer isolated, relatively impure, in the pioneering study of Lunde and Zechmeister.[38] Its relationship to *ctt*-DPH was established in that study by the observation that it underwent thermal isomerization at 4 °C in the dark to yield *ctt*- and *ttt*-DPH. Because *ctc*-DPH is the remaining DPH dicis isomer that can form by one bond photoisomerization only from *ctt*-DPH and because, furthermore, *ctc*-DPH should yield thermally the ctt and ttt isomers as reported earlier,[38] we feel confident in assigning the 1,5-dicis geometry to this product. The ctt → ctc quantum yield increases strongly with increasing *ctt*-DPH concentration in both MCH and AN. Because *ctc*-DPH does not form on fluorenone sensitization,[14,22] a triplet quantum chain process can be ruled out as the source of this concentration dependence. Assuming that the ϕ_{ctc} values in Tables 1 and 2 are accurate (samples were irradiated and analyzed at ~20 °C, and the thermal lability of *ctc*-DPH was not determined under our conditions), it seems clear that the singlet mechanism for its formation differs from the mechanisms that apply to the other isomers. One possibility is that, in contrast to ^{1}tpt* and ^{1}ptt*, ^{1}ctp* is a transition state instead of an intermediate on the path of a small ^{1}ctt* → ^{1}ctc* adiabatic channel. Participation of ^{1}ctc* in a singlet quantum chain process could then account for the pronounced concentration dependence exhibited by ϕ_{ctc}. This and other possibilities will be investigated in future work.

Interconversion of *tct*-DPH and *ctt*-DPH requires two-bond isomerization, which is known to occur in the triplet state. That triplets are involved in these photoisomerizations is revealed by the concentration dependence of the quantum yields (with the notable exception of ϕ_{ctt} in AN starting from *tct*-DPH, see below). Because the equilibrium distribution of the DPH triplet strongly favors the all-trans geometry, the greater involvement of ^{3}ttt* in the quantum chain photoisomerizations of *ctt*- and *tct*-DPH leads to very high fluorenone-sensitized quantum yields in ctt → ttt and tct → ttt directions ($\phi_{ttt} \geq 10$ in benzene at 20 °C for [*ctt*-DPH] or [*tct*-DPH] $= 1.0 \times 10^{-3}$ M).[14] Quantitative evaluation of the quantum yields for the photoisomerization of the cis isomers requires knowledge of triplet parameters in eqs analogous to 12 and 13. Unfortunately, for the cis isomers these parameters are known in benzene but not in MCH or AN.[14] Qualitative analysis of these quantum yields can be based on the known behavior of the triplets in benzene, because, as has been shown starting from *ttt*-DPH,[14] triplet photoisomerization quantum yields are expected to be relatively insensitive to these solvent changes.

Use of the triplet parameters determined for the cis isomers in benzene to estimate the behavior of the triplets in MCH leads to the conclusion that ϕ_{is}^{o} can be no higher than 0.02 for either *ctt*- or *tct*-DPH. Starting from *ctt*-DPH all ϕ_{ttt} and ϕ_{tct}, values in Table 1 are accounted for nearly quantitatively with $\phi_{is}^{o} = 0.018$ and the assumption that all photoisomerization occurs via this minor triplet pathway. If a lower value of $\phi_{is} = 0.015$ were assumed, then the singlet contributions for the direct photoisomerization of *ctt*-DPH would be no higher than $\phi_{ttt}^{S} = 0.04$ and $\phi_{tct}^{S} = 0.003$. Similarly, starting from *tct*-DPH the ϕ_{ttt} quantum yields are quantitatively accounted for with $\phi_{is}^{o} = 0.020$ if all the isomerization is again assigned to the triplet state. Somewhat higher ϕ_{is} values are predicted from the ϕ_{ctt} values ($\phi_{is}^{o} = 0.03-0.04$), which are consistent with $\phi_{is}^{o} = 0.020$ if we allow for a small singlet component, $\phi_{ctt}^{S} = 0.002$. However, even this small ϕ_{ctt}^{S} value is an upper limit because its calculation neglects formation of ctt by sequential two photon absorption (tct $\xrightarrow{h\nu}$ ttt $\xrightarrow{h\nu}$ ctt). We conclude that photoisomerization by torsional relaxation in the singlet excited state is very inefficient for both *ctt*- and *tct*-DPH in MCH.

