

shift to the carbenic center. There is a 7-fold increase in lifetime from *p*-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C̄Cl to *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C̄Cl. This effect is much smaller than the magnitude predicted by theoretical calculations,<sup>2</sup> but this is to be expected. The substituent effect is obviously less when the substituent is placed on the phenyl ring, as in our case, rather than on the carbene center, as considered in the theoretical study. Nevertheless, the present work represents a first quantitative study of the substituent effect on 1,2-H shift to a carbene.

### Experimental Section

3-[*p*-(Trifluoromethyl)benzyl]-3-chlorodiazirine (1) and 3-(*p*-chlorobenzyl)-3-chlorodiazirine (2) were prepared by Graham's method<sup>15</sup> and purified by chromatography on silica gel.

**Product Studies: Photolysis of Diazirine 1 in TME.** Diazirine 1 ( $3 \times 10^{-3}$  mol) and TME ( $3 \times 10^{-2}$  mol) were dissolved in isooctane (40 mL), and the solution was photolyzed (350 nm) for 30 h at 25 °C. The unreacted TME and solvent were distilled off under reduced pressure. The residue was chromatographed on a column of silica gel and eluted with hexane containing 2% ethyl acetate. The products were (*Z*)- and (*E*)-*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH=CHCl (30%) [MS *m/e* 208 (33), 206 (100, M<sup>+</sup>), 171 (94)] and 1-chloro-1-[*p*-(trifluoromethyl)benzyl]-2,2,3,3-tetra-

methylcyclopropane (65%) [MS *m/e* 290 (2), 271 (10), 255 (100); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.10 (s, 6 H, CH<sub>3</sub>), 1.20 (s, 6 H, CH<sub>3</sub>), 3.15 (s, 2 H, CH<sub>2</sub>), 7.1-7.6 (m, 4 H, Ar H)]. Authentic samples of the styrene and cyclopropane were used to calibrate the gas chromatograph, and the absolute yields of the products were determined from the integrated areas of the components in the GC analysis. Bibenzyl was used as the GC internal standard. It is to be noted that no azine was formed under the above experimental conditions.

Photolysis of neat diazirine 1 yielded chlorostyrene (40%) and the expected azine (50%), (*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CCl=N-)<sub>2</sub> [MS *m/e* 440 (10, M<sup>+</sup>), 159 (100); UV broad absorption 250-350 nm ( $\epsilon \sim 10^4$ )]. The product analysis<sup>5</sup> for diazirine 2 and the laser flash photolysis setup<sup>4</sup> have been described previously.

**Acknowledgment.** M.T.H.L. thanks the Natural Sciences and Engineering Research Council of Canada for an International Collaborative Research Grant.

**Registry No.** 1, 139913-92-1; 1 azine derivative, 139913-96-5; 2, 91309-66-9; fluoro[*p*-(trifluoromethyl)benzyl]carbene, 139913-93-2; (*E*)-1-chloro-2-[*p*-(trifluoromethyl)phenyl]ethene, 139913-94-3; (*Z*)-1-chloro-2-[*p*-(trifluoromethyl)phenyl]ethene, 139913-95-4; pyridine, 110-86-1; pyridinium (*p*-trifluoromethyl)benzylidene, 139913-97-6; tetramethylethene, 563-79-1; 1-chloro-1-[*p*-(trifluoromethyl)benzyl]-2,2,3,3-tetramethylcyclopropane, 139913-98-7; chloro(*p*-chlorobenzyl)carbene, 88211-10-3; pyridinium *p*-chlorobenzylidene, 139913-99-8.

(15) Graham, W. H. *J. Am. Chem. Soc.* 1965, 87, 4396.

## Evidence for Ground-State *s*-cis Conformers in the Fluorescence Spectra of *all-trans*-1,6-Diphenyl-1,3,5-hexatriene

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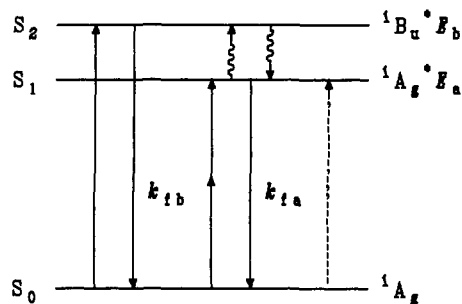
**Abstract:** The temperature and excitation wavelength dependencies of the fluorescence spectrum of *all-trans*-1,6-diphenyl-1,3,5-hexatriene were studied in methylcyclohexane. As previously reported, the increase in *T* leads to relatively enhanced emission at the onset and tail portions of the fluorescence spectrum. Enhanced emission at the tail portion of the fluorescence spectrum is also observed at constant *T* by moving to longer excitation wavelengths. The results are consistent with thermal repopulation of the <sup>1</sup>B<sub>u</sub> state leading to enhanced onset emission and with population of excited *s*-cis conformers of the triene either by increasing their ground-state concentration (higher *T*) or by selective excitation (longer  $\lambda_{exc}$ ) leading to enhanced tail emission. Application of principal-component analysis with self-modeling to matrices composed of fluorescence spectra for different  $\lambda_{exc}$  and constant *T* (30.0 or 91.0 °C) allows their resolution into two components, one of which is the combined <sup>2</sup>A<sub>g</sub>/<sup>1</sup>B<sub>u</sub> fluorescence from the *all-s-trans* conformer and the other of which is an emission spectrum that we assign to *s*-cis conformers. The fractional contribution of *s*-cis conformer fluorescence in observed spectra for  $\lambda_{exc} = 355$  nm increases from 6 to 25% as *T* is increased from -3.2 to +91.0 °C and is significantly higher at longer  $\lambda_{exc}$ , leading to an estimated enthalpy difference for conformer equilibration of  $3.4 \pm 0.4$  kcal/mol.

