Polycyclic Aromatic Hydrocarbon Solute Probes. Part IX: Evaluation of Additional Pentaphene, Pentacene, and Pyranthrene Compounds as Possible Solvent Polarity Probes

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Fluorescence emission spectra are reported for benzo[*rst*]dinaphtho[2,1-8,7defg;2',1',8',7'ijkl]pentaphene, dibenzo[*a,rs*]naphtho[8,1,2cde]pentaphene, dibenzo[*fg,ij*]pentaphene (also called dibenzo[*b,n*]perylene), dibenzo[*de,kl*]naphtho[1,2,3,4rst]pentaphene, dibenzo[*h,rs*]pentaphene, pyranthrene, tetrabenzo[*de,hi,op,st*]pentacene, and dinaphtho[2,1,8,7defg;2',1',8',7'opqr]pentacene dissolved in various organic solvents. Results of these measurements are used to screen PAHs for potential solvent polarity behavior. Of the eight PAHs examined, only dibenzo[*h,rs*]pentaphene exhibited probe behavior as evidenced by selective, systematic emission intensity enhancement of band I with increasing solvent polarity.

Index Headings: Fluorescence; Spectroscopic techniques.

INTRODUCTION

Fluorescence spectroscopy is an extremely versatile, sensitive experimental technique used in identification/quantification of numerous environmentally important polycyclic aromatic hydrocarbons (PAHs), polycyclic aromatic nitrogen heterocycles (PANHs), and polycyclic aromatic sulfur heterocycles (PASHs). Earlier papers¹⁻⁸ have been primarily concerned with measuring the photophysical behavior of dissolved PAH solutes in order to identify probe molecules for future applications. The emission spectrum of the PAH monomer consists of several major vibronic bands labeled I, II, etc., in progressive order, starting with the 0-0 vibronic band. Previous measurements revealed that pyrene, benzo[*ghi*]perylene, ovalene, coronene, benzo[*a*]coronene, naphtho[8,1,2abc]coronene, naphtho[2,3a]coronene, dibenzo[*a,j*]coronene, benzo[*e*]pyrene, dinaphtho[8,1,2abc;2',1',8'klm]coronene, dibenzo[*def,p*]chrysene, benzo[*rst*]pentaphene, and phenanthro[5,4,3,2efghi]perylene exhibit selective emission intensity enhancement of vibronic band I relative to band III (or band II or IV) in polar solvents. The ratio of emission intensities serves as a quantitative measure of solvent polarity and structure. Interestingly, not all PAH, PASH and PANH molecules behave in a similar fashion. Various emission intensity ratios of perylene, dibenzo[*bc,ef*]coronene, benzo[*a*]pyrene, benzo[*pqr*]naphtho[8,1,2bcd]perylene, 1-azapyrene, 2-azapyrene, 4-azapyrene, and several other PAHs remained essentially constant, irrespective of solvent polarity. Our measurements have further revealed that PASH molecules behave differently than their PAH counterparts, perhaps

because of either the reduced "double bond conjugation" or the $\pi^* \rightarrow n$ transitions arising from the divalent sulfur atoms. Emission spectra of thianthrene, 1,6-dithiapyrene, 1,7-dithiaperylene, and 3,10-dithiaperylene contained relatively few bands of low emission intensity. Significant band broadening and very poor spectral resolution were noted in many of the more polar solvents examined.

PAH identification and quantification in unknown mixtures requires accurate fluorescence emission intensity measurements and availability of a large spectral data file for comparing the unknown's spectrum against PAH standards. Kalman filtering and Gaussian or other curve-fitting techniques may be needed to uncouple overlapping spectra if more than one fluorescent species is present.⁹⁻¹³ To prevent misidentification, the data file should include both polar and nonpolar solvents since electronic interactions between a solvent dipole and an excited PAH solute can lead to spectral distortions, wavelength shifts, and/or intensity ratio variations. Solvent-induced fluorescent spectral changes can be rationalized qualitatively in a relatively straightforward manner. Excitation promotes the PAH solute from a ground state of low dipole moment to one of the vibrational levels of the first electronic excited state, S_1^* , with an accompanying electron distribution in the surrounding solvent molecules. Insufficient time exists, however, for solvational-sphere molecules to physically reorient with the new PAH dipole moment. Relaxation from the vibrationally excited S_1^* level to the excited S_1^0 level occurs whenever solvent molecules rotationally reorient to a more stable dipole configuration during the excited state's lifetime. Emission of the fluorescent photon returns both the PAH molecule to the ground S_0 state and solvational molecules to their initial electronic configuration. Subsequent rotation of solvent molecules back to the ground-state dipole orientation restores the system to its original state. Transition probabilities and energy separations between the different energy levels vary with each solute-solvent pair, and give rise to observed intensity ratio changes and emission wavelength shifts.^{13,14}

