suggest that the association rate is dominated by ligand to metal donor interactions. Further investigations on the origin of barriers to ligand addition and a comparison of the relative reactivity of $Cr(CO)_5$ and $Cr(CO)_4$ will be reported in a subsequent paper.[10]

Acknowledgment is made to the National Science Foundation (CHE-8500713) for support for this research.

Resolution and Structural Assignment of the Three Components in *trans*-1,2-Di(2-naphthyl)ethene Fluorescence[1]

J. Saltiel,*[†] D. F. Sears, Jr.,[†] F. B. Mallory,[‡] C. W. Mallory,[§] and C. A. Buser[‡]

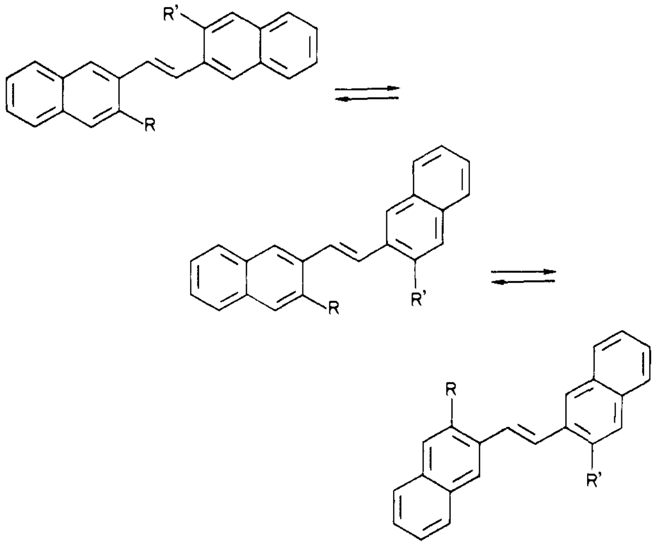
Chemistry Departments, The Florida State University
Tallahassee, Florida 32306
Bryn Mawr College, Bryn Mawr, Pennsylvania 19010
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Received November 7, 1985

The dependence of the 1,2-diarylethene fluorescence spectral shape on excitation wavelength, λ_{exc}, and other variables,[2] and fluorescence decay results requiring multiexponential fits[3] are attributed to the presence of equilibrating mixtures of aryl-rotational conformers. Electronic excitation reverses double- and single-bond character "freezing" ground-state conformers into noninterconverting populations of excited-state species exhibiting different intrinsic properties.[2,3] Pure component fluorescence spectra were obtained for *trans*-1-phenyl-2-(2-naphthyl)ethene, *t*-2-NPE, by application of principal component analysis (PCOMP), a curve resolution technique,[4] and structures were assigned by comparison with spectra from analogues.[5] We now report the application of the PCOMP/analogue approach to the resolution of three-component spectra using *trans*-1,2-di(2-naphthyl)ethene, DNE, and its conformationally restricted (steric hindrance) 3-methyl, MDNE, and 3,3′-dimethyl, DMDNE, derivatives.

Corrected fluorescence spectra of DNE, MDNE, and DMDNE ($\sim 10^{-5}$ M in methylcyclohexane, 30.0 °C) were measured as previously described,[5] except that the fluorimeter was interfaced to a CompuPro System 816 series microcomputer and digitized intensities were recorded at 1.0-nm increments. Changes in DNE fluorescence spectral shape with λ_{exc} and with $[O_2]$ agreed with earlier reports (Figure 1).[2,3] Subtle changes were observed for MDNE, but the fluorescence spectrum of DMDNE was insensitive to changes in λ_{exc} and $[O_2]$.