Several reviews of polyene spectroscopy are available.<sup>1-4</sup> Numerous experimental<sup>5-10</sup> and theoretical<sup>11-15</sup> investigations have

- (1) Hudson, B. S.; Kohler, B. E. *Annu. Rev. Phys. Chem.* 1974, 25, 437.
- (2) Hudson, B. S.; Kohler, B. E.; Schulten, K. *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982; Vol. 6, p 1.
- (3) Allen, M. T.; Whitten D. G. *Chem. Rev.* 1989, 89, 1691.
- (4) Saltiel, J.; Sun, Y.-P. *Photochromism, Molecules and Systems*; Bouas-Laurent, H., Dürr, H., Eds.; Elsevier: Amsterdam, 1990; p 64.
- (5) Bensasson, R.; Lafferty, J.; Land, E. J.; Sinclair, R. S.; Truscott, T. *G. Chem. Phys. Lett.* 1976, 41, 333.
- (6) Nikitina, A. N.; Ponomareva, N. A.; Yanovskaya, L. A.; Dombrovskii, V. A.; Kucherov, V. F. *Opt. Spectrosc. (Engl. Transl.)* 1976, 40, 144.
- (7) Anderson, R. J. M.; Holtom, G. R.; McClain, W. M. *J. Chem. Phys.* 1979, 710, 4310.
- (8) Fang, H. L.-B.; Thrash, R. J.; Leroi, G. E. *J. Chem. Phys.* 1977, 57, 3389.
- (9) Fang, H. L.-B.; Thrash, R. J.; Leroi, G. E. *Chem. Phys. Lett.* 1978, 57, 59.
- (10) Brey, L. A.; Schuster, G. B.; Drickamer, H. G. *J. Chem. Phys.* 1979, 71, 2765.
- (11) Tavan, P.; Schulten, K. *Chem. Phys. Lett.* 1978, 56, 200.

confirmed Hudson and Kohler's assignment of the fluorescence spectrum of *all-trans*-1,8-diphenyl-1,3,5,7-octatetraene to the <sup>2</sup>A<sub>g</sub> → <sup>1</sup>A<sub>g</sub> transition, and spectroscopic evidence similarly supports the <sup>2</sup>A<sub>g</sub> assignment to the lowest excited singlet state of *all-trans*-1,6-diphenyl-1,3,5-hexatriene, DPH (Figure 1). The <sup>2</sup>A<sub>g</sub> ← <sup>1</sup>A<sub>g</sub> transition is symmetry forbidden in the single-photon absorption spectrum and allowed in the two-photon absorption (fluorescence excitation) spectrum; the converse applies for the <sup>1</sup>B<sub>u</sub> ← <sup>1</sup>A<sub>g</sub> transition. Effective experimental radiative rate constants,  $k_f^{obsd} = \phi_f^{obsd} / \tau_f^{obsd}$ , for DPH and higher polyenes are much smaller than calculated theoretical radiative rate constants,  $k_f^{th}$ ,<sup>18,19</sup> in agreement with assignments of  $k_f^{obsd}$  and  $k_f^{th}$  to  $k_{fa}$  and

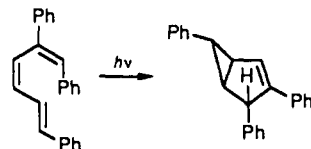
- (12) Schulten, K.; Karplus, M. *Chem. Phys. Lett.* 1972, 14, 305.
- (13) Schulten, K.; Ohmine, I.; Karplus, M. *J. Chem. Phys.* 1976, 64, 4422.
- (14) Ikeyama, T.; Azumi, T. *J. Chem. Phys.* 1982, 76, 5672.
- (15) Henneker, W. H.; Siebrand, W.; Zgierski, M. *Z. J. Chem. Phys.* 1983, 79, 2495.
- (16) Hudson, B. S.; Kohler, B. E. *J. Chem. Phys.* 1973, 59, 4984.
- (17) Andrews, J. R.; Hudson, B. S. *J. Chem. Phys.* 1978, 68, 4587.



**Figure 1.** The Hudson and Kohler model for DPH and higher polyene fluorescence.<sup>1,2,16,17</sup>

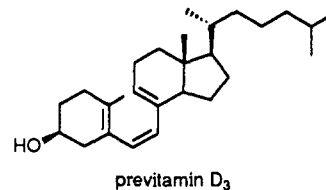
$k_{tb}$ , respectively. The magnitude of  $k_{ta}$  depends on the degree of mixing between the  $1^1B_u$  and  $2^1A_g$  states and is predicted to be proportional to  $\Delta E_{ba}^{-2}$ , where  $\Delta E_{ba}$  is the  $1^1B_u$ - $2^1A_g$  energy gap.<sup>17,20</sup> Since  $E_b$  decreases with increasing medium polarizability and  $E_a$  is not affected,  $\Delta E_{ba}$  becomes smaller as the refractive index,  $n$ , of the medium is increased, being a linear function of  $\alpha = (n^2 - 1)/(n^2 + 2)$ .<sup>21,17</sup>  $\Delta E_{ba}$  in DPH is sufficiently small to allow thermal repopulation of the  $1^1B_u$  state as reflected in delayed  $1^1B_u$  fluorescence that is readily observable as a shoulder at the onset of DPH fluorescence spectra.<sup>21-24</sup>

Fluorescence spectra, lifetimes, quantum yields, and the small intersystem crossing yields of DPH have all been reported to be independent of  $\lambda_{exc}$ .<sup>25-28</sup> Accordingly, only the all-*s-trans* conformer has been assumed to contribute significantly to DPH fluorescence and absorption spectra. In contrast, excitation of the parent 1,3,5-hexatrienes and of alkyl-substituted conjugated trienes gives product distributions that are sensitive to  $\lambda_{exc}$ ,<sup>29-36</sup> and it was for these systems and specifically for trienes in the vitamin D field that Havinga's NEER (nonequilibration of excited rotamers) principle was proposed.<sup>37</sup> Furthermore, the major photoproducts from the irradiation of two phenyl-substituted DPH isomers are triphenylbicyclo[3.1.0]hex-2-enes that appear to require selective excitation of unique *s-cis* conformers,<sup>38,39</sup> e.g.