The same procedure can be applied to the quantum yields in AN, Table 2. Starting from *ctt*-DPH, use of $\phi_{is}^{o} = 0.038 \pm 0.002$ predicts all the observed ϕ_{ttt} and ϕ_{tct} values quantitatively on the assumption that all photoisomerization occurs in the triplet state. Starting from *tct*-DPH, the ϕ_{ttt} values predict $\phi_{is}^{o} = 0.015 \pm 0.001$ if all *ttt*-DPH formed in the triplet state. This sets an upper limit for ϕ_{is} that is significantly lower than ϕ_{is}^{o} values (0.13−0.35) estimated by assigning all two-bond isomerization (i.e., the ϕ_{ctt} values) to the triplet pathway. With the use of $\phi_{is}^{o} = 0.015$ to estimate the triplet contributions, ϕ_{ctt}^{T}, to the photoisomerization we obtain $\phi_{ctt}^{S} = 0.031 \pm 0.002$, independent of [*tct*-DPH]. The prediction that nearly all tct → ctt photoisomerization occurs in the singlet excited state is consistent with the observed concentration independence of the ϕ_{ctt} values in Table 2. Thus, the conclusion reached earlier on the basis of preliminary data, that there is “a significant two-bond/photon isomerization pathway in the tct → ctt direction” in AN and not in MCH is confirmed here. What is remarkable is that this appears to be the major photoisomerization channel open to ^{1}tct*. Apparently the polar solvent enhances access to ^{1}ptt* for both *ttt*- and *tct*-DPH. If ^{1}ptt* were indeed the precursor for *ctt*-DPH starting from *tct*-DPH, then the assumption that this twisted intermediate decays with equal probability to *ctt*- and *ttt*-DPH predicts $\phi_{ctt}^{S} = \phi_{ttt}^{S} = 0.031$. Applying this correction to the ϕ_{ttt} values in Table 2 leads to a small downward adjustment in ϕ_{is}^{o} for *tct*-DPH in AN to 0.014.

The Effect of Fumaronitrile. The possible role of DPH radical cations, 2DPH$^{\bullet+}$, in the photoisomerization was investigated by using FN to induce their formation. This part of the work was prompted by the elegant studies of charge-transfer quenching of ^{1}*ttt*-DPH* by Löhmannsröben and Schael.[31,32,39,40] Interactions between ^{1}*ttt*-DPH* and several electron acceptors, including FN, were investigated in a series of solvents of varying polarity (toluene to AN) using fluorescence and transient absorption measurements.[31,40] Exciplexes formed in nonpolar solvents have charge-transfer character and in polar solvents, such as AN, dissociate into free radical ion pairs. Intersystem crossing in the contact radical ion pair followed by back electron transfer leads to ^{3}DPH* as an important decay channel especially in nonpolar solvents.[31] Diffusion-controlled *ttt*-DPH fluorescence quenching by FN was demonstrated in both toluene ($k_q^f = 1.40 \times 10^{10}$ M^{-1} s^{-1}) and AN ($k_q^f = 2.10 \times 10^{10}$ M^{-1}s^{-1}).[31]

Assuming that neither the exciplex nor DPH radical cations contribute to the photoisomerization of *ttt*-DPH, the following steps must be included in order to account for photoisomerization quantum yields in the presence of FN:

$$^1\text{ttt}^* + \text{FN} \xrightarrow{k_q^f} {}^1(\text{ttt}\cdot\text{FN})^* \tag{14}$$

$$^1(\text{ttt}\cdot\text{FN})^* \xrightarrow{k_{ed}} {}^1\text{ttt} + \text{FN} \tag{15}$$

$$^1(\text{ttt}\cdot\text{FN})^* \xrightarrow{k_{eis}} {}^3(\text{ttt}\cdot\text{FN})^* \tag{16}$$

$$^1(\text{ttt}\cdot\text{FN})^* \rightarrow {}^2\text{ttt}^{\bullet+} + {}^2\text{FN}^{\bullet-} \tag{17}$$

$$^3(\text{ttt}\cdot\text{FN})^* \rightarrow {}^3\text{eet}^* + \text{FN} \tag{18}$$

The singlet exciplex, ^{1}(ttt•FN)*, includes strong resonance contributions from the contact radical ion pair structure, $^1(\text{ttt}^{\bullet+} \cdot \text{FN}^{\bullet-})^*$. For simplicity, we neglect the reverse of eq 14 which may contribute to deviations from monoexponential fluorescence decay of ^{1}ttt* in the presence of FN.[31] We also neglect radical ion re-encounters which in polar solvents can give singlet and triplet exciplexes. No interaction between FN and DPH triplets need be considered because we find that the presence of 0.016 M FN in AN has no effect on the fluorenone-sensitized photoisomerization of *ttt*-DPH.

