*J. Am. Chem. Soc.* **1995,** *117,* 10761−10762 10761

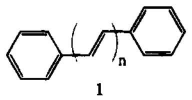
# Absorption and Fluorescence Spectra of a Rigid Analogue of *all-trans*-1,6-Diphenyl-1,3,5-hexatriene. Solvent-Controlled Order Inversion of $2^1A_g$ and $1^1B_u$ Energy Levels

Jack Saltiel* and Shujun Wang

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

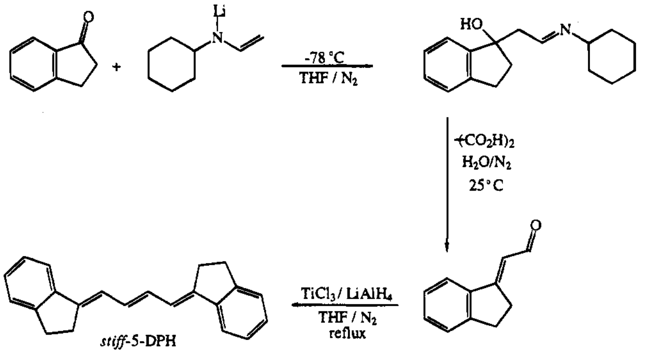
*Received July 19, 1995*

α,ω-Diphenylpolyenes, **1**, of which stilbene is the first member, have attracted a great deal of attention as models of the retinyl polyenes that are related to vitamin A and visual pigments.[1] Until recently studies of the higher members (**1**, $n$ > 2) were focused on their spectroscopic properties. We initiated our studies[2] of the photochemistry of *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) primarily because it is the shortest family member whose spectroscopy mimics that of the longer polyenes by having as the lowest excited singlet state, $S_1$, the forbidden doubly excited $2^1A_g$ state.[1a,b] Single photon absorption gives initially the $1^1B_u$ state that relaxes rapidly to a thermal equilibrium mixture with the $2^1A_g$ state. Since the energy gap, $\Delta E_{ba}$, between the two lowest excited states is small and the radiative rate constant, $k_{fb}$, of the symmetry-allowed $1^1B_u \rightarrow 1^1A_g$ transition is large, emission from the $1^1B_u$ state is readily observed at ambient temperatures as a shoulder at the onset of DPH fluorescence.[3] The bulk of DPH fluorescence is assigned to the symmetry-forbidden $2^1A_g \rightarrow 1^1A_g$ transition, which is rendered somewhat allowed (radiative rate constant $k_{fa}$) via vibronic mixing with the nearby $1^1B_u$ state.[4,5] Named after Hudson and Kohler,[1a,b] this model for higher polyene fluorescence accounts nicely for the pronounced sensitivity of $k_{fa}$ to solvent changes. An increase in medium polarizability [$\alpha = (n^2 - 1)/(n^2 + 2)$ where $n$ is the solvent's refractive index] selectively stabilizes the $1^1B_u$ state and diminishes $\Delta E_{ba}$.[1b,3d,4,6] More effective $1^1B_u/2\,^1A_g$ mixing ensues and is reflected in the enhancement of $k_{fa}$ ($k_{fa} \propto \Delta E_{ba}^{-2}$).[4,5] Relationships between these well-understood photophysical properties of DPH and its trans → cis photoisomerization remain obscure. Following usual practice[7] and by analogy with stilbene,[1e,f] Birks proposed that deviations of $\phi_f$ from unity reflect radiationless decay along photoisomerization channels.[5,8] In view of low intersystem crossing yields ($\phi_{is} \le 0.02$[9−11]) such processes presumably involve torsional motions in $S_1$ to twisted intermediates at the terminal, $^1$ptt*, and central, $^1$tpt*, double bonds.[2b,5,8] Recognizing that, within the Orlandi and Siebrand model for stilbene photoisomerization,[12] the $2^1A_g$ state experiences no barriers along isomerization coordinates, greater stabilization due to stronger $1^1B_u/2^1A_g$ mixing was postulated at the planar DPH geometry.[8] The relative energy of the $1^1B_u$ state has also been postulated to be strongly dependent on the degree of nonplanarity along the phenyl−vinyl bonds.[13] Studies of rigid analogues of stilbene[14] and of *trans,trans*-1,4-diphenyl-1,3-butadiene[15] (DPB) have yielded valuable insights concerning the role of specific torsional motions in controlling their photochemical and photophysical properties. We report here a study of the rigid analogue of DPH, *all-trans*-diindanylidene-2-butene (*stiff*-5-DPH) with frozen phenyl−vinyl torsional motions.