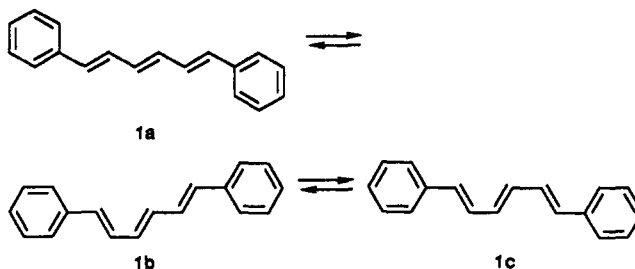


- (18) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814.  
 (19) Birks, J. B.; Dyson, D. J. *Proc. R. Soc. London, A* **1963**, *275*, 135.  
 (20) Birks, J. B.; Tripathi, G. N. R.; Lumb, M. D. *Chem. Phys.* **1978**, *33*, 185.  
 (21) Alford, P. C.; Palmer, T. F. *Chem. Phys. Lett.* **1982**, *86*, 248.  
 (22) Alford, P. C.; Palmer, T. F. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 433.  
 (23) Jones, G. R.; Cundall, R. B. *Chem. Phys. Lett.* **1986**, *126*, 129.  
 (24) Itoh, T.; Kohler, B. E. *J. Phys. Chem.* **1987**, *91*, 1760.  
 (25) Görner, H. *J. Photochem.* **1982**, *19*, 343.  
 (26) Cehelnik, E. D.; Cundall, R. B.; Lockwood, J. R.; Palmer, T. F. *Chem. Phys. Lett.* **1974**, *27*, 586.  
 (27) Cehelnik, E. D.; Cundall, R. B.; Lockwood, J. R.; Palmer, T. F. *J. Phys. Chem.* **1975**, *79*, 1369.  
 (28) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 4507.  
 (29) Dauben, W. G.; McInnis, E. L.; Michno, D. M. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 91.  
 (30) Vroegop, P. J.; Lugtenburg, J.; Havinga, E. *Tetrahedron* **1973**, *29*, 1393.  
 (31) Meinwald, J.; Mazzochi, P. H. *J. Am. Chem. Soc.* **1966**, *88*, 2850.  
 (32) Srinivasan, R. *J. Am. Chem. Soc.* **1961**, *83*, 2807.  
 (33) Srinivasan, R. *J. Chem. Phys.* **1963**, *38*, 1039.  
 (34) Gielen, J. W. J.; Jacobs, H. J. C.; Havinga, E. *Tetrahedron Lett.* **1976**, 3751.  
 (35) Brouwer, A. M.; Conelisse, J.; Jacobs, H. J. C. *Tetrahedron* **1987**, *43*, 435.  
 (36) Brouwer, A. M. Ph.D. Thesis, University of Leiden, Leiden, The Netherlands, 1987.  
 (37) Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1979**, *11*, 305.  
 (38) Padwa, A.; Clough, S. *J. Am. Chem. Soc.* **1970**, *92*, 5803.  
 (39) Padwa, A.; Brodsky, L.; Clough, S. *J. Am. Chem. Soc.* **1972**, *94*, 6767.

However, the importance of ground-state conformer control in accounting for  $\lambda_{exc}$  effects on the photochemistry of previtamin D<sub>3</sub><sup>40,41</sup> has been challenged.



Itoh and Kohler have reported that both the red and blue edges of DPH fluorescence spectra undergo comparable increases in relative intensity with increasing  $T$  in methylcyclohexane, MCH.<sup>42</sup> While the change in the blue side was attributed to fluorescence from the increased  $1^1B_u$  population, the change at the red edge was tentatively assigned to "hot-band" emission from the  $2^1A_g$  state.<sup>42</sup> Since enhanced red-edge emission could reveal fluorescence from increased populations of *s-cis* conformers, we were encouraged to reinvestigate the  $T$  and  $\lambda_{exc}$  effects of DPH fluorescence. As will be shown below, we have succeeded in resolving DPH fluorescence spectra into two components, one consisting of  $T$ -dependent  $1^1B_u/2^1A_g$  combined fluorescence and the second consisting of a red-shifted, relatively  $T$ -independent, spectrum whose contribution increases with  $T$  and with  $\lambda_{exc}$ . Our results suggest strongly that the red-shifted component corresponds to excitation of one or both of the hitherto elusive *s-cis* conformers of DPH, **1b** and/or **1c**.



## Experimental Section

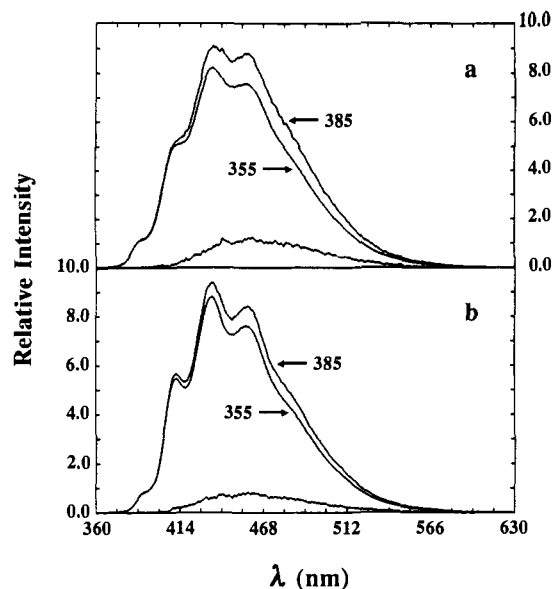
**Materials.** *all-trans*-1,6-Diphenyl-1,3,5-hexatriene from Aldrich, 98% purity, was chromatographed on silica gel with ethyl acetate/petroleum ether (1:99 v/v) as eluent and then twice recrystallized from *n*-hexane (Aldrich, Spectrophotometric grade). Methylcyclohexane from Baker or Aldrich, reagent grade, was washed with concentrated sulfuric acid, stirred over several portions of fuming sulfuric acid, washed with water followed by aqueous sodium bicarbonate, dried over sodium sulfate, and distilled. In all instances, the UV transparency of purified MCH matched or exceeded that of Baker Photorex MCH. Petroleum ether from Baker, reagent grade, was distilled prior to use.

**Fluorescence Measurements.** All luminescence measurements were made with a modified Hitachi/Perkin-Elmer MPF-2A spectrophotometer equipped with a 150-W Xe arc source and a Hamamatsu R106UH photomultiplier tube. Absorption spectra were measured with a Perkin-Elmer Lambda-5 spectrophotometer. Both spectrophotometers were interfaced to a PC's limited Dell 80286/87 (12 MHz) microcomputer.

Fluorescence spectra of DPH ( $\sim 1.3 \times 10^{-6}$  M) in MCH in the  $-3.2$  to  $+91.0$  °C range were measured for Ar-outgassed MCH solutions,  $\lambda_{exc} = 355$  nm (triplicate spectra at each of 14  $T$ 's) and 385 (duplicate spectra at each of 7  $T$ 's). Sets of spectra were also obtained as a function of  $\lambda_{exc}$  at 30.0 and 91.0 °C. MCH solutions of DPH ( $(2.1-4.4) \times 10^{-6}$  M) were outgassed with Ar, using a prebubler, for 30 min prior to collection of data. A few spectra were also recorded using air-saturated solutions. Fluorescence intensities were recorded in the 340.0-630.0-nm range in 0.25-nm increments. Spectra were recorded by systematically increasing the excitation wavelength, and the procedure was repeated five times. No change could be discerned between the first and the fifth set of spectra,

(40) Jacobs, H. J. C.; Gielen, J. W. H.; Havinga, E. *Tetrahedron Lett.* **1980**, *21*, 4013.