To better understand the photophysical properties of PAHs dissolved in fluid solutions at the molecular level, we initiated a series of studies designed to identify PAH solutes exhibiting solvent polarity probe behavior as evidenced by selective emission intensity enhancement of the I vibronic band. Thus far, the enhancement phenom-

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FIG. 1. Molecular structures of PAH compounds: (AK) benzo[*rst*]dinaphtho[2,1,8,7defg;2',1',8',7'ijkl]pentaphene; (AL) dibenzo[*de,kl*]naphtho[1,2,3,4rst]pentaphene; (AM) dibenzo[*h,rst*]pentaphene; (AN) dibenzo[*a,rst*]naphtho[8,1,2cde]pentaphene; (AO) dibenzo[*fg,ij*]pentaphene; (AP) tetrabenzo[*de,hi,op,st*]pentacene; (AQ) dinaphtho[2,1,8,7defg;2',1',8',7'opqr]pentacene; and (AR) pyranthrene.

ena has not been explained well enough to enable *a priori* prediction of which PAH molecules will exhibit probe character. We have put forth several preliminary ideas based upon the number of Kekulé resonance structures,⁵ the point groups and symmetry elements,⁴ the dissimilarities between a given molecule's excitation and emission spectra,⁴ and the relative length of the center aromatic row in the case of the coronene derivatives.^{4,5} To expand our spectral data file, we report the fluorescence emission behavior of benzo[*rst*]dinaphtho[2,1,8,7defg;2',1',8',7'ijkl]pentaphene, dibenzo[*a,rst*]naphtho[8,1,2cde]pentaphene, dibenzo[*fg,ij*]pentaphene (also called dibenzo[*b,n*]perylene), dibenzo[*de,kl*]naphtho[1,2,3,4rst]pentaphene, dibenzo[*h,rst*]pentaphene, pyranthrene, tetrabenzo[*de,hi,op,st*]pentacene, and dinaphtho[2,1,8,7defg;2',1',8',7'opqr]pentacene dissolved in nonelectrolyte organic solvents of varying polarity. Molecular structures of the eight PAHs are depicted in Fig. 1. Results of these measurements are used to classify the PAHs as

FIG. 2. Fluorescence emission spectra of benzo[*h,rst*]pentaphene dissolved in [A (—)] *n*-hexadecane; [B (---)] dichloromethane; [C (— · —)] butyl acetate; and [D (····)] dimethyl sulfoxide. In butyl acetate major emission peaks occur at 416, 441, and 469 nm.

FIG. 3. Fluorescence emission spectra of dibenzo[*de,kl*]naphtho[1,2,3,4rst]pentaphene dissolved in [A (—)] *n*-hexadecane and [B (---)] dimethyl sulfoxide. *n*-Hexadecane was the only solvent studied in which a second band (shoulder) appeared. Spectra were recorded on a Perkin-Elmer MPF-66 spectrofluorometer.

either solvent polarity probes or nonprobe molecules depending upon whether the observed emission intensity ratios vary systematically with solvent polarity.

MATERIALS AND METHODS

The five pentaphenes, two pentacenes, and pyranthrene were synthesized and purified by procedures described in the chemical literature.¹⁵⁻¹⁷ Stock solutions were prepared by dissolving the various solutes in dichloromethane. Small aliquots of the stock solutions were transferred into test tubes, allowed to evaporate, and diluted with the solvent of interest. Final solute concentrations were sufficiently dilute to allow exclusion of both primary and secondary inner filtering artifacts. Solvents were of HPLC, spectroquality, or AR grade, purchased commercially from Aldrich, Fisher Scientific, or Lancaster Synthesis.

Fluorescence spectra were recorded at ambient room temperature on a Shimadzu RF-5000U spectrofluorome-

FIG. 4. Fluorescence emission spectra of benzo[*rst*]dinaphtho[2,1,8,7defg;2',1',8',7'ijkl]pentaphene dissolved in [A (—)] *n*-hexadecane; [B (---)] dichloromethane; [C (— · —)] butyl acetate; and [D (····)] dimethyl sulfoxide. In butyl acetate major emission bands occur at 438, 469, and 499 nm.

