Effect of Solvent Polarity and Acidity on Fluorescence Emission Fine Structures of Select Aza-Polynuclear Aromatics and Dibenzo[b,n]perylene Hetero-Atom Derivatives

SHERYL A. TUCKER, WILLIAM E. ACREE, JR.,* MARY J. TANGA, MAXIMILIAN ZANDER, JOHN C. FETZER, SUMIO TOKITA, KIMIHIRO HIRUTA, KIYOSHI KITAHARA, and HISAO NISHI

Department of Chemistry, University of North Texas, Denton, Texas 76203-5068, U.S.A. (S.A.T., W.E.A.); SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025, U.S.A. (M.J.T.); Rütgerswerke AG, Kekuléstrasse 30, D-4620 Castrop-Rauxel, Germany (M.Z.); Chevron Research and Technology Company, Richmond, California 94802-0627, U.S.A. (J.C.F.); and Department of Applied Chemistry, Saitama University, Shimo-Ohkubo, Urawa-shi 338, Japan (S.T., K.H., K.K., H.N.).

Fluorescence emission spectra are reported for 1-azabenz[a]anthracene, 2-azabenz[a]anthracene, 9-azabenz[a]anthracene, 4-azachrysene, 1,2,7,8-tetraazacoronene, dibenzo[2,3:10,11]perlyo[1,12bcd]furan, dibenzo[2,3:10,11]perlyo[1,12bcd]thiophene, and dibenzo[2,3:10,11]perlyo[1,12bcd]selenophene dissolved in various organic solvents. Results of these measurements are used to classify the solutes into probe or nonprobe molecules depending upon whether emission intensity ratios vary systematically with solvent polarity. Of the eight aromatic solutes examined, only the three azabenzanthracenes showed slight probe character.

Index Headings: Fluorescence; Spectroscopic techniques.

INTRODUCTION

This paper continues a systematic, experimental investigation of the effect that solvent polarity and acidity have on photophysical properties of large, multi-ring polycyclic aromatic compounds, in order to identify probe molecules for future applications. The emission spectrum of a polycyclic aromatic hydrocarbon (PAH) monomer consists of several major vibronic bands labeled I, II, etc., in progressive order. Previous measurements¹⁻⁶ revealed that pyrene, benzo[ghi]perylene, ovalene, coronene benzo[a]coronene, naphtho[2,3a]coronene, benzo[e]pyrene, naphtho[8,1,2abc]coronene, dinaphtho[8,1,2abc;2',1',8'klm]coronene, dibenzo[def,p]chrysene, phenanthro[5,4,3,2efghi]perylene, and benzo[rst]pentaphene 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, only 17 of 45 PAHs studied to date behave in this fashion. Various emission intensity ratios of perylene, dibenzo[bc,ef]coronene, benzo[a]pyrene, benzo[pqr]naphtho[8,1,2bcd]perylene, dibenzo[fg,ij]pentaphene, and several other PAHs remained essentially constant, irrespective of solvent polarity.

Concurrent with the aforementioned PAH studies, we have undertaken a systematic spectrofluorometric investigation of the corresponding hetero-atom compounds

in hopes of identifying still more solvent polarity and solvent acidity probe molecules. Preliminary measurements^{7,8} on four azapyrene and three phenanthroisoquinoline derivatives indicate that polycyclic aromatic nitrogen heterocycles (PANHs) can also be divided into probe and nonprobe molecules on the basis of their fluorescence properties. Phenanthro[2,3h]isoquinoline, phenanthro[3,2h]isoquinoline, and 12-azabenz[a]pyrene showed modest probe character, as evidenced by decreased I/II or I/III band emission intensity ratios with increased solvent polarity. Emission intensity ratios for 1-azapyrene, 2-azapyrene, 4-azapyrene, and phenanthro[9,10g]isoquinoline, on the other hand, remained essentially constant in all thirteen solvents investigated. Alcoholic solvents such as 2,2,2-trifluoroethanol protonate the nitrogen hetero-atom, resulting in loss of emission fine structure accompanied by a sizeable redshift in emission intensity.