(41) (a) Dauben, W. G.; Phillips, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 5781. (b) Dauben, W. G.; Share, P. E.; Ollmann, R. R., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2548. (c) Dauben, W. G.; Disanayaka, B.; Funhoff, D. J. H.; Kohler, B. E.; Schilke, D. E.; Zhou, B. *J. Am. Chem. Soc.* **1991**, *113*, 8367.  
 (42) Itoh, T.; Kohler, B. E. *J. Phys. Chem.* **1987**, *91*, 1760.



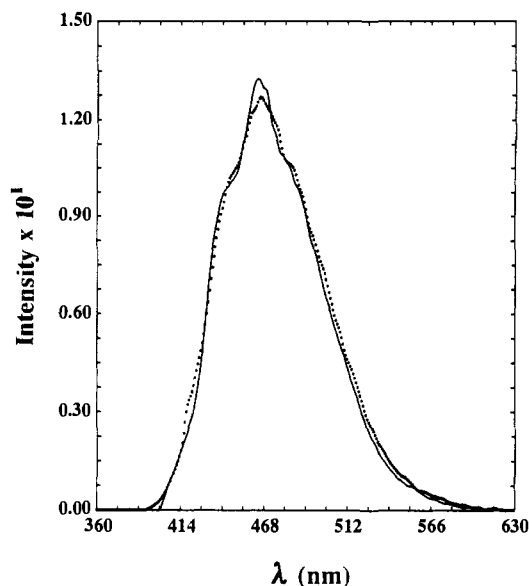
**Figure 2.** Fluorescence spectra (uncorrected for nonlinear instrumental response) of DPH in Ar-outgassed MCH for  $\lambda_{\text{exc}} = 355$  and  $385$  nm at (a)  $91.0$  °C and (b)  $30.0$  °C. Difference spectra were obtained after normalizing the spectra at the onset region ( $360.0$ – $375.0$  nm).

and each set of quintuplicate spectra was averaged to give a single baseline-corrected spectrum at each  $\lambda_{\text{exc}}$ . Temperatures were maintained to within  $\pm 0.1$  °C using a Haake-FN constant- $T$  circulator or a Neslab-RTE 4DD circulation bath. Solution temperatures were measured with an Omega Engineering Model 199 RTD digital thermometer. Use of a more dilute DPH solution ( $1.15 \times 10^{-6}$  M) in MCH gave identical results at  $30.0$  °C, but these somewhat noisier spectra were not included in the analysis.

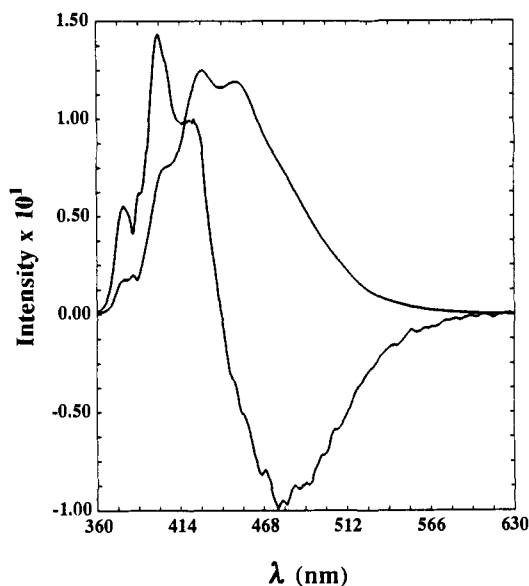
**Data Analyses.** Principal-component analyses with self-modeling (PCA-SM) calculations were performed on a PC's limited Dell 80486/87 (25 MHz) using FORTRAN language as previously described.<sup>43–45</sup>

## Results

**The Red-Shifted-Component Fluorescence Spectrum.** In disagreement with previous claims that DPH fluorescence spectra are independent of  $\lambda_{\text{exc}}$ ,<sup>27</sup> we find that excitation at the onset of DPH absorption,  $\lambda_{\text{exc}} \geq 380$  nm, leads to significant broadening of the tail portion of fluorescence spectra. Furthermore, the  $\lambda_{\text{exc}}$  effect shows a regular increase with increasing  $T$  (Figure 2). Resolution of the red-shifted-component, *sc*-DPH, fluorescence spectrum was facilitated by assuming that the onset portion ( $360.0$ – $375.0$  nm) of the experimental fluorescence spectra is strictly  $\lambda_{\text{exc}}$  independent. Sets of *sc*-DPH spectra were generated for  $91.0$  and  $30.0$  °C as differences of pairs of averaged spectra whose areas were matched in the  $360.0$ – $375.0$ -nm region. The  $360.0$ – $375.0$ -nm region in the difference spectra was within experimental uncertainty indistinguishable from a zero baseline, confirming the assumption that fluorescence in this region is independent of  $\lambda_{\text{exc}}$ . Pairs of  $\lambda_{\text{exc}}$  in nanometers selected for generation of difference spectra were as follows.  $91.0$  °C:  $380, 310$ ;  $385, 310$ ;  $390, 310$ ;  $380, 350$ ;  $385, 350$ ;  $390, 350$ .  $30.0$  °C:  $380, 350$ ;  $385, 350$ ;  $390, 350$ . Noise reduction was achieved by performing principal-component analysis ( $340.0$ – $630.0$  nm,  $1.0$ -nm increments) separately on the sets of six ( $91.0$  °C) and three ( $30.0$  °C) difference spectra and assigning the major eigenvector from each calculation to *sc*-DPH (neglected eigenvectors consisted of imperfectly subtracted Rayleigh scattering lines and baseline noise). Prior to use in subsequent calculations, the *sc*-DPH spectra were first smoothed five times; the  $375.0$ – $390.0$ -nm region was then smoothed 100 times to eliminate distortions due to residual Rayleigh scattering lines, and the  $340$ – $375$ -nm region was set to



**Figure 3.** Principal eigenvectors from PCA-SM analysis of difference spectra at  $30.0$  °C (—) and  $91.0$  °C (⋯).



**Figure 4.** The two major eigenvectors from PCA-SM analysis of the  $91.0$  °C spectral matrix. The structure in the  $380$ – $395$ -nm region is due to imperfectly subtracted excitation Rayleigh lines.

exactly zero intensity (Figure 3).