PCOMP analyses of emission spectra have been described.[5-7] Spectroexcitational emission input matrices (up to 150 × 150) were employed, each row of which represented a digitized, normalized fluorescence spectrum obtained at one of eight λ_{exc} in the presence or absence of O_2. Matrix columns differed by 1.0-nm increments spanning the fluorescence spectra. Recognition of significant eigenvectors was based on the magnitude of the eigenvalues. Both DNE and MDNE, treated separately, gave two-component solutions which accounted for >99% of the total variance of all measured spectra. In each case a vibronic structure was well resolved in the shorter wavelength component spectrum and much less so in the longer wavelength component spectrum; moreover, the fluorescence spectrum of DMDNE showed a better developed vibronic structure than the second MDNE component. In pursuing a three-component solution for DNE, it was assumed that (1) the longer wavelength DNE component spectrum is a combination of DNE_2 and DNE_3 fluorescence and (2) the subtle changes in the ratio of $MDNE_1/MDNE_2$ fluorescence in experimental spectra lead to poor estimates of the coefficients for the $MDNE_2$ fluorescence spectrum. The assumptions were tested by including the appropriately shifted DNE_2/DNE_3 composite solution spectrum and the DMDNE spectrum in the MDNE spectroexcitational matrix (see below). A two-component solution resulted with *eigenvectors nearly identical with those obtained for MDNE alone.* Thus, using MDNE and DMDNE fluorescence spectra to define the coefficients for resolved spectra for $MDNE_1$ and $MDNE_2$ allows separation of the broad DNE component spectrum into DNE_2 and DNE_3 contributions.[8] Finally, PCOMP was applied to a matrix of experimental spectra of DNE, MDNE (2-nm blue-shifted), and DMDNE (9-nm blue-shifted). The three pure component fluorescence spectra and the composite DNE_2/DNE_3 solution obtained when the DNE spectra are treated separately are shown in Figure 1. The three-component PCOMP solution gives a set of coefficients $(\alpha_i,\beta_i,\gamma_i)$ which define linear combinations of the eigenvectors V_α, V_β, V_γ that represent best fit approximations of the experimental spectra, i.e., the spectrum corresponding to the *i*th row of the matrix is $S_i = \alpha_i V + \beta_i V + \gamma_i V$.[9] For a well-behaved solution, all points of a plot of the coefficients in Cartesian coordinates fall within a triangle whose edges represent coefficients for two-component mixtures and whose corners represent coefficients for the pure component spectra. Orthogonal and edge views of the triangle are shown in Figure 2. DNE points are clustered about a line representing a 55:45 DNE_2/DNE_3 ratio, hence the two-component solution when DNE spectra are treated alone and the essential role of the methyl derivative spectra in locating two corners of the triangle. Significantly, MDNE points are distributed about a 37:63 $MDNE_1/MDNE_2$ composition suggesting that the shift from the DNE_2/DNE_3 ratio reflects mainly the statistical factor of 2 (there



	DNE_1	DNE_2	$MDNE_1$	DNE_3	$MDNE_2$	DMDNE
R	H	H	H	H	H	CH_3
R′	H	H	CH_3	H	CH_3	CH_3
K_{sv}, M^{-1}	218 ± 33	90 ± 13	52 ± 16	90 ± 13	65 ± 2	52 ± 2

[†] The Florida State University.

[‡] Bryn Mawr College.

[§] University of Pennsylvania.

(1) Presented in part at the 33rd Southwest/37th Southeast Regional American Chemical Society Meeting, October 1985, Memphis, TN; Abstr. No. 307.

(2) For reviews, see: (a) Scheck, Y. B.; Kovalenko, N. P.; Alfimov, M. V. *J. Lumin.* **1977**, *15*, 157. (b) Fischer, E. *J. Photochem.* **1981**, *17*, 231. (c) Mazzucato, U. *Pure Appl. Chem.* **1982**, *54*, 1705.

(3) For key references, see: (a) Haas, E.; Fischer, G.; Fischer, E. *J. Phys. Chem.* **1978**, *82*, 1638. (b) Birks, J. B.; Bartocci, G.; Aloisi, G. G.; Dellonte, S.; Barigelleti, F. *Chem. Phys.* **1980**, *51*, 113.

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

(5) Saltiel, J.; Eaker, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 7624.

(6) Warner, I. M.; Christian, G. D.; Davidson, E. R.; Callis, J. B. *Anal. Chem.* **1977**, *49*, 564.

(7) Aartsma, T. J.; Gouterman, M.; Jochum, C.; Kwiram, A. L.; Pepich, B. V.; Williams, L. D. *J. Am. Chem. Soc.* **1982**, *104*, 6278.

(8) 3-Methyl substitution on the naphthyl group of 2-NPE causes broadening of vibrational bands;[5] it is likely, therefore, that in an exact solution DNE_2 and DNE_3 spectra would have better resolved vibrational structure than the spectra of the methyl derivatives.

(9) See supplementary material.

