

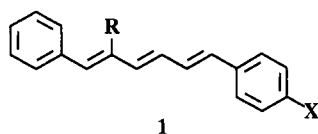
# Differential Medium Effects on the Trans → Cis Photoisomerization of *all-trans*-1,6-Diphenyl-1,3,5-hexatriene. Competing Diradicaloid vs Zwitterionic Pathways

Jack Saltiel,\* Dong-Hoon Ko, and Steven A. Fleming\*,†

Department of Chemistry  
Florida State University  
Tallahassee, Florida 32306-3006

Received December 6, 1993

Interest in the electronically excited-state properties of vitamin A and the visual pigments has given rise to numerous studies of the  $\alpha,\omega$ -diphenylpolyenes.<sup>1–4</sup> The Orlandi and Siebrand proposal<sup>5</sup> that the  $2^1A_g$  state plays a key role in stilbene photoisomerization is adopted generally as the central feature of most discussions of  $\alpha,\omega$ -diphenylpolyene trans → cis photoisomerization.<sup>3,4,6,7</sup> *all-trans*-1,6-Diphenyl-1,3,5-hexatriene (*ttt*-DPH, **1**, R = X = H) is special because it is the shortest family member that mimics the spectroscopy of the longer polyenes by having the  $2^1A_g$  state as its lowest excited singlet state.<sup>1–4</sup> Vibronic coupling of the



$2^1A_g$  and  $1^1B_u$  states bestows transition probability to the forbidden  $2^1A_g \rightarrow 1^1A_g$  radiative process.<sup>1–4</sup> Retention of  $1^1A_g$  and  $1^1B_u$  designations for the mixed states indicates the major contributor in each case. Though the bulk of the fluorescence of *ttt*-DPH corresponds to the  $2^1A_g \rightarrow 1^1A_g$  transition, the  $1^1B_u$  excited state is repopulated thermally and contributes at the onset of the fluorescence spectrum.<sup>8</sup> Since *ttt*-DPH fluorescence lifetimes are on the nanosecond time scale,<sup>9</sup> but  $1^1B_u \rightleftharpoons 2^1A_g$  equilibration is complete within 30 ps,<sup>10–12</sup> both states are viable candidates for photoisomerization. The interest in the photochemistry of *ttt*-DPH is heightened by its use as a microenvironment fluorescence probe in biochemical media<sup>5,13</sup> and as a molecule exhibiting highly nonlinear optical properties.<sup>14</sup>

We have confirmed Zechmeister's qualitative findings<sup>15</sup> by isolating and characterizing the primary photoproducts *tct*- and *ctt*-DPH.<sup>16</sup> HPLC analyses show that *cct*-DPH is a secondary photoproduct.<sup>16</sup> Changing the solvent from methycyclohexane, MCH, to acetonitrile, AN, dramatically increases the *ctt*-DPH

† Permanent address: Department of Chemistry, Brigham Young University, Provo, UT 84602.

(1) Hudson, B. S.; Kohler, B. E. *Annu. Rev. Phys. Chem.* **1974**, *25*, 437–460.

(2) Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982; Vol. 6, p 1.

(3) (a) Allen, M. T.; Whitten, D. G. *Chem. Rev.* **1989**, *89*, 1691–1702. (b) Whitten, D. G. *Acc. Chem. Res.* **1993**, *26*, 502–509.

(4) Saltiel, J.; Sun, Y.-P. In *Photochromism, Materials and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 64.

(5) Orlandi, G.; Siebrand, W. *Chem. Phys. Lett.* **1975**, *30*, 352.

(6) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415–436.

(7) Kohler, B. E. *Chem. Rev.* **1993**, *93*, 41–54.

(8) Itoh, T.; Kohler, B. E. *J. Phys. Chem.* **1987**, *91*, 1760–1764.

(9) Cehelnik, E. D.; Cundall, R. B.; Lockwood, J. R.; Palmer, T. J. *J. Phys. Chem.* **1975**, *79*, 1369–1380.

(10) Felder, T. C.; Choi, K.-J.; Topp, M. R. *Chem. Phys.* **1982**, *64*, 175–180.