**The  $A_g/B_u$  Mixture Spectra.** The PCA-SM procedure was applied separately to spectral matrices consisting of baseline-corrected spectra at  $91.0$  and  $30.0$  °C and the corresponding *sc*-DPH spectrum described above. Both matrices behaved cleanly as two-component systems. The eigenvectors and normalization line for the  $91.0$  °C matrix are shown in Figures 4 and 5, respectively. Determination of the combination coefficients for the  $A_g/B_u$  mixture spectra was achieved by moving on the normalization lines until calculated differences between the fractional contributions of *sc*-DPH at  $\lambda_{\text{exc}} = 385.0$  and  $350.0$  nm,  $\Delta x_2$ , matched the fractional area of the *sc*-DPH difference spectrum described in the preceding section,  $0.125$  and  $0.0755$  for  $91.0$  and  $30.0$  °C, respectively. This procedure served as a refinement of the Lawton and Sylvestre approach for defining pure-component combination coefficients.<sup>43–46</sup> Resulting pure-component  $2^1A_g/1^1B_u$  spectra are shown in Figure 6. Fractional contributions of *sc*-DPH as a function of  $\lambda_{\text{exc}}$  at each of the two  $T$ 's are shown in Table I. Also shown in Table I are fractional contributions

(43) Sun, Y.-P.; Sears, D. F., Jr.; Saltiel, J. *J. Am. Chem. Soc.* **1987**, *99*, 2515.

(44) Sun, Y.-P.; Sears, D. F., Jr.; Saltiel, J.; Mallory, F. B.; Mallory, C. W.; Buser, C. A. *J. Am. Chem. Soc.* **1988**, *110*, 6974.

(45) Sun, Y.-P.; Sears, D. F., Jr.; Saltiel, J. *J. Am. Chem. Soc.* **1989**, *111*, 706.

(46) Lawton, W. H.; Sylvestre, E. A. *Technometrics* **1971**, *13*, 617.

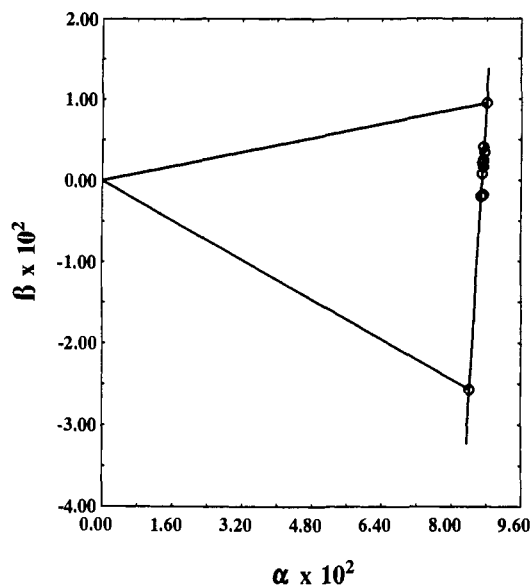


Figure 5. Normalization line of the vectors in Figure 4. The points are combination coefficients for the spectra in the input matrix.

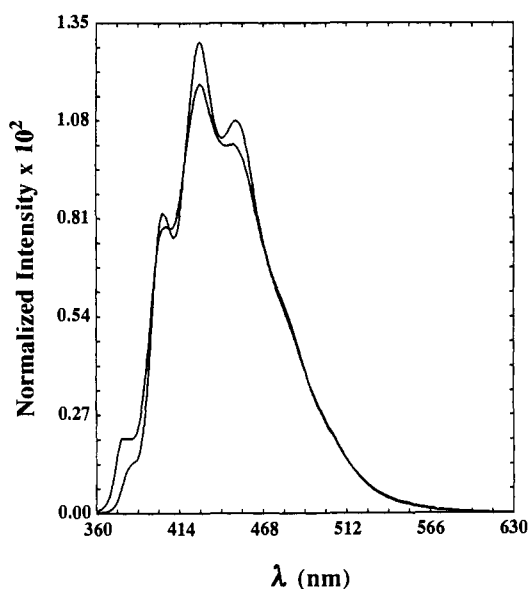


Figure 6. Pure-component  $2^1A_g/1^1B_u$  mixture spectra at 30.0 and 91.0 °C (broader spectrum).

based on spectra that are corrected for nonlinearity in spectrophotometer response (Figure 7).<sup>47</sup>

***T* Dependence of *sc*-DPH Fractional Contributions.** The *T* dependence of  $x_2$  (Table I) was extended to other *T*'s using two earlier sets of slightly noisier DPH fluorescence spectra measured with  $\lambda_{exc} = 355$  and 385 nm as a function of *T*. The spectra at each *T* together with the *sc*-DPH spectra from Figure 3 (the 30 °C *sc*-DPH spectrum was used for  $T \leq 30.0$  °C, and a weighted average, based on *T*, of the 30.0 and 91.0 °C *sc*-DPH spectra was used for  $T > 30.0$  °C) were treated separately by PCA-SM analysis. The uncertainty in identifying the combination coefficients of each pure  $A_g/B_u$  mixture spectrum was reduced by using the fractional contributions at 355.0 nm from Table I as guides at 30.0 and 91.0 °C. Self-consistency between different *T*'s was achieved by carrying out additional PCA-SM calculations for matrices containing spectra from two or three *T*'s. The resulting fractional contributions are shown in Table II. They are in excellent agreement with an approximate set of fractional contributions, obtained independently, based on the dependence of

Table I. Fractional Contributions of *sc*-DPH as a Function of  $\lambda_{exc}$  in MCH<sup>a</sup>

<i>T</i> = 30.0 °C			<i>T</i> = 91.0 °C		
$\lambda_{exc}$ , nm	$x_2$	$x_{2c}^b$	$\lambda_{exc}$ , nm	$x_2$	$x_{2c}^b$
350.0	0.0928	0.1084	265.0	0.1841	0.2115
355.0	0.0948	0.1107	310.0	0.1651	0.1903
360.0	0.1006	0.1173	350.0	0.2097	0.2398
365.0	0.1041	0.1214	355.0	0.2139	0.2444
370.0	0.0996	0.1162	360.0	0.2215	0.2527
375.0	0.0993	0.1159	365.0	0.2199	0.2150
380.0	0.1103	0.1284	370.0	0.2152	0.2458
385.0	0.1677	0.1932	375.0	0.2189	0.2499
390.0	0.2091	0.2391	380.0	0.2575	0.2919
395.0	0.1833	0.2106	385.0	0.3352	0.3747
350.0	0.1048 <sup>c</sup>	0.1222	350.0	0.2150 <sup>c</sup>	0.2456
355.0	0.1151 <sup>c</sup>	0.1339	350.0	0.2332 <sup>c,d</sup>	0.2655
380.0	0.1309 <sup>c</sup>	0.1529	355.0	0.2180 <sup>c</sup>	0.2489
385.0	0.1685 <sup>c</sup>	0.1941	355.0	0.2148 <sup>c,d</sup>	0.2454
390.0	0.2322 <sup>c</sup>	0.2644	385.0	0.3307 <sup>c</sup>	0.3700
			385.0	0.3357 <sup>c,d</sup>	0.3753

<sup>a</sup>Unless otherwise indicated [DPH] =  $4.37 \times 10^{-6}$  and  $4.09 \times 10^{-6}$  M in Ar-outgassed solutions at 30.0 and 91.0 °C, respectively. <sup>b</sup>Corrected for nonlinearity of instrumental response. <sup>c</sup>[DPH] =  $21.4 \times 10^{-6}$  M. <sup>d</sup>Air-saturated solution.