0002-7863/86/1508-1688$01.50/0

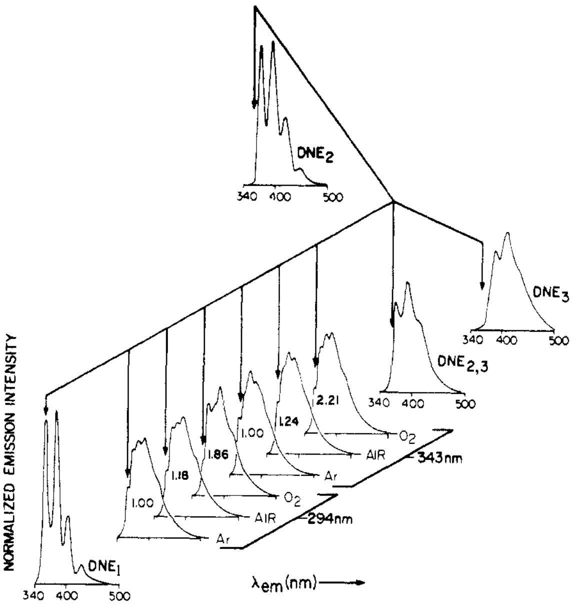


Figure 1. Typical DNE fluorescence spectra in the presence of argon, air, and O_2 at two λ_{exc}. Numbers are relative normalization factors. PCOMP component spectra are given at either end: two components for DNE alone, DNE_1 and $DNE_{2,3}$; three components for DNE, MDNE, and DMDNE together DNE_1, $DNE_2(MDNE_1)$, and $DNE_3(DMDNE)$. Arrows indicate position of λ = 360 nm for each spectrum.

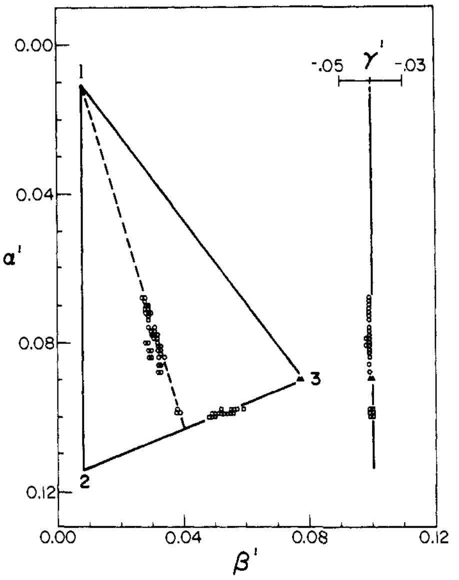


Figure 2. Orthogonal and edge views of triangle from plot of coefficients for a three-component solution, DNE (○), MDNE (□), and DMDNE (△); most points represent several independent spectra (148 total).

are two equivalent DNE_2 structures).

Stern–Volmer constants, K_{sv}, for O_2 quenching, obtained from the dependence of normalization factors and fractional contributions on $[O_2]$,[5] are given below the structures. Since, in contrast to NPE,[5] these K_{sv}'s are independent of λ_{exc}, it appears that in DNE each conformer exhibits one characteristic fluorescence lifetime.[3a,10,11] Assuming k_q = 3.0 × 10^{10} M^{-1} s^{-1} for O_2 quenching,[12] fluorescence lifetimes are 7.3 ± 1.1, 3.0 ± 0.5, ad 3.0 ± 0.5 ns for DNE_1, DNE_2, and DNE_3 and 1.7 ± 0.5, 2.2 ± 0.1, and 1.7 ± 0.1 ns for $MDNE_1$, $MDNE_2$, and DMDNE, respectively. Biexponential fits of DNE fluorescence decay curves have given 7.3 ± 0.1 and 2.2 ± 0.1 ns in methylcyclohexane at room temperature[3a] and 8.6 ± 0.7 and 1.92 ± 0.04 ns in cyclohexane at 20 °C.[10] Excitation of DNE at 373 nm, which should favor absorption by DNE_3, gives monoexponential decay with τ = 1.7 ns.[3a] It is likely, therefore, that the lifetime of DNE_3 is somewhat shorter than that of DNE_2, as was inferred from differential quenching of DNE_2/DNE_3 composite fluorescence by CCl_4.[10a] The similarity of DNE_2 and DNE_3 lifetimes is reflected in the early gated time-resolved fluorescence spectrum of DNE which shows mainly strong contributions from DNE_2 and DNE_3.[10b] Assignment of DNE_3 to the most red-shifted fluorescence spectrum conforms with observations in rigid media using nonequilibrium conformer mixtures of *t*-DNE obtained from *c*-DNE isomerization.[13] Assignments of DNE_1 and DNE_2 to the other spectra agree with those based on the quasiline fluorescence spectrum of DNE obtained at 4 K in a polycrystalline *n*-hexane matrix.[14,15]

Acknowledgment. We thank P. Tunnel for technical assistance in interfacing the fluorimeter to the microcomputer. This work was supported by NSF Grant CHE 84-00706.