Parallel Stern−Volmer plots in the presence or absence of air are consistent with the assumption that exciplex formation, eq 14, is irreversible in both MCH and AN. At the very least they show that, if reversibly formed, the exciplex is too short-lived to be quenched by oxygen.[41] The SV constants in MCH give $k_q^f = (2.21 \pm 0.10) \times 10^{10}$ M^{-1} s^{-1}, assuming $\tau_o^f = 13.5$ ns,[23] close to the value expected for diffusion controlled quenching. This strong fluorescence quenching should apply with equal force to the singlet components of the photoisomerization quantum yields. However, the observed quantum yields for [DPH] = 1.21×10^{-3} M in MCH, Table 3, are remarkably independent of the concentration of FN. As will be shown below, diminution of the singlet contributions to photoisomerization is exactly compensated by enhanced DPH triplet formation from the exciplex. A relevant precedent is the formation of stilbene triplets via intersystem crossing from the stilbene/FN exciplex.[42−44]

With the inclusion of exciplex formation, eqs 12 and 13 can be used to calculate photoisomerization quantum yields, provided that τ_S^o is replaced by $\tau_S = (k_f + k_{nr} + k_{is} + k_1 + k_3 + k_q^f[\text{FN}])^{-1}$ and ϕ_{is}^o is replaced by ϕ_{is}^{FN}, the intersystem crossing yield in the presence of FN. As described by Schael,[31] the dependence of ϕ_{is}^{FN} on [FN] is given by

$$\phi_{is}^{FN} = \frac{\phi_{is}^o + f_T k_q^f \tau_S^o[\text{FN}]}{1 + k_q^f \tau_S^o[\text{FN}]} \tag{19}$$

where f_T is the fraction of exciplexes that decays to DPH triplets. The condition that the decrease in ϕ_{xxt}^S due to FN quenching be exactly compensated by the increase in ϕ_{xxt}^T is fulfilled if

$$f_T = \frac{\alpha' k_1 \tau_S^o + \phi_{is}^o \phi_{ctt}^{T\circ}}{\phi_{ctt}^{T\circ}} = \frac{\beta' k_3 \tau_S^o + \phi_{is}^o \phi_{tct}^{T\circ}}{\phi_{tct}^{T\circ}} \tag{20}$$

where $\phi_{ctt}^{T\circ}$ and $\phi_{tct}^{T\circ}$ are the known triplet quantum yields[13] at a specific [DPH] that correspond to unit probability of DPH triplet formation. With the use of $10^2\alpha' k_1 \tau_S^o = 0.28$ and $10^2\beta' k_1 \tau_S^o = 0.98$ from Table 5 and by taking $\phi_{is}^o = 0.029$, as above, eq 20 gives $f_T = 0.062$ and 0.057 in MCH from the ctt and tct parameters, respectively. The average of these two values, $f_T = 0.060 \pm 0.005$ can be compared to $f_T = 0.11 \pm 0.03$, the value determined spectroscopically by Schael in toluene.[31] It follows from eq 20 that our value of f_T in MCH is independent of the magnitude of k_q^f. Overall photoisomerization quantum yields independent of [FN] result, which are well within experimental uncertainty of the experimental values, Table 7 (compare average calculated values of ϕ_{ctt} and ϕ_{tct} equal to 0.0052 and 0.020_5, respectively, with corresponding experimental values of 0.0053(3) and 0.0205(7) from Table 3 for [DPH] = 1.21×10^{-3} M).