Table II. Fractional Contributions of *sc*-DPH as a Function of *T* at  $\lambda_{exc} = 355$  nm in MCH

<i>T</i> , °C	$\lambda_{exc} = 355$ nm		$\lambda_{exc} = 385$ nm	
	$x_2$	$x_{2c}^a$	$x_2$	$x_{2c}^a$
-3.2	0.0488	0.0575	0.0754	0.0884
-1.3	0.0558	0.0656		
3.9	0.0690	0.0815	0.0963	0.1124
10.7	0.0806	0.0944		
18.2	0.0979	0.1143	0.1557	0.1798
25.4	0.1092	0.1272		
29.8	0.1150 <sup>b</sup>	0.1338	0.1836	0.2109
37.9	0.1248	0.1449		
48.0	0.1434	0.1660		
56.8	0.1629	0.1879	0.2532	0.2872
65.9	0.1788	0.2056		
74.6	0.1967	0.2254	0.3076	0.3456
82.9	0.2045	0.2340		
91.0	0.2140 <sup>b</sup>	0.2445	0.3254	0.3644

<sup>a</sup>Corrected for nonlinearity in instrumental response. <sup>b</sup>Base values from Table I; see text.

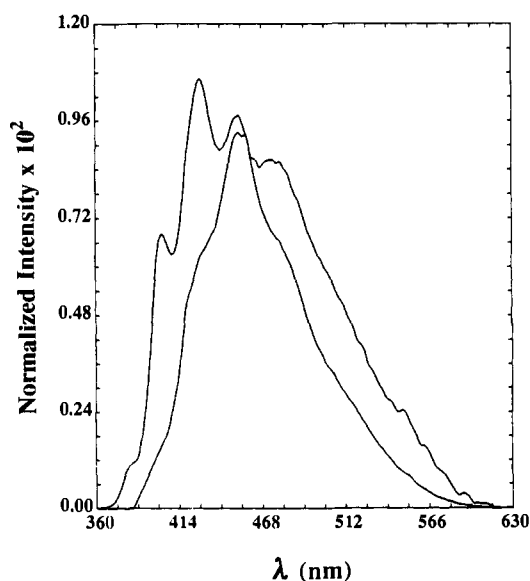


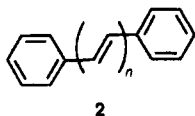
Figure 7. Pure-component *st*-DPH ( $2^1A_g/1^1B_u$  mixture) and *sc*-DPH spectra at 30.0 °C corrected for nonlinearity of instrumental response.

$\Delta x_2$  on *T* (see above). Pure  $2^1A_g/1^1B_u$  spectra generated by subtraction of the fraction of *sc*-DPH at each *T* are nearly coincident at the tail portion of the spectra.

(47) Parker, C. A. *Photoluminescence of Solutions*; Elsevier: Amsterdam, 1968; pp 252–258.

## Discussion

Interest in  $\alpha,\omega$ -diphenylpolyenes, **2**, has been motivated in large part by the goal of understanding the photophysical and photochemical properties of molecules whose electronic systems better



approximate those of the retinylpolyenes that are related to vitamin A and visual pigments.<sup>1-4</sup> Especially important have been spectroscopic studies<sup>5-10</sup> demonstrating that with increasing number of conjugated olefinic double bonds a reversal in the order of the lowest two excited singlet states occurs. Thus, in *trans*-stilbene (**2**,  $n = 1$ ) the  $1^1B_u$  state lies somewhat lower in energy than the  $2^1A_g$  state and is responsible for fluorescence, whereas in *all-trans*-DPH (**2**,  $n = 3$ ) the  $2^1A_g$  state lies lower than the  $1^1B_u$  state. In the latter case, fluorescence originates predominantly from the  $2^1A_g$  state but the  $1^1B_u$  state also contributes because of thermal repopulation from the  $2^1A_g$  state. Much work has focused on determining the factors controlling the energy gap between these two states and its effect on the degree of mixing between them. These two states are also proposed to be crucial in the mechanisms of *trans*  $\rightarrow$  *cis* olefinic-double-bond photoisomerization.<sup>3,4,48-50</sup> In comparison with that of the stilbenes, the photochemistry of the longer diphenylpolyenes remains largely unexplored.<sup>4</sup> We selected DPH for the extension of our work in this area because it affords opportunities (a) to determine the behavior of the  $2^1A_g$  state in photoisomerization much more directly than does stilbene and (b) to investigate quantitatively the effect of rotamerism in the photochemistry and photophysics of a conjugated triene.

This paper addresses the question of rotamerism in DPH. Our success in deconvoluting three rotamer fluorescence spectra of *trans*-1,2-bis(2-naphthyl)ethene by applying PCA-SM analysis<sup>44</sup> prompted us to reexamine the  $\lambda_{exc}$  dependence of DPH fluorescence. Until now, all spectroscopic observations on DPH have been attributed to the all-*s-trans* conformer, **1a**. We suspect that earlier studies claiming that the fluorescence spectrum of DPH is independent of  $\lambda_{exc}$  confined themselves to  $\lambda_{exc} < 380$  nm.<sup>27</sup> As described above, use of  $\lambda_{exc} \geq 380$  nm has allowed deconvolution of DPH into two pure-component fluorescence spectra. A rough analogy with 1,3-butadiene suggests that introduction of each *s-cis*-1,3-butadiene moiety in DPH should raise the energy by about 3 kcal/mol.<sup>51-54</sup> Molecular mechanics calculations on the parent *trans*-1,3,5-hexatriene agree with this view, predicting increases in total energy of 2.7 and 5.6 kcal/mol as one (tTt  $\rightarrow$  cTt) and two (tTt  $\rightarrow$  cTc) *s-cis* bonds are introduced into the triene, respectively.<sup>55</sup> Accordingly, it is likely that the major component represents  $2^1A_g/1^1B_u$  mixed fluorescence from *all-s-trans*-DPH (**1a**), while the minor component corresponds to emission from *s-cis*-DPH (**1b**). At present, we cannot exclude the possibility that the new emission corresponds to **1c** or to a mixture of **1b** and **1c**. In this connection it is important to recall that fluorescence spectra of DNE at different  $\lambda_{exc}$  also behaved as a two-component system and further resolution of one of these components into two required use of a quencher that differentially quenched their fluorescence.<sup>44</sup> Structures were assigned to the three DNE fluorescence spectra by comparison with spectra of conformationally restricted derivatives.<sup>44</sup> Similar experiments for DPH are planned. Though the structure of the red-shifted spectrum is less well defined than the structure of the spectrum of the all-*s-trans* conformer, the two spectra bear a strong resemblance (Figure 7). Thus the possibility exists that the spectrum