Supplementary Material Available: Details of the PCOMP analyses, description of the composition of spectroexcitational matrices, and tables of eigenvectors and coefficients (20 pages). Ordering information is given on any current masthead page.

---

(10) (a) Ghiggino, K. P. *J. Photochem.* **1980**, *12*, 173. (b) Matthews, A. C.; Sakurovs, R.; Ghiggino, K. P. *Ibid* **1982**, *19*, 235.

(11) Fischer, E. *J. Photochem.* **1985**, *28*, 139.

(12) Patterson, L. K.; Porter, G.; Topp, M. R. *Chem. Phys. Lett.* **1970**, *7*, 612. Gijzeman, O. L. J.; Kaufman, K.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 708.

(13) Castel, N.; Fischer, E. *J. Mol. Struct.* **1985**, *127*, 159.

(14) Muszkat, K. A.; Wismontski-Knittel, T. *Chem. Phys. Lett.* **1981**, *83*, 87.

(15) Syntheses of DNE, MDNE, and DMDNE and application of PCOMP to fluorescence excitation spectra will be reported in the full paper.

Tetramethylallene and 2,4-Dimethyl-1,3-pentadiene as Hydrogen Atom Acceptors in Reactions with $HMn(CO)_5$ and $HCo(CO)_4$

John F. Garst,* T. Michael Bockman, and Rajnish Batlaw

Department of Chemistry, School of Chemical Sciences
The University of Georgia, Athens, Georgia 30602

Received August 19, 1985
Revised Manuscript Received January 27, 1986

Conjugated hydrocarbons such as anthracene,[1] 1,1-diphenylethylene,[2] styrene,[3] and phenylacetylene[4] react with $HMn(CO)_5$ or $HCo(CO)_4$ through initial molecule-assisted homolysis (MAH) steps,[5] hydrogen atom transfers, giving radical-pair intermediates (eq 1). For analogous reactions of 1,3-

$$\mathrm{C{=}C{-}C{=}C + HM \rightarrow [C{=}C{-}C{-}C{-}H\ {\cdot}M] \rightarrow products; \quad M = Mn(CO)_5\ or\ Co(CO)_4} \quad (1)$$

dienes, the natures of the initial steps are uncertain,[6,7] while for

---

(1) (a) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186. (b) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335. (c) Sweany, R.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487.

(2) (a) Orchin, M. In "Catalytic Transition Metal Hydrides"; Slocum, E. W., Moser, W. R., Eds.; *Ann. N.Y. Acad. Sci.* **1983**, *415*, 129. (b) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *182*, 299. (c) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1981**, *222*, C5. (d) Nalesnik, T. E.; Freudenberger, J. H.; Orchin, M. *J. Mol. Catal.* **1982**, *16*, 43.

(3) Bockman, T. M.; Garst, J. F.; King, R. B.; Marko, L.; Ungvary, F. *J. Organomet. Chem.* **1985**, *279*, 165.

(4) Bockman, T. M.; Garst, J. F. *Abstr. Pap.—Am. Chem. Soc.* **1985**, *189th*, INOR 68.

(5) (a) Pryor, W. A. In "Organic Free Radicals"; Pryor, W. A., Ed.; American Chemical Society: Washington, DC, 1978; ACS Symp. Ser. No. 69, Chapter 3, pp 33–62. (b) Harmony, J. A. K. In "Methods in Free-Radical Chemistry"; Huyser, E. S., Ed.; Dekker: New York, 1974; Vol. 5, Chapter 2, pp 101–176.

(6) Ungvary, F.; Marko, L. *Organometallics* **1984**, *3*, 1466.

0002-7863/86/1508-1689$01.50/0 © 1986 American Chemical Society