TABLE 6: Intersystem Crossing and Isomerization Channels for the Singlet Excited States of the DPH Isomers, 366 Nm, 20 °C

	MCH		AN	
isomer	ϕ_{is}[a]	$2(\phi_{xtt}^S + \phi_{txt}^S)$	ϕ_{is}[a]	$2(\phi_{xtt}^S + \phi_{txt}^S)$
ttt-DPH	0.029[b]	0.025	0.010[c]	0.17
ctt-DPH	0.015	0.008	0.038	0
tct-DPH	0.020	0	0.014	0.06

[a] Upper limits unless otherwise indicated, see text. [b] Reference 30. [c] Reference 31.

TABLE 7: Calculated Singlet and Triplet Contributions to *ttt*-DPH Photoisomerization Quantum Yields in MCH in the Presence of FN

10^3[DPH] or 10^3 [FN], M	$10^2\phi_{ctt}^T$	$10^2\phi_{ctt}^S$	$10^2\phi_{ctt}$[a]	$10^2\phi_{tct}^T$	$10^2\phi_{tct}^S$	$10^2\phi_{tct}$[a]
			DPH[b]			
0.400	0.20	0.08_7	0.29	0.82	0.30	1.13
0.800	0.32	0.08_7	0.41	1.33	0.30	1.64
1.20	0.42	0.08_7	0.51	1.76	0.30	2.06
1.60	0.51	0.08_7	0.60	2.13	0.30	2.43
2.00	0.58	0.08_7	0.67	2.44	0.30	2.74
			FN[c]			
1.0	0.30	0.22	0.52	1.27	0.76	2.02
2.0	0.34	0.18	0.52	1.42	0.62	2.04
3.4	0.38	0.14	0.52	1.56	0.49	2.05
4.0	0.39	0.13	0.52	1.61	0.45	2.06
5.0	0.40	0.11	0.51	1.67	0.40	2.06

[a] Sum of singlet and triplet contributions. [b] ϕ_{xxt}^T values calculated with $f_T = 0.060$ for [FN] = 7.6×10^{-3} M. [c] ϕ_{xxt}^T values calculated with ϕ_{is}^{FN} values from eq 19 with $f_T = 0.062$, see text; [DPH] = 1.21×10^{-3} M.

The quenching of ^{1}*ttt*-DPH* by FN in AN had been studied previously by steady state and transient fluorescence measurements at room temperature.[31] The fluorescence lifetime of ^{1}*ttt*-DPH* obtained under these conditions, 4.1 ns,[31] agrees with the value reported earlier for 22 °C.[23] The rate constant k_q^f differed somewhat depending on the method of measurement: $k_q^f = (1.60 \pm 0.10) \times 10^{10}$ and 2.10×10^{10} M^{-1}s^{-1} from stationary and transient fluorescence measurements, respectively.[31] Our Stern−Volmer constants for the quenching of DPH fluorescence by FN in AN give $k_q^f = (2.15 \pm 0.08) \times 10^{10} \times$ M^{-1}s^{-1}, in excellent agreement with the value obtained from the transient measurements.[45] As for MCH, the fact that the slopes of the two lines are identical shows that FN and O$_2$

TABLE 8: Singlet and Triplet Contributions to *ttt*-DPH Photoisomerization Quantum Yields in AN in the Presence of FN[a]

10^3[FN],M	$10^2\phi_{is}^{FN b}$	$10^2\phi_{ctt}^{T}$	$10^2\phi_{ctt}^{S}$	$10^2\phi_{tct}^{T}$	$10^2\phi_{tct}^{S}$
0.00	1.00	0.10_6	5.53	0.59_3	2.93
3.03	1.61	0.17_1	4.15	0.95_5	2.42
6.05	2.00	0.21_2	2.98	1.19	2.02
9.08	2.28	0.24_2	2.92	1.35	1.81
12.1	2.48	0.26_3	2.66	1.47	1.45
15.1	2.64	0.28_0	2.37	1.57	1.26

[a] [*ttt*-DPH] = 1.0×10^{-3} M. [b] Calculated with $f_T = 0.039$, $k_q^f = 2.15 \times 10^{10}$ M^{-1}s^{-1} and $\tau_S^o = 4.1$ ns, see text.