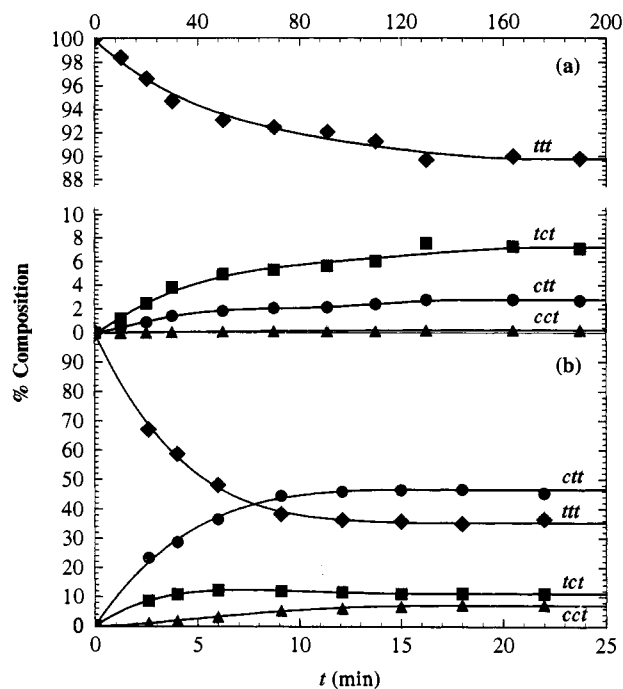
(11) Rullière, C.; Declémy, A. *Chem. Phys. Lett.* **1987**, *135*, 213–218.

(12) Hilinski, E. F.; McGowan, W. M.; Fleming, S. A.; Sears, D. F., Jr.; Saltiel, J., unpublished results.

(13) (a) Fiorini, R.; Valentino, M.; Wang, S.; Glaser, M.; Gratton, E. *Biochemistry* **1987**, *26*, 3864. (b) Parasassi, T.; De Stasio, G.; Rusch, R. M.; Gratton, E. *Biophys. J.* **1991**, *59*, 466.

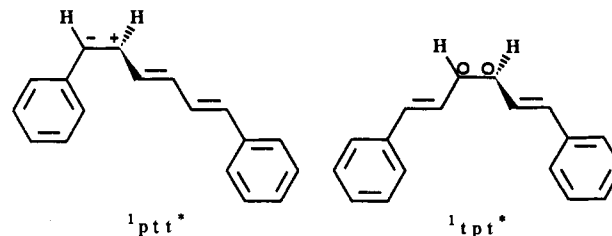
(14) Rodenberger, D. C.; Heflin, J. R.; Garito, A. F. *Nature* **1992**, *359*, 309.

(15) Lunde, K.; Zechmeister, L. *J. Am. Chem. Soc.* **1954**, *76*, 2308–2313.



**Figure 1.** Photostationary-state determinations starting from  $1.05 \times 10^{-3}$  M *ttt*-DPH. (a) Degassed in MCH,  $\lambda_{exc} = 366$  nm, 21.1 °C. (b)  $N_2$ -purged in AN,  $\lambda_{exc} = 404$  nm, 20.3 °C.

content of the photostationary state, Figure 1. The quantum yield for central bond isomerization,  $\phi_{ttt \rightarrow tct}$ , is insensitive to solvent polarity, whereas terminal bond isomerization,  $\phi_{ttt \rightarrow ctt}$ , is enhanced 7-fold on changing the solvent from MCH to AN, Table 1. The quantum yields are small and, at least for MCH, insensitive to *ttt*-DPH concentration. Much larger values were expected on the basis of the assumption that deviations of *ttt*-DPH fluorescence quantum yields,  $\phi_f$ , from unity are due entirely to torsional relaxation along trans → cis photoisomerization coordinates.<sup>3,9,23,25</sup> For instance, if, by analogy with stilbene,<sup>4,6,24</sup> nearly equal partitioning from twisted excited intermediates  $^1ptt^*$  and  $^1tpt^*$  to trans and cis ground-state double bonds is assumed, then  $(\phi_{ttt \rightarrow tct} + \phi_{ttt \rightarrow ctt}) = 0.18$  and 0.44 would be expected from  $\phi_f$  in MCH and in AN at 30 °C, respectively.<sup>9</sup> It



follows that twisted intermediates are not formed efficiently due to competing direct  $^1ttt^* \rightarrow ^1ttt$  radiationless decay and/or that decay from  $^1ptt^*$  and/or  $^1tpt^*$  overwhelmingly favors the *ttt* isomer. In view of preliminary observations<sup>27</sup> indicating lower

(16) Saltiel, J.; Sears, D. F., Jr.; Ko, D.-H.; Park, K. M. In *Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-O., Eds.; CRC Press: London, in press.

(17) Excitation at the onset of DPH absorption should reflect larger participation of excited *s-cis* conformers;<sup>18</sup>  $\lambda_{exc} = 366$  nm in AN at 29.8 °C gives 0.587, 0.291, 0.098, and 0.024 as photostationary fractions of *ttt*-, *ctt*-, *tct*-, and *cct*-DPH, respectively.