Polycyclic aromatic sulfur heterocycles (PASHs) show behavior that is different from that of their PAH/PANH counterparts, perhaps because of either $\pi^* \rightarrow n$ electronic transitions or reduced “double bond conjugation” resulting from divalent sulfur atom substitution into the six-membered benzenoid ring system. 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 in many of the more polar solvents examined make these four PASHs unsuitable as solvent polarity probes.⁵ If probe behavior and Kekulé resonance structure count are somehow related, as our preliminary observations suggest,^{4,5} then one could argue on this basis that hetero-atom placement at a perimeter methylene bridge position on a cyclopentadiene ring offers one possible method for incorporating Periodic Table group 16 atoms into the PAH molecule without necessarily disrupting aromatic character. To pursue this idea further and to expand our hetero-atom compound spectral file, we report in this communication the fluorescence behavior of dibenzo[2,3:10,11]perylene[1,12bcd]furan (DBP-O), dibenzo[2,3:10,11]perylene[1,12bcd]thiophene (DBP-S), dibenzo[2,3:10,11]perylene[1,12bcd]selenophene (DBP-Se), 1-azabenz[a]anthracene (1-AzBA), 2-azabenz[a]anthracene (2-AzBA), 9-azabenz[a]anthra-

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* Author to whom correspondence should be sent.

FIG. 1. Molecular structures of polycyclic aromatic hetero-atom solutes: (A) 1-azabenz[a]anthracene; (B) 2-azabenz[a]anthracene; (C) 9-azabenz[a]anthracene; (D) 4-azachrysene; (E) 1,2,7,8-tetraazacoronene; and (F) dibenzo[2,3:10,11]perylene, dibenzo[2,3:10,11]perylene[1,12bcd]thiophene and dibenzo[2,3:10,11]perylene[1,12bcd]selenophene for Periodic Table Group 16 hetero-atoms $X = O, S,$ and $Se,$ respectively. The remaining member of the series, the tellurium-derivative with $X = Te,$ has not been synthesized to date.

cene (9-AzBA), 4-azachrysene (4-AzCh), and 1,2,7,8-tetraazacoronene (AzCo) (see Fig. 1 for molecular structures) dissolved in various nonelectrolyte organic solvents.

MATERIALS AND EXPERIMENTAL METHODS

The eight aromatic hetero-atoms were synthesized and purified by procedures described in the literature.⁹⁻¹⁶ 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 spectrofluorometer (UNT) or at 25°C on a Perkin-Elmer MPF-66 spec-

FIG. 2. Fluorescence emission spectra of dibenzo[2,3:10,11]perylene[1,12bcd]furan dissolved in [A (—•—)] *n*-hexadecane; [B (—)] dichloromethane; [C (—)] butyl acetate; and [D (—•—)] dimethyl sulfoxide. In *n*-hexadecane major emission peaks occurred at ~425 and 453 nm, with a minor peak near 483 nm.

trofluorometer (Chevron). Solutions were excited at 370 nm (DBP-O), 380 nm (DBP-S), 380 nm (DBP-Se), 300 nm (4-AzCh), 340 nm (1-AzBA), 340 nm (2-AzBA), 300 nm (9-AzBA), and 400 nm (AzCo) 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 emission spectra of the three dibenzo[b,n]perylene hetero-atom solutes dis-

FIG. 3. Fluorescence emission spectra of dibenzo[2,3:10,11]perylene[1,12bcd]thiophene dissolved in [A (—•—)] *n*-hexadecane; [B (—)] dichloromethane; [C (—)] butyl acetate; and [D (—•—)] dimethyl sulfoxide. In *n*-hexadecane emission peaks occurred at about 411, 438, and 466 nm.

FIG. 4. Fluorescence emission spectra of dibenzo[2,3:10,11]perylene-1,12-bis(selenophene) dissolved in [A (—•—)] *n*-hexadecane; [B (—)] dichloromethane; [C (—•—)] butyl acetate; and [D (—)] dimethyl sulfoxide. In *n*-hexadecane emission peaks occurred at about 418, 443, and 472 nm.

solved in *n*-hexadecane, butyl acetate, dichloromethane, and dimethyl sulfoxide are depicted in Figs. 2–4. The four nonelectrolyte solvents were judiciously selected so as to encompass the entire range of solvent polarity from the nonpolar *n*-hexadecane hydrocarbon to the moderately polar butyl acetate and dichloromethane solvents to the very polar dimethyl sulfoxide, which is the most polar solvent considered in the present investigation. Examination of the three figures reveals that DBP-O, DBP-S, and DBP-Se, like their PAH counterpart, fluoresce strongly and have two major resolvable emission bands of approximately equal intensity (I/II ratios of 1.25 ± 0.15 and 1.23 ± 0.12 for DBP-S and DBP-Se, respectively) in the 400–500 nm spectral region, whereas dibenzo[*b,n*]perylene had an additional weak emission band

FIG. 5. Fluorescence emission spectra of 9-azabenz[a]anthracene dissolved in [A (—•—)] *n*-hexadecane; [B (—)] dichloromethane; [C (—•—)] butyl acetate; and [D (—)] dimethyl sulfoxide. In *n*-hexadecane emission bands occurred at about 390, 414, and 438 nm.