**1**

**Scheme 1**



*stiff*-5-DPH was prepared in 30% overall yield from 1-indanone (Aldrich) in three steps as outlined in Scheme 1: orange crystals, mp 203.0−203.7 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 2.93−2.96 (m, 4H), 3.04−3.08 (m, 4H), 6.55−6.60 (m, 2H), 6.70−6.74 (m, 2H), 7.17−7.29 (comp m, 6H), 7.50−7.54 (m, 2H).[16] Absorption and fluorescence spectra[17] of *stiff*-5-DPH in benzene (B), methylcyclohexane (MCH), and perfluoroheptane (PFH) are shown in Figure 1. The absorption spectra are unexceptional, being consistent with those of the parent DPH. Alkyl substitution and the blocking of torsional motions along phenyl−vinyl bonds are reflected in better resolved vibronic structure and in a 2100 cm$^{-1}$ lowering of the $1^1B_u \leftarrow 1^1A_g$

---

(1) For reviews, see: (a) Hudson, B. S.; Kohler, B. E. *Annu. Rev. Phys. Chem.* **1974**, *25*, 437−460. (b) Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982; Vol. 6, p 1. (c) Allen, M. T.; Whitten, D. G. *Chem. Rev.* **1989**, *89*, 1691−1702. (d) Whitten, D. G. *Acc. Chem. Res.* **1993**, *26*, 502−509. (e) Saltiel, J.; Sun, Y.-P. In *Photochromism, Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 64. (f) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415−436.

(2) (a) Saltiel, J.; Sears, D. F., Jr.; Sun, Y.-P.; Choi, J.-O. *J. Am. Chem. Soc.* **1992**, *114*, 3607−3612. (b) Saltiel, J.; Ko, D.-H.; Fleming, S. A. *J. Am. Chem. Soc.* **1994**, *116*, 4099−4100.

(3) (a) Alford, P. C.; Palmer, T. F. *Chem. Phys. Lett.* **1982**, *86*, 248−253. (b) Alford, P. C.; Palmer, T. F. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 433−447. (c) Jones, G. R.; Cundall, R. B. *Chem. Phys. Lett.* **1986**, *126*, 129−133. (d) Itoh, T.; Kohler, B. E. *J. Phys. Chem.* **1987**, *91*, 1760−1764.

(4) Andrews, J. R.; Hudson, B. S. *J. Chem. Phys.* **1978**, *68*, 4587−4594.

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

(6) Sklar, L. A.; Hudson, B. S.; Petersen, M.; Diamond, J. *Biochemistry* **1977**, *16*, 813.

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

(8) (a) Birks, J. B.; Birch, D. J. S. *Chem. Phys. Lett.* **1975**, *31*, 608−610. (b) Birks, J. B. *Chem. Phys. Lett.* **1978**, *54*, 430−434.

(9) (a) Chattopadhyay, S. K.; Das, P. K. *Chem. Phys. Lett.* **1982**, *87*, 145−150. (b) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 4504−4514.

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

(11) Görner, H. *J. Photochem.* **1982**, *19*, 343−356.

(12) Orlandi, G.; Siebrand, W. *Chem. Phys. Lett.* **1975**, *30*, 352−354.