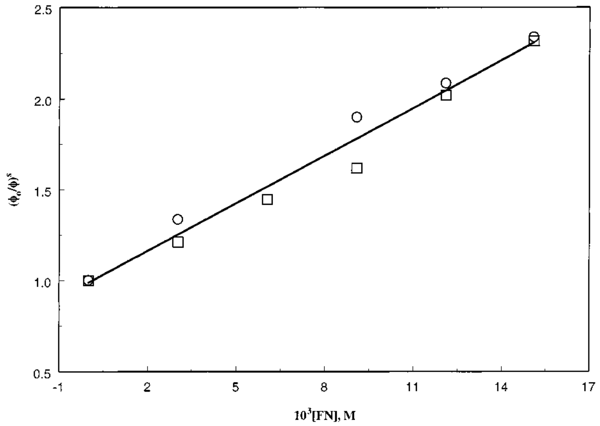


Figure 2. Quenching of the singlet contribution to *ttt*-DPH photoisomerization by FN in AN. The circles and squares are for ttt → ctt and ttt → tct, respectively.

quenching of ^{1}*ttt*-DPH are strictly additive. No cooperativity is observed as would be expected if a reversibly formed ^{1}(DPH · FN)* exciplex were quenched by O_2.[41] The exciplex is known to dissociate to radical ion pairs in AN[31,37]and is probably too short-lived to be quenched by O_2.

Inspection of the photoisomerization quantum yields in Table 4 shows that FN strongly quenches *ctt*-DPH formation but has a much smaller effect on *tct*-DPH formation (slopes of ϕ^o/ϕ vs [FN] plots are 69 and 16 M^{-1} for *ctt*- and *tct*-DPH, respectively). This behavior is consistent with enhanced triplet participation in the presence of FN since the DPH triplets favor tct over ctt formation (5.7:1.0 in AN).[14] In eq 19 all parameters for the calculation of ϕ_{is}^{FN} are known except for f_T. The value of f_T was varied systematically and, for each f_T, values of ϕ_{is}^{FN} were calculated with the use of eq 19 for the *ttt*-DPH concentrations in Table 4. Triplet contributions to the photoisomerization quantum yields were calculated as was described above for the MCH data, and these were subtracted from the observed quantum yields to obtain ϕ_{ctt}^{S} and ϕ_{tct}^{S} values, Table 8. For each f_T value Stern−Volmer plots of the singlet contributions, $(\phi_o^S/\phi^S) = 1 + K_{SV}[FN]$, were compared with our experimental value for fluorescence quenching. The best agreement was achieved for $f_T = 0.039$. Derived values of $K_{SV} = 87.6 \pm 3.9$ and 86.8 ± 5.7 M^{-1} for ctt and tct formation, via the singlet pathway respectively, are in excellent agreement with each other and with the values obtained from the fluorescence measurements. The global Stern−Volmer plot has $K_{SV} = 87.5 \pm 4.5$ M^{-1} (the slope/intercept ratio is 88.6 M^{-1}), Figure 2.

Conclusion

Quantum yields for intersystem crossing and isomerization decay channels of the singlet excited states of the DPH isomers are summarized in Table 6. Clearly, torsional relaxation leading to cis−trans photoisomerization is not a significant decay channel of the excited singlet state of any of the three DPH isomers. Earlier, we showed that the extra conjugation afforded by the two additional double bonds in DPH stabilizes planar triplet geometries much more than twisted geometries.[13,22] Consequently, instead of the twisted state being an intermediate, as in the triplet photoisomerization of stilbene, twisted states are transition states in the interconversion of planar DPH triplets. Apparently, the stabilization of the planar excited singlet states of DPH is even more pronounced, and torsional motions in the excited singlet potential energy surface leading to photoisomerization experience much higher activation barriers.[46] We assume that these barriers correspond to the transition states leading to the twisted intermediates ^{1}ptt* and ^{1}tpt*, as there is no evidence in the fluorescence spectra of ^{1}*ttt*-DPH for adiabatic formation of either ^{1}ctt* or ^{1}tct*.[33]

Fluorescence measurements show that FN quenches the singlet excited state of *ttt*-DPH irreversibly at close to the diffusion controlled rate in both MCH and AN. However, the concomitant quenching of the photoisomerization is compensated exactly in MCH and in part in AN because the quenching interactions open an intersystem crossing channel that populates ^{3}DPH*. The fractions of exciplexes, f_T, that give DPH triplets are 0.060 and 0.039 in MCH and AN, respectively.

Acknowledgment. This research was supported by NSF, most recently by Grant CHE 9985895.

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