FIG. 6. Fluorescence emission spectra of 1,2,7,8-tetraazacoronene dissolved in 1,2,4-trichlorobenzene. The spectrum was recorded on a Perkin-Elmer MPF-66 spectrofluorometer and represents the average of fifty scans.

near 505 nm. All three hetero-atom compounds fluoresced strongly. Quantifiable signals were obtained at solute concentrations approaching 10^{-6} Molar. For DBP-O, spectral resolution decreased markedly with increased solvent polarity, to the point where only a single unsymmetrical emission band was observed in dimethyl sulfoxide. Solvent polarity had a much smaller effect on DBP-S and DBP-Se fluorescence behavior, both in terms of spectral resolution and in terms of systematic changes in emission intensity ratios. The small ± 0.15 change in intensity ratios between the various solvents appeared to be random, and not correlated to solvent polarity.

Interestingly, three of the five polycyclic aromatic nitrogen heterocyclic solutes showed slight probe character, as evidenced by a systematic decrease in the calculated I/II band emission intensity ratio with increasing solvent polarity (see Figs. 5 and 6 for representative spectra). The two exceptions noted in Table I, namely methanol and 2-propanol, will be discussed in the next para-

FIG. 7. Fluorescence emission spectra of the neutral (A, in dimethyl sulfoxide) and protonated (B, in trifluoroethanol and in HClO_4 -trifluoroethanol) forms of 1-azabenz[a]anthracene. Protonation of the nitrogen hetero-atom results in loss of emission fine structure accompanied by a sizeable redshift in emission wavelengths.

TABLE I. Ratios of fluorescence emission intensities of 1-azabenz[a]anthracene, 2-azabenz[a]anthracene, and 9-azabenz[a]anthracene dissolved in select nonelectrolyte organic solvents.

Solvent	Py ^a	1-AzBA ^b	2-AzBA ^c	9-AzBA ^d
Cyclohexane	0.58	1.81	1.39	1.74
Isooctane	0.59	1.80	1.39	1.74
<i>n</i> -Hexadecane	0.60	1.75	1.33	1.68
<i>n</i> -Butyl ether	0.84	1.64	1.22	1.52
Benzene	1.05	1.53	1.11	1.50
2-Propanol	1.09	1.28	0.92	1.20
Chloroform	1.25	Rxn	Rxn	Rxn
Butyl acetate	1.35	1.54	1.06	1.38
Methanol	1.35	1.16	0.88	1.10
Dichloromethane	1.35	1.37	1.00	1.38
Acetonitrile	1.79	1.36	0.97	1.33
Dimethyl formamide	1.81	1.31	0.97	1.33
Dimethyl sulfoxide	1.95	1.31	0.98	1.18
Dynamic range	1.37	0.50	0.42	0.56

^a Defined as the ratio of band I (at ~373 nm)/band III (~383 nm) for pyrene. Experimental values are from Dong and Winnik.³⁵

^b Defined as the ratio of band I (at 384–396 nm)/band II (at 406–418 nm) for 1-azabenz[a]anthracene.

^c Defined as the ratio of band I (at 381–391 nm)/band II (at 404–412 nm) for 2-azabenz[a]anthracene.