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

(14) (a) Saltiel, J.; Zafiriou, O. C.; Megarity, E. D.; Lamola, A. A. *J. Am. Chem. Soc.* **1968**, *90*, 4759−4760. (b) Saltiel, J.; D'Agostino, J. *J. Am. Chem. Soc.* **1972**, *94*, 6445−6457. (c) Doany, F. E.; Heilweil, E. J.; Moore, R.; Hochstrasser, R. M. *J. Chem. Phys.* **1984**, *80*, 201−206. (d) Vogel, J.; Schneider, S.; Dörr, F.; Lemmen, P.; Lenoir, D. *Chem. Phys.* **1984**, *90*, 387−398. (e) Ogawa, K.; Suzuki, H.; Futakami, M. *J. Chem. Soc., Perkin Trans. 2* **1988**, 39−43.

(15) (a) Yee, W. A.; Horwitz, J. S.; Goldbeck, R. A.; Einterz, C. M.; Kliger, D. S. *J. Phys. Chem.* **1983**, *87*, 380−382. (b) Lee, M.; Bain, A. J.; McCarthy, P. J.; Haseltine, J. N. ; Smith, A. B., III; Hochstrasser, R. M. *J. Chem. Phys.* **1986**, *85*, 4341−4347. (c) Lee, M.; Haseltine, J. N.; Smith, A. B., III; Hochstrasser, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 5044−5051. (d) Wallace-Williams, S. E.; Schwartz, B. J.; Møller, S.; Goldbeck, R. A.; Yee, W. A.; El-Bayoumi, M. A.; Kliger, D. S. *J. Phys. Chem.* **1994**, *98*, 60−67.

(16) Consistent with the $^1$H NMR spectrum of the analogous *stiff*-5-DPB in ref 15c.

(17) Absorption and fluorescence spectra were measured at ambient temperature (~23 °C) as previously described.[18]

(18) Saltiel, J.; Sears, D. F., Jr.; Choi, J.-O.; Sun, Y.-P.; Eaker, D. W. *J. Phys. Chem.* **1994**, *98*, 35−46.

0002-7863/95/1517-10761$09.00/0

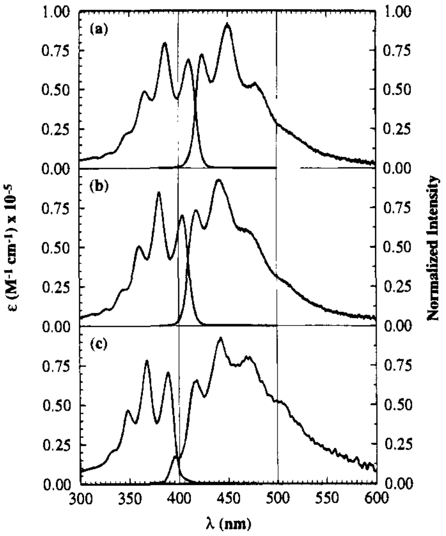


**Figure 1.** Absorption and fluorescence spectra of *stiff-5*-DPH at room temperature in B, MCH, and PFH, panels a, b, and c, respectively. Fluorescence spectra have been corrected for nonlinear instrumental response.

transition origin. Similar changes have been observed for the spectra of the analogous structural models of stilbene[14b,e] and of DPB.[15] The striking difference between DPH and the other two cases is that the lower $1^1B_u$ energy in *stiff-5*-DPH leads to a reversal of the order of the two lowest excited singlet states in the more polarizable benzene solvent. The $2^1A_g$ and $1^1B_u$ states of *stiff-5*-DPH are nearly isoenergetic in MCH. The mirror image symmetry between absorption and fluorescence spectra shows that, in contrast to DPH, the fluorescence spectra of *stiff-5*-DPH in these two solvents are dominated by the $1^1B_u \rightarrow 1^1A_g$ transition. The $2^1A_g \rightarrow 1^1A_g$ transition is seen in the fluorescence spectrum of *stiff-5*-DPH in PFH, where the low solvent polarizability sufficiently raises the energy of the $1^1B_u$ state as to restore the normal state order. The energy levels associated with the spectra in Figure 1 are shown in Figure 2.