FIG. 5. Fluorescence emission spectra of dibenzo[fg,ij]pentaphene dissolved in [A (—)] *n*-hexadecane; [B (---)] dichloromethane; [C (— · —)] butyl acetate; and [D (—)] dimethyl sulfoxide. In butyl acetate major emission peaks occur at 441, 470, and 501 nm.

ter (UNT) or at 25°C on a Perkin-Elmer MPF-66 spectrofluorometer (Chevron). Solutions were excited at 315 nm (AK), 375 nm (AL), 366 nm (AM), 300 nm (AN), 300 nm (AO), 375 nm (AP), 410 nm (AQ), and 300 nm (AR) in a 1-cm² quartz cuvette with excitation and emission slit width settings of either 15 nm and 3 nm (UNT) or 2 nm and 5 nm (Chevron), respectively. All fluorescence spectra were solvent blank corrected and verified by repetitive measurements.

RESULTS AND DISCUSSION

Representative fluorescence spectra of the various solutes dissolved in *n*-hexadecane, butyl acetate, dichloromethane, and dimethyl sulfoxide are given in Figs. 2–9. The four nonelectrolyte solvents were selected so as to encompass the entire range of solvent polarity, from

FIG. 6. Fluorescence emission spectra of dinaphtho[2,1,8,7defg; 2',1',8',7'opqr]pentacene dissolved in [A (—)] *n*-hexadecane; [B (---)] dichloromethane; [C (— · —)] butyl acetate; and [D (—)] dimethyl sulfoxide. In butyl acetate major emission peaks occur at 486 and 522 nm.

FIG. 7. Fluorescence emission spectra of tetrabenzo[de,hi,op,st]pentacene dissolved in [A (—)] *n*-hexadecane and [B (---)] dimethyl sulfoxide. Spectra were recorded on a Perkin-Elmer MPF-66 spectrofluorometer.

the nonpolar *n*-hexadecane hydrocarbon to the moderately polar butyl acetate and dichloromethane solvents to the very polar dimethyl sulfoxide. The selection of this particular set of four solvents differs somewhat from our initial recommendations of using cyclohexane, methanol, carbon tetrachloride, and dimethyl sulfoxide to screen PAHs for possible probe behavior. Unfortunately, the larger solutes do not readily redissolve into cyclohexane and methanol from the test tube walls, and it was difficult to measure accurately the fluorescence emission intensities of many of the weaker bands, even at the higher detector sensitivity on the Shimadzu spectrofluorometer. To overcome this problem, we replaced cyclohexane ($Py = 0.58$)¹⁸ and methanol ($Py = 1.35$)¹⁸ with solvents of comparable pyrene scale polarity—namely, *n*-hexadecane ($Py = 0.60$)¹⁸ and butyl acetate ($Py =$

FIG. 8. Fluorescence emission spectra of dibenzo[a,rst]naphtho[8,1,2,cde]pentaphene dissolved in [A (—)] *n*-hexadecane; [B (---)] dichloromethane; [C (— · —)] butyl acetate; and [D (—)] dimethyl sulfoxide. In butyl acetate major emission peaks occur at 413, 435, 483, and 512 nm.

FIG. 9. Fluorescence emission spectra of pyranthrene dissolved in [A (---)] *n*-hexadecane; [B (—)] dichloromethane; [C (---)] butyl acetate; [D (—)] dimethyl sulfoxide; and [E (●—●)] binary 1,1,2-trichlorotrifluoroethane + perfluoro-1,3-dimethylcyclohexane solvent. In dichloromethane major emission peaks occur at 394, 416, and 441 nm, with a broad unresolved band located in the 460–520 nm spectral region.

1.35)¹⁸—in hopes of facilitating faster redissolution. Dichloromethane has now replaced carbon tetrachloride as the recommended chlorinated hydrocarbon because many PAHs are known to undergo rapid photochemical reactions in carbon tetrachloride.^{19–24} Reactions between PAH molecules and dichloromethane appear to be much slower and, on the basis of our past studies, are not expected to significantly affect the emission intensity ratios. A fifth screening solvent, a 50% by weight binary mixture of 1,1,2-trichlorotrifluoroethane plus perfluoro-1,3-dimethylcyclohexane, is being reported for the first time. This particular mixed solvent has a solvent polarity comparable to that of *n*-hexadecane and is capable of resolving overlapping bands in the pyranthrene emission spectrum into distinct peaks (see Fig. 9), which could better facilitate PAH identification in unknown mixtures.