(18) Saltiel, J.; Sears, D. F., Jr.; Sun, Y.-P.; Choi, J.-O. *J. Am. Chem. Soc.* **1992**, *114*, 3607–3612.

(19) Saltiel, J.; Marinari, A.; Chang, D. W.-L.; Mitchener, J. C.; Megarity, E. D. *J. Am. Chem. Soc.* **1979**, *101*, 2982.

(20) Hammond, H. A.; Demeyer, D. E.; Williams, J. L. R. *J. Am. Chem. Soc.* **1969**, *91*, 5180.

**Table 1.** Photoisomerization Quantum Yields, 366 nm, 30 °C<sup>a</sup>

I: R, X	solvent	$\phi_{\text{tct} \rightarrow \text{ctt}}$	$\phi_{\text{tct} \rightarrow \text{tct}}$	$\phi_{\text{ctt} \rightarrow \text{tct}}$	$\phi_{\text{tct} \rightarrow \text{tct}}$
H, H <sup>b</sup>	MCH	0.0110(8)	0.048(4)	0.139(5)	0.221(7)
H, H	AN	0.075(3)	0.049(2)	0.171(5)	0.138(5)
H, CN <sup>c,d</sup>	MCH	0.0063(5)	0.010(1)		
H, CN	AN	0.24(2)	0.022(2)		
H, OCH <sub>3</sub> <sup>c,e</sup>	MCH	0.042(1)	0.025(1)		
H, OCH <sub>3</sub>	AN	0.23(1)	0.10(2)		
CH <sub>3</sub> , CN	B		0.110(1)		
CH <sub>3</sub> , CN	AN		0.108(1)		

<sup>a</sup> Degassed solutions irradiated in a merry-go-round apparatus as previously described;<sup>19</sup> conversions corrected for back-reaction; actinometry based on the benzophenone-sensitized photoisomerization of *trans*-stilbene in benzene;<sup>19-21</sup> numbers in parentheses indicate uncertainties in the last digit shown from duplicate determinations. <sup>b</sup> Independent of [DPH] in range  $(4.4-13.3) \times 10^{-4}$  M in MCH; [DPH] =  $1.10 \times 10^{-3}$  M in AN. <sup>c</sup> Prepared from cinnamaldehyde via aldol condensation with acetaldehyde followed by a Wittig reaction; details to be presented later. <sup>d</sup> [DPH] =  $1.0 \times 10^{-4}$  M. <sup>e</sup> [DPH] =  $3.6 \times 10^{-4}$  M. <sup>f</sup> From ref 22, B is benzene.

$\phi_f$  values for *ctt*- and *tct*- than for *tct*-DPH, the latter possibility is unattractive since its corollary that unusually high *ctt*  $\rightarrow$  *tct* and *tct*  $\rightarrow$  *tct* quantum yields obtain is not borne out, Table 1. Remarkably, a significant two-bond/photon isomerization pathway in the *tct*  $\rightarrow$  *ctt* direction,  $\phi_{\text{tct} \rightarrow \text{ctt}} = 0.071$ , is observed in AN. This pathway is negligible in MCH and is inoperative in both solvents in the reverse direction. Since  $\phi_{\text{tct} \rightarrow \text{ctt}}$  almost equals  $\phi_{\text{ctt} \rightarrow \text{tct}}$  in AN, it appears that <sup>1</sup>ptt\* is formed from <sup>1</sup>tct\* and <sup>1</sup>tct\* with nearly equal efficiencies in the polar solvent.

The nature of possible twisted intermediates on the potential energy surface of lowest excited singlet states of olefins is a subject of current interest and debate.<sup>3,4,6</sup> The differential medium effects in the singlet photoisomerizations of *tct*-DPH and *tct*-DPH suggest that competing torsional relaxations about terminal and central bonds lead to zwitterionic, <sup>1</sup>ptt\*, and diradicaloid, <sup>1</sup>tpt\*, twisted intermediates, respectively. Observations with unsymmetrically substituted *tct*-DPH (1, R = H, X = CN or OCH<sub>3</sub>) are consistent with the charge distribution shown above for <sup>1</sup>ptt\* of the parent, Table 1. Photoisomerization of the cyano derivative in AN shows selective and marked enhancement of 1-cis isomer formation, while no 5-cis isomer is observed. Though AN similarly enhances the formation of the 1-cis isomer of the methoxy derivative, the crucial distinction between the two substituents is that in this case the 5-cis isomer forms in both solvents and its formation is

(21) Valentine, D., Jr.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 3449.