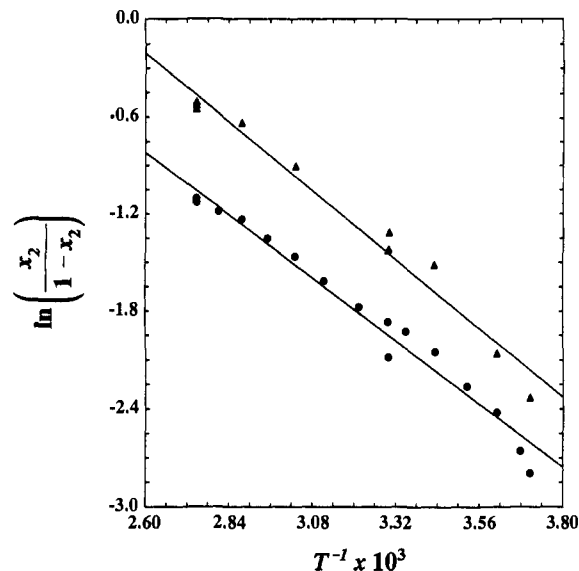


Figure 8. van't Hoff plots of the fractional contributions for 355-nm (●) and 385-nm (▲) excitation (Tables I and II).

assigned to *s-cis* conformers is also a mixture of  $2^1A_g/1^1B_u$  fluorescence.

Aside from providing strong spectroscopic evidence for the validity of the NEER principle in a conjugated triene, the present study is essential for a quantitative interpretation of  $2^1A_g/1^1B_u$  decay characteristics in the *all-s-trans*-DPH conformer (**1a**). The resolution of  $2^1A_g/1^1B_u$  fluorescence spectra into pure-component  $2^1A_g$  and  $1^1B_u$  spectra is best accomplished after subtraction of the *s-cis*-DPH fluorescence from experimental spectra.<sup>56</sup> Similarly, the gradual decrease in  $\phi_f$  of DPH in MCH ( $\phi_f = 0.74$  at  $T = -24$  °C and  $\phi_f = 0.44$  at  $T = 101$  °C) and other hydrocarbon solvents with increasing  $T$ <sup>27</sup> cannot safely be associated with the behavior of the  $2^1A_g$  state of **1a** nor even with the pair of equilibrated  $1^1B_u/2^1A_g$  states of **1a**. A significant part of the decrease in  $\phi_f$  could be due to the  $T$  dependence of the *s-cis*-DPH fluorescence quantum yield ( $\phi_2$ ). Needless to say, this important question must be addressed if the fluorescence quantum yields of DPH are to be quantitatively related to its photochemistry. A careful reexamination of the  $\lambda_{exc}$  dependence of  $\phi_f$  in MCH is, therefore, in progress in our laboratory.

As can be seen in Table II, the fractional contributions of *s-cis*-DPH fluorescence increase strongly with increasing  $T$ . Clearly, the increase in the concentration of *s-cis* conformer(s) responsible for this emission far outpaces any decrease in  $\phi_2$  as  $T$  is increased. Assuming, for the moment, that only two conformers contribute to the fluorescence of DPH, a preliminary interpretation of the  $T$  dependence on  $x_2$  can be based on relationships 1 and 2, where  $\epsilon_1$  and  $\epsilon_2$  are the decadic absorptivities

$$\frac{[s\text{-DPH}]}{[st\text{-DPH}]} = \frac{\epsilon_1 \phi_1 x_2}{\epsilon_2 \phi_2 x_1} \quad (1)$$

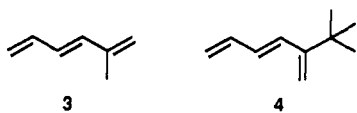
$$\ln \frac{x_2}{1-x_2} = \ln \frac{\epsilon_2 \phi_2}{\epsilon_1 \phi_1} + \frac{\Delta S_{21}}{R} - \frac{\Delta H_{21}}{RT} \quad (2)$$

of the *s-trans*- and *s-cis*-DPH conformers, respectively, and  $\Delta S_{21}$  and  $\Delta H_{21}$  are the entropy and enthalpy differences between the two conformers. In the absence of information concerning the  $T$  dependence of  $\phi_1$  and  $\phi_2$  separately, we assume them to vary with  $T$  in the same way; i.e.,  $(\phi_2/\phi_1) = \text{constant}$ . The plots of  $\ln [x_2/(1-x_2)]$  vs  $T^{-1}$  (Figure 8) give  $\Delta H_{21} = 3.21 \pm 0.13$  and  $3.51 \pm 0.19$  kcal/mol for the data at 355.0 and 385.0 nm, respectively. Discarding data points below 3.9 °C gives  $\Delta H_{21} = 2.95 \pm 0.11$  and  $3.29 \pm 0.17$  kcal/mol, in the same order. It is well established that *s-cis* conformers of conjugated polyenes have

(48) Orlandi, G.; Siebrand, W. *Chem. Phys. Lett.* **1975**, *30*, 352.  
 (49) Birks, J. B. *Chem. Phys. Lett.* **1978**, *54*, 430.  
 (50) Hohlneicher, G.; Dick, B. *J. Photochem.* **1984**, *27*, 215.  
 (51) Sun, Y.-P.; Sears, D. F., Jr.; Saltiel, J. *J. Am. Chem. Soc.* **1988**, *110*, 6277 and references cited.  
 (52) Mui, P. W.; Grunwald, E. *J. Am. Chem. Soc.* **1982**, *104*, 6562.  
 (53) Wiberg, K. B.; Rosenberg, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1509.  
 (54) Arnold, B. R.; Balaji, V.; Michl, J. *J. Am. Chem. Soc.* **1990**, *112*, 1808.  
 (55) Tai, J. C.; Allinger, N. L. *J. Am. Chem. Soc.* **1976**, *98*, 7928.