Inspection of Figs. 2–9 reveals that the eight PAH solutes can be divided into two categories, probe or non-probe molecules, depending upon whether the ratio of emission intensities changes systematically with solvent polarity. For dibenzo[h,rst]pentaphene (DBPP), significant enhancement of the I band (circa 414–418 nm) emission intensity to the V band (circa 469–473 nm) is observed with increasing solvent polarity. Calculated I/V intensity ratios range from DBPP = 1.90 for cyclohexane to DBPP = 4.24 for dimethyl sulfoxide. The I/IV band ratio also varied with solvent polarity; however, the dynamic range was considerably smaller, from I/IV = 0.72 for cyclohexane to I/IV = 1.31 for dimethyl sulfoxide. Numerical emission intensity ratios, along with literature Py values,¹⁸ are summarized in Table I. Estimated uncertainties in the measured intensity ratio are believed to be on the order of ± 0.05 (or less) on the basis of

TABLE I. Ratios of fluorescence emission intensities for dibenzo[h,rst]pentaphene dissolved in select solvents.

Solvent	Py ^a	Dibenzo[h,rst]pentaphene ^b	
		I/IV	I/V
<i>n</i> -Hexane	0.58	0.73	1.90
Cyclohexane	0.58	0.72	1.90
Methylcyclohexane	0.58	0.73	1.91
2,2,4-Trimethylpentane	0.59	0.73	1.90
<i>n</i> -Hexadecane	0.60	0.75	1.95
C ₂ Cl ₃ F ₃ + C ₈ F ₁₆ ^c		0.80	2.10
<i>n</i> -Butyl ether	0.84	0.97	2.78
Benzene	1.05	1.10	3.37
2-Propanol	1.09	1.13	3.45
Butyl acetate	1.35	1.13	3.49
Dichloromethane	1.35	1.20	3.73
Methanol	1.35	1.18	3.62
Acetonitrile	1.79	1.23	3.77
N,N-Dimethylformamide	1.81	1.27	4.09
Dimethyl sulfoxide	1.95	1.31	4.24

^a Experimental Py values are from Dong and Winnik.¹⁸

^b The various bands are defined as follows: I band at 414–418 nm, IV band at 439–444 nm, and V band at 469–473 nm.

^c A 50% by weight binary mixture of 1,1,2-trichlorotrifluoroethane + perfluoro-1,3-dimethylcyclohexane.

replicate measurements for select solvents. Dibenzo[a,rst]naphtho[8,1,2cde]pentaphene initially appeared to show “probe-like” character in our four screening solvents. Upon closer examination of the fluorescence behavior in fifteen organic solvents, it was noted that emission intensity ratios did not vary systematically with solvent polarity. Abnormally low I (at 409–415 nm)/III (at 480–492 nm) ratios of I/III $\approx$ 0.50–0.60 in methanol, ethanol, and 2-propanol prevent dibenzo[a,rst]naphtho[8,1,2cde]pentaphene from being labeled as a PAH solvent polarity probe, in accordance with our past classification scheme.

Emission intensity ratios for dinaphtho[2,1,8,7defg; 2',1',8',7'opqr]pentacene, benzo[rst]dinaphtho[2,1,8,7defg; 2',1',8',7'ijkl]pentaphene, and dibenzo[fg,ij]pentaphene remained essentially constant, irrespective of solvent polarity. Extremely weak, one-band emission intensities were observed in the case of both tetrabenzo[de,hi,op,st]pentacene and dibenzo[de,kl]naphtho[1,2,3,4rst]pentaphene, even at the higher solute concentrations studied. Both dissolved compounds did possess additional excitation and emission bands in the 350–550 nm spectral region, which could be a result of trace PAH impurities, as the observed signal was just barely above the solvent blank and background noise. Attempts to work at higher PAH concentrations failed to significantly increase signal intensities. In addition, the stock solution of dibenzo[de,kl]naphtho[1,2,3,4rst]pentaphene was blue in color. These latter two compounds are thus labeled nonprobes, as only one major band was observed in the emission spectrum and even the calculated ratios based on the much smaller 350–550 nm emission signals were nearly constant, at least to within the experimental uncertainty. For pyranthrene (see Fig. 9), the number of resolvable peaks varied anywhere from 4 to 7 depending upon the solvent being examined, and it was impossible to assign a common set of bands to all 15 solvents.