(22) Baretz, B. H.; Singh, A. K.; Liu, R. S. H. *New J. Chem.* **1981**, *5*, 297-303.

(23) Birks, J. B.; Birch, D. J. S. *Chem. Phys. Lett.* **1975**, *31*, 608-610.

(24) Birks, J. B.; Tripathi, G. N. R.; Lumb, M. D. *Chem. Phys.* **1978**, *33*, 185-194.

(25) Birks, J. B. *Chem. Phys. Lett.* **1978**, *54*, 430-434.

(26) Saltiel, J.; Waller, A. S.; Sears, D. F., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 2453.

(27) Saltiel, J.; Zhang, Y.; Sears, D. F., Jr., unpublished results.

enhanced in AN (the photostationary-state composition for 366-nm excitation in AN includes 31.1% *tct*, 30.2% *ctt*, 14.8% *tct*, and 12.1% *tct*). Provided that twisted intermediates are indeed involved in the photoisomerization, formation of the 5-cis isomer shows that the electron-donating stabilization afforded by the methoxy substituent fails to suppress the normal pathway leading to the indicated charge distribution for <sup>1</sup>ptt\*. Interestingly, it appears that methoxy substitution also opens an alternative torsional relaxation channel leading to <sup>1</sup>ptt\* with reverse charge distribution, as reflected in enhanced 1-cis isomer formation in AN. The results on 1, R = H, X = CN, appear to be in conflict with a report of solvent-independent photoisomerization of 1, R = CH<sub>3</sub>, X = CN, exclusively at the central bond.<sup>22</sup> HPLC analyses were carried out directly on our irradiated samples, as solvent removal or replacement occasionally results in loss of terminal bond *cis* isomers due to catalyzed *cis*  $\rightarrow$  *trans* isomerization.

Low *tct*-DPH photoisomerization quantum yields are responsible in large measure for the insensitivity of  $\tau_f$  to *T* changes, especially in MCH.<sup>9</sup> Activated photoisomerization channels are minor contributors to overall <sup>1</sup>tct\* decay in nonpolar solvents, contrary to previous assumptions.<sup>9,23,25</sup> The Birks photoisomerization model, involving photoisomerization via irreversible torsional motion over a small barrier in the 2<sup>1</sup>A<sub>g</sub> state,<sup>3</sup> is not valid as that analysis<sup>24</sup> disregards both the thermal repopulation of the 1<sup>1</sup>B<sub>u</sub> state<sup>8</sup> and the presence of a significant <sup>1</sup>tct\*  $\rightarrow$  <sup>1</sup>tct radiationless decay path. A mechanism that decouples  $\tau_f$  and  $\phi_f$  dependencies on *T* involves rapid photoisomerization from the initially formed 1<sup>1</sup>B<sub>u</sub> state in competition with relaxation to the lower 2<sup>1</sup>A<sub>g</sub> state.<sup>4</sup> This mechanism is inconsistent with azulene quenching experiments that give  $k_q\tau_f = 87 \pm 5$  M<sup>-1</sup> in MCH when the azulene effect is determined on either  $\phi_{\text{tct} \rightarrow \text{ctt}}$  or  $\phi_{\text{tct} \rightarrow \text{tct}}$ . Since triplet transient absorption was not detected following direct *tct*-DPH excitation,  $\phi_{\text{is}} \leq 0.02$ , triplet states have been eliminated as significant photoisomerization intermediates.<sup>28-31</sup> This conclusion is strengthened by the absence of residual azulene-insensitive photoisomerization pathways.

Activated torsional relaxation of the 2<sup>1</sup>A<sub>g</sub> state and/or the thermally accessible 1<sup>1</sup>B<sub>u</sub> state provides viable mechanisms for *tct*-DPH photoisomerization.

**Acknowledgment.** This research was supported by NSF Grants CHE 90-14060 and CHE 93-12918. Support To S.A. F. toward his sabbatical stay from the Florida State University and Brigham Young University is gratefully acknowledged.

(28) Görner, H. *J. Photochem.* **1982**, *19*, 343-356.

(29) Chattopadhyay, S. K.; Das, P. K. *Chem. Phys. Lett.* **1982**, *87*, 145-150.

(30) Goldbeck, R. A.; Twarowski, A. J.; Russell, E. L.; Rice, J. K.; Birge, R. R.; Switkes, E.; Kliger, D. S. *Chem. Phys.* **1982**, *77*, 3319-3328.

(31) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 4504-4514.