On the basis of the Birks mechanism for DPH photoisomerization,[5,8] reversal of the $2^1A_g/1^1B_u$ state order should profoundly affect radiationless decay dynamics. *stiff-5*-DPH, having the same state order as stilbene,[1] might be expected to exhibit stilbene-like properties in hydrocarbon solvents. This would produce roughly 20-fold and 100-fold attenuations in fluorescence quantum yield and lifetime, respectively, relative to the parent DPH.[1] These expectations are not borne out experimentally. The fluorescence quantum yield of *stiff-5*-DPH in MCH at 25 °C, 0.66, is identical, within experimental uncertainty, to that of DPH.[7] The near degeneracy of $2^1A_g$ and $1^1B_u$ states of *stiff-5*-DPH in MCH is reflected in only a modest decrease in fluorescence lifetime (5 ns, based on $K_{sv}$ = 133 $M^{-1}$ for $O_2$ quenching of *stiff-5*-DPH fluorescence, vs 13 ns for DPH[7]). Photoisomerization results for the analogue are similar to those reported for the parent.[2b] The two major primary photoproducts, *tct*- and *ctt-stiff-5*-DPH, were isolated by preparative HPLC and characterized by $^1H$ NMR. Photoisomerization quantum yields ($\lambda_{exc}$ = 366 nm) are generally small and show enhancement for the terminal bond in a more polar solvent: $\phi_{ttt\rightarrow tct}$ = 0.018 and 0.0064, $\phi_{ttt\rightarrow ctt}$ = 0.011 and 0.085 at 30 °C in MCH and acetonitrile, respectively. As with DPH, it appears that the major radiationless decay channel of *ttt-stiff-5*-DPH is not along photoisomerization coordinates. Nor can phenyl–vinyl torsional motions contribute in promoting radiationless decay since they are effectively eliminated in the rigid analogue.

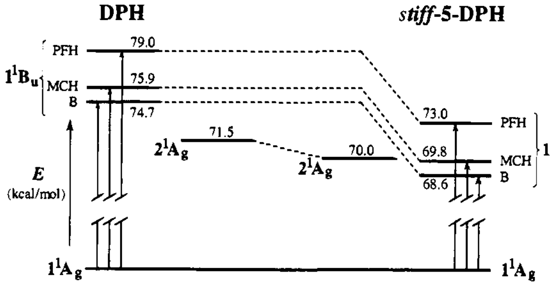


**Figure 2.** Effect of solvent on the energies of the two lowest excited singlet states of DPH and *stiff-5*-DPH.

Preliminary studies of the temperature dependence of photoisomerization quantum yields of DPH[19] and of *stiff-5*-DPH indicate activation energies for torsional motion in the range of 6–10 kcal/mol, well in excess of $\Delta E_{ba}$. We conclude that neither of these states is stabilized by torsional motion along photoisomerization coordinates and that equilibration between the two lowest excited singlet states is complete prior to photoisomerization. Since the order of the two lowest states does not significantly influence the efficiency of trans → cis photoisomerization, the energetics of a third state may be controlling. For instance, a mechanism analogous to the Hohlneicher and Dick modification[20] of the Orlandi and Siebrand model[12] for stilbene photoisomerization may apply to DPH. Of course, although the Birks mechanism[5,8] for polyene photoisomerization must be abandoned, photoisomerization over a large torsional barrier from either the $2^1A_g$ or the $1^1B_u$ state could also account for our results. Our results with DPH[2b] and with *stiff-5*-DPH differ sharply from observations on *trans, trans*- and *cis,trans*-1,3,5,7-octatetraene, for which adiabatic photoisomerization over a very small barrier in the $2^1A_g$ state has been reported.[21]

**Acknowledgment.** This research was supported by NSF Grant CHE 93-12918.

JA952382S

---

(19) Saltiel, J.; Ko, D.-H. Unpublished results.

(20) Hohlneicher, G.; Dick, B. *J. Photochem.* **1984**, *27*, 215.

(21) (a) Ackerman, J. R.; Kohler, B. E. *J. Am. Chem. Soc.* **1984**, *106*, 3681–3682. (b) Kohler, B. E. *Chem. Rev.* **1993**, *93*, 41–54.