As additional PAHs are studied, it is important to re-examine our preliminary observations regarding possible

TABLE II. Summary of the fluorescence probe character vs. molecular structure for polycyclic aromatic hydrocarbons.^a

Compound	Molecular formula	Probe	π -electrons	Point group ^b	Kekulé SC
C	C ₃₂ H ₁₆	Yes	4n	C _{2v}	48
D	C ₃₂ H ₁₆	Yes	4n	D _{2h}	57
I	C ₃₀ H ₁₆	No	4n + 2	D _{2h}	35
W	C ₃₄ H ₁₆	Yes	4n + 2	C _{2v}	70
X	C ₃₀ H ₁₆	No	4n + 2	D _{2h}	27
Y	C ₃₂ H ₁₆	NA ^c	4n	C _{2v}	36
Z	C ₃₄ H ₁₈	NA ^c	4n + 2	C _{2v}	41
AB	C ₃₄ H ₁₆	No	4n + 2	C _{2h}	66
AF	C ₃₂ H ₁₆	No	4n	C _s	49
AG	C ₂₈ H ₁₆	No	4n	C _s	23
AK	C ₃₄ H ₁₆	No	4n + 2	C _{2v}	70
AL	C ₃₄ H ₁₈	No	4n + 2	C _{2v}	36
AM	C ₂₈ H ₁₆	Yes	4n	C _{2v}	27
AN	C ₃₄ H ₁₈	No	4n + 2	C _s	49
AO	C ₂₈ H ₁₆	No	4n	C _{2v}	25
AP	C ₃₄ H ₁₈	No	4n + 2	C _{2h}	36
AQ	C ₃₂ H ₁₆	No	4n	C _{2h}	36
AR	C ₃₀ H ₁₆	NA ^c	4n + 2	C _{2h}	25

^a Continuation of Table I from Ref. 5. PAH solutes are: (C) naphtho[2,3a]coronene; (D) dibenzo[a,j]coronene; (I) tetrabenzo[de,hi,mn,qr]naphthacene; (W) dibenzo[fg,ij]phenanthro[2,1,10,9,8,7pqrstuv]pentaphene; (X) tribenzo[de,kl,rst]pentaphene; (Y) dinaphtho[2,1,8,7defg;2',1',8',7'ijkl]pentaphene; (Z) benzo[rst]anthra[9,1,2cde]pentaphene; (AB) benzo[cd]chryseno[4,5,6,7fghijk]perylene; (AF) dibenzo[cd,k]naphtho[8,1,2fghi]perylene; and (AG) benzo[a]naphtho[8,1,2cde]naphthacene.

^b Point groups are assigned on the basis of planar structures.

^c NA indicates that the molecule is unacceptable as a probe because either a common set of bands could not be assigned in all solvents studied or new spectral bands appeared in select solvents. The molecule may exhibit selective enhancement of band I.

probe character vs. molecular structure correlations. Table II lists molecular formulas, point groups, number of π -electrons, and Kekulé structure counts for compounds AK–AR. Also included in this tabulation are any previously investigated PAHs having molecular formulas of C₃₄H₁₆, C₃₄H₁₈, C₂₈H₁₆, C₃₂H₁₆, and C₃₀H₁₆. Careful examination reveals that there is no correlation between probe character and overall molecular symmetry, even if one considers just the pentaphene derivatives. For example, dibenzo[fg,ij]phenanthro[2,1,10,9,8,7pqrstuv]pentaphene, benzo[rst]dinaphtho[2,1,8,7defg;2',1',8',7'ijkl]pentaphene, dibenzo[h,rst]pentaphene, and dibenzo[fg,ij]pentaphene possess C_{2v} point group symmetry, having a major twofold rotation axis and two vertical mirror planes. Only dibenzo[fg,ij]phenanthro[2,1,10,9,8,7pqrstuv]pentaphene and dibenzo[h,rst]pentaphene exhibit probe character as evidenced by selective enhancement of band I intensity. Exhibition of probe character by dibenzo[h,rst]pentaphene (SC = 27) is in agreement with our earlier observation that if solute probes exist in any given molecular formula family then they generally (not always) possess a greater number of Kekulé resonance forms than do nonprobe family members. Dibenzo[h,rst]pentaphene has more Kekulé structures than