(56) Sun, Y.-P.; Sears, D. F., Jr.; Choi, J.-O.; Saltiel, J. Manuscript in preparation.

lower molar absorptivities than corresponding *s-trans* conformers. Of relevance here are *trans*-2-methyl- (3) and *trans*-2-*tert*-butyl-1,3,5-hexatriene (4), which exist predominantly in confor-



mations analogous to **1a** and **1b**, respectively.<sup>35,36</sup> Since the UV absorption spectrum of **3** has  $\epsilon = 4.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , while the spectrum of **4** has  $\epsilon = 1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , both at  $\lambda_{\text{max}} = 258 \text{ nm}$ ,<sup>36</sup> it seems reasonable to expect that in the 350–380-nm region, for which  $x_2$  is nearly constant,  $1.0 \leq (\epsilon_1/\epsilon_2) \leq 3.0$ . The fluorescence quantum yield of DPH in MCH at  $T$  close to 30 °C is reported to be 0.65.<sup>27</sup> It follows that  $(\phi_1/\phi_2) \geq 0.65$ , since the fluorescence quantum yield of *s-cis*-DPH,  $\phi_2$ , cannot exceed unity. Assuming an upper limit for  $(\phi_1/\phi_2) \leq 2.0$  gives  $0.65 \leq (\epsilon_1\phi_1/\epsilon_2\phi_2) \leq 6.0$  which, on the basis of the intercept of the 355-nm plot in Figure 8, gives  $5.9 \text{ eu} \leq \Delta S_{21} \leq 10.3 \text{ eu}$  (excluding the two lowest  $T$  data points gives  $5.1 \text{ eu} \leq \Delta S_{21} \leq 9.5$ ). Since **1b** can form from **1a** in two ways, a correction of  $R \ln 2$  would have to be applied to  $\Delta S_{21}$  if the structure of *s-cis*-DPH can be assigned exclusively to **1b**.

### Conclusion

DPH fluorescence has been resolved into two components, the major of which consists of a mixture of  $2^1A_g/1^1B_u$  fluorescence spectra from the all-*s-trans* conformer **1a** and the minor of which

is a red-shifted spectrum assigned to *s-cis* conformers whose structure is most probably **1b**. Consistent with this assignment, the contribution of the red-shifted emission is enhanced by excitation at the red edge of the DPH absorption spectrum and by increasing  $T$ . Analysis of the  $T$  dependence of fractional contribution ratios of the two components in the fluorescence spectra indicates that the ground-state enthalpy difference between the conformers giving rise to these emissions is  $3.4 \pm 0.4 \text{ kcal/mol}$ , consistent with the **1a**  $\rightleftharpoons$  **1b** hypothesis.<sup>55</sup> The  $\lambda_{\text{exc}}$  dependence of the relative contribution of the two resolved spectra shows that the rotamers responsible for DPH fluorescence do not interconvert freely in the two lowest excited singlet states, thus providing strong evidence for the adherence to Havinga's NEER principle by a conjugated triene. In this regard, it would be highly surprising if selective excitation of the less favorable previtamin D<sub>3</sub> all-*s-cis* conformer shown above did not contribute, at least in part, to the pronounced  $\lambda_{\text{exc}}$  effects on photoproduct quantum yields that have been observed for previtamin D<sub>3</sub>.<sup>40,41</sup> Additional  $\lambda_{\text{exc}}$  effects due to selective formation of  $1^1B_u$  and  $2^1A_g$  states, whose different photochemical behavior competes with their equilibration, are an attractive possibility, as has been suggested.<sup>41c</sup> We have proposed a similar mechanism for the *trans*  $\rightarrow$  *cis* photoisomerization of all-*trans*-DPH,<sup>4,56</sup> and we are in the process of testing it experimentally.

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## Control of Porphyrin Orientation in Thermotropic Liquid Crystals by Molecular Design. A Time-Resolved EPR Study

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**Abstract:** Molecular compatibility of a guest porphyrin in a thermotropic nematic liquid crystalline host phase was shown to control the orientation of the porphyrin chromophore. In this manner, the normal alignment of a porphyrin plane parallel to the director in a nematic phase was inverted to a perpendicular orientation by attachment of mesogenic type appendages orthogonal to a porphyrin ring on one side of the ring plane. This molecular design also leads to a head-to-tail ordering of the porphyrin even in isotropic phases. The conclusions reached are based on detection and analysis of time-resolved EPR spectra of photoexcited triplet states.

### Introduction

The study of photochemical processes in organized systems such as lyotropic and thermotropic liquid crystals are of importance owing to their relevance to such diverse fields as reaction mechanism and transport in chemical and biological systems<sup>1</sup> and the electronic and mechanical properties of synthetic liquid crystals (LC).<sup>2</sup> The former are important in the understanding of the orientation dependence of chemical reactions and of biological membrane behavior, whereas the latter are intensively being exploited for applied purposes. In recent years the chemistry of porphyrins and metalloporphyrins has attracted a great deal of attention because of the important part the porphyrin moiety plays in chemical and biological related processes, such as dioxygen and electron transfer, catalytic oxygenation,<sup>3</sup> as well as in artificial

and model photosynthesis.<sup>4</sup> Since many of these processes generally occur in organized media and not in isotropic matrices, we found it important to be able to control the orientation of a

(1) (a) Chapman, D. In *Liquid Crystals and Plastic Crystals*; Gray, G. W., Winsor, P. A., Eds.; Ellis Horwood Ltd.: Chichester, 1974. (b) Friberg, S. E. *Lyotropic Liquid Crystals Adv. Chem. Ser.* 1976, No. 152. (c) Weiss, R. G. *Tetrahedron* 1988, 44, 3413.

(2) (a) Gray, G. W. *Thermotropic Liquid Crystals*; Wiley: New York, 1987. (b) Blinov, L. M. *Electro-optical and Magneto-optical Properties of Liquid Crystals*; Wiley: New York, 1983. (c) Meier, G.; Sackmann, E.; Grabmair, J. G. *Applications of Liquid Crystals*; Springer: Berlin, 1975.

(3) (a) Collman, J. P.; Halbert, T. R.; Suslick, K. S. In *Metal Ion Activation of Dioxygen*; Spiro, T. G., Ed.; Wiley: New York, 1980; p 1. (b) Papa, S.; Lorusso, M. In NATO ASI Ser. A 76, *Biomembranes*; Butron, R. M., Guerra, F. C., Eds.; Plenum: New York, 1986; p 257. (c) Ortiz de Montellano, P. *Cytochrome P-450*; Plenum: New York, 1986.

(4) (a) Willner, I.; Willner, B. In *Topics in Current Chemistry*; Mattay, J., Ed.; Springer-Verlag: Berlin, 1991; Vol. 159, p 153. (b) Gust, D.; Moore, T. A. *Ibid.*, p 103.

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<sup>†</sup> Casali Institute of Applied Chemistry.