^d Defined as the ratio of band I (at 389–402 nm)/band II (at 412–425 nm) for 9-azabenz[a]anthracene.

graph. Numerical values of 1-AzBA range from 1.81 for the nonpolar cyclohexane solvent to 1-AzBA = 1.31 for both dimethyl formamide and dimethyl sulfoxide. Similarly, 2-azabenz[a]anthracene and 9-azabenz[a]anthracene values ranged from 2-AzBA = 1.39 and 9-AzBA = 1.74 for cyclohexane to lower values of 2-AzBA = 0.98 and 9-AzBA = 1.18 for dimethyl sulfoxide. Estimated uncertainties in the numerical ratios are believed to be on the order of ± 0.04 or less, on the basis of replicate measurements for select solvents. As an example, measured values for butyl acetate over a five-day period of 1-AzBA = 1.58, 1.51, 1.54, 1.53, and 1.54 indicate very good reproducibility. Examination of Table I further reveals that, with the exception of the two alcohols, the ranking of solvents by polarity is nearly unchanged, at least to within the propagated experimental uncertainties. Better discrimination of solvent polarity is permitted by the much larger pyrene (Py) dynamic range, 1.37 for Py versus ~0.50 for PANHs. Presently, there appears to be no compelling reason for us to recommend using these three azabenzanthracene derivatives in place of pyrene, coronene, ovalene, and benzo[ghi]perylene. For informational purposes, we note that pyrene was one of the first PAH solvent polarity probes to be identified and characterized. A number of practical applications, ranging from characterization of heterogeneous chromatographic surfaces and of organized solvent media to determination of critical micelle concentrations, are based on pyrene fluorescence behavior.^{17–25} 4-Azachrysene and 1,2,7,8-tetraazacoronene are both classified as nonprobe PANH molecules. Emission intensity ratios for 4-AzCh failed to vary with solvent polarity ($I/II = 1.10 \pm 0.10$), whereas fluorescence signals for AzCo were much too weak in many solvents to permit accurate determination of intensity ratios. Fifty scans had to be averaged in order to obtain the fluorescence spectra of AzCo dissolved in 1,2,4-trichlorobenzene, which is depicted in Fig. 6. After fifty scans there is still considerable noise in the 520–650 nm spectral region.

Abnormally low I/II band intensity ratios noted in methanol and 2-propanol can be rationalized in terms of acid-base equilibria or strong hydrogen bonding. Protonation of the nitrogen lone electron pair by a hydrogen ion results in the loss of emission fine structure accompanied by a sizeable redshift in emission wavelengths. Trifluoroethanol completely protonates 4-azachrysene and the three azabenzanthracene derivatives (see Fig. 7 for representative spectra). The original three-band emission spectrum of 4-AzCh at ~360–405 nm disappeared and is replaced by a fairly broad, single band redshifted by over 100 nm into the 460–560 nm spectral region. The spectra remained unchanged whenever a small drop of perchloric acid was added to the solvent. As expected, the protonation is completely reversible. Addition of sodium hydroxide to a HClO₄-propanol solution restored the original “unprotonated” PANH spectrum, though a slight loss in emission intensity was observed. Partial protonation of a PANH solute by an alcoholic solvent would more than likely give erroneously low I/II band intensity ratios, particularly if the redshifted emission spectrum were to overlap or selectively tail into band II. Strong hydrogen bonding between the PANH and alcohol offers a second plausible reason for the erroneously low I/II intensity ratio, as the fluorescence spectrum of the resulting PANH-H-OR intermediate would be redshifted to a much lesser extent. For methanol and 2-propanol, the entire 350–600 nm spectral region was scanned, but no measurable degree of protonation was observed. It should be noted that Bortolus *et al.*²⁶ first recommended 2,2,2-trifluoroethanol as a solvent for discriminating the fluorescence of polynuclear aza-aromatic compounds from that of the corresponding PAH molecule.

During the course of these measurements, unusual fluorescence behavior was noted for the PANH solutes dissolved in chloroform. The PANH fluorescence emission spectra varied significantly with irradiation time, to the point where it was impossible to obtain reproducible spectra. Chemical reactions between amines and halogenated compounds are fairly well documented in the chemical literature. Most reactions occur at elevated temperatures and involve the formation of an alkylammonium bromide salt. Nevstad and Songstad²⁷ recently published results of a kinetic study on reactions of various amines with dichloromethane at 25°C. Liberation of one mole of chloride ion suggested formation of N-chloromethyldialkylammonium and N-chloromethylammonium cation intermediates, which were rapidly deprotonated by the reacted amine. One cannot dismiss the possibility that chloroform (and other chlorinated solvents) might react with PANHs at sites other than the nitrogen hetero-atom, since carbon tetrachloride is known to undergo irreversible photochemical reactions with several PAHs.^{28–34} Unfortunately, at the very low 10^{-6} (or less) molar solute concentrations used in the fluorescence studies, we were unable to conclusively identify any reaction products which might have been formed.

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