benzo[a]naphtho[8,1,2cde]naphthacene (SC = 23) and dibenzo[fg,ij]pentaphene (SC = 25), which are two other members of the C₂₈H₁₆ family. The rule is not without exception, as benzo[rst]dinaphtho[2,1,8,7defg;2',1',8',7'ijkl]pentaphene has a structure count of SC = 70, yet unlike dibenzo[fg,ij]phenanthro[2,1,10,9,8,7pqrstuv]pentaphene, this C₃₄H₁₆ family member fails to show probe behavior. Although one additional exception has been found in the present study, we still believe that the Kekulé structure count provides a useful criterion with which to initially screen PAHs for future studies. It is still the case that the only definitive method for determining whether a given PAH behaves as a solvent polarity probe is to actually measure its fluorescence properties in various organic solvents.

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1. R. Waris, M. A. Rembert, D. M. Sellers, W. E. Acree, Jr., K. W. Street, Jr., C. F. Poole, P. H. Shetty, and J. C. Fetzer, *Appl. Spectrosc.* **42**, 1525 (1988).
2. R. Waris, M. A. Rembert, D. M. Sellers, W. E. Acree, Jr., K. W. Street, Jr., and J. C. Fetzer, *Analyst* **114**, 195 (1989).
3. R. Waris, K. W. Street, Jr., W. E. Acree, Jr., and J. C. Fetzer, *Appl. Spectrosc.* **43**, 845 (1989).
4. W. E. Acree, Jr., S. A. Tucker, A. I. Zvaigzne, K. W. Street, Jr., J. C. Fetzer, and H.-F. Grutzmacher, *Appl. Spectrosc.* **44**, 477 (1990).
5. W. E. Acree, Jr., S. A. Tucker, L. E. Cretella, A. I. Zvaigzne, K. W. Street, Jr., J. C. Fetzer, K. Nakasuji, and I. Murata, *Appl. Spectrosc.* **44**, 951 (1990).
6. W. E. Acree, Jr., A. I. Zvaigzne, and J. C. Fetzer, *Appl. Spectrosc.* **44**, 1193 (1990).
7. S. A. Tucker, W. E. Acree, Jr., and M. J. Tanga, *Appl. Spectrosc.* **45**, 57 (1991).
8. S. A. Tucker, I.-L. Teng, W. E. Acree, Jr., and J. C. Fetzer, *Appl. Spectrosc.* **45**, 186 (1991).
9. R. E. Kalman, *J. Basic Eng.* **82**, 34 (1960).
10. S. C. Rutan, *J. Chemom.* **1**, 7 (1987).
11. S. D. Brown, *Anal. Chim. Acta* **181**, 1 (1986).
12. S. C. Rutan, D. D. Gerow, and G. E. Hartmann, *Intell. Lab. Sys.* **3**, 61 (1988).
13. T. L. Cecil and S. C. Rutan, *Anal. Chem.* **62**, 1998 (1990).
14. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (Plenum Press, New York, 1983).
15. J. C. Fetzer and W. R. Biggs, *J. Chromatogr.* **295**, 161 (1984).
16. J. C. Fetzer and W. R. Biggs, *J. Chromatogr.* **322**, 275 (1985).
17. E. Clar and M. Zander, *J. Chem. Soc.* 1861 (1958).
18. D. C. Dong and M. A. Winnik, *Can. J. Chem.* **62**, 2560 (1984).
19. N. Selvarajan, M. M. Panicker, S. Vaidyanathan, and V. Ramakrishnan, *Indian J. Chem.* **18A**, 23 (1979).
20. M. V. Encinas, M. A. Rubio, and E. Lissi, *Photochem. Photobiol.* **37**, 125 (1983).
21. M. V. Encinas, M. A. Rubio, and E. A. Lissi, *J. Photochem.* **18**, 137 (1982).
22. W. M. Wiczak and T. Tatowski, *Z. Naturforsch.* **42A**, 1290 (1987).
23. E. J. Bowen and K. K. Rohatgi, *Disc. Faraday Soc.* **14**, 146 (1953).
24. S. A. Tucker, L. E. Cretella, R. Waris, K. W. Street, Jr., W. E. Acree, Jr., and J. C. Fetzer, *Appl. Spectrosc.* **44**, 269 (1990).