Effect of Solvent Polarity on the Fluorescence Emission Spectra of Select Five- and Six-Ring Pyrene Derivatives

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The fluorescence properties of dibenzo[def,p]chrysene, benzo[*rst*]pentaphene, and anthranthrene dissolved in eleven organic non-electrolyte solvents are reported. Measurements indicate that both dibenzo[def,p]chrysene and benzo[*rst*]pentaphene exhibit probe character, as evidenced by the selective enhancement of the intensity of vibronic band I relative to band II with increased solvent polarity. Emission ratios of anthranthrene remained nearly constant, irrespective of solvent polarity. These results, combined with previously reported data for benzo[ghi]perylene, benzo[a]pyrene, benzo[e]pyrene, and dibenzo[a,e]pyrene, are used to examine molecular structure-probe character correlations of select five- and six-ring pyrene derivatives.

Index Headings: Fluorescence; Spectroscopic techniques.

INTRODUCTION

This paper continues a systematic, experimental investigation¹⁻⁵ of the effect that solvent polarity has on the photophysical properties of polycyclic aromatic hydrocarbons (PAHs) and polycyclic aromatic sulfur heterocycles (PASHs). Pertinent photophysical processes of PAHs dissolved in fluid solution are summarized below:

The emission spectrum of the PAH monomer consists of several major vibronic bands labeled I, II, etc., in progressive order. Previous measurements revealed that pyrene, benzo[ghi]perylene, ovalene, coronene, benzo[a]coronene, naphtho[2,3a]coronene, dibenzo[a,j]cornene, dinaphtho[8,1,2abc;2',1',8'klm]coronene, naphtho[8,1,2abc]coronene, and benzo[e]pyrene exhibit selective emission intensity enhancement of vibronic band I relative to III (or band II or IV) in polar solvents.

Surprisingly, not all PAH and PASH molecules behave in an identical manner. Approximately one-half of the molecules studied thus far showed an enhancement effect. The various emission intensity ratios of perylene, dibenzo[bc,ef]coronene, benzo[a]pyrene, benzo[pqr]naphtho[8,1,2bcd]perylene, naphtho[1,2,3,4ghi]perylene, tribenzo[de,kl,*rst*]pentaphene, benzo[1,2,3bc;4,5,6b'c']dicononene, naphth[2',1',8',7':4,10,5]anthra[1,9,8abcd]coronene, tetrabenzo[de,hi,mn,qr]naphthacene, dibenzo[a,e]pyrene, and benz[4,10]anthra[1,9,

8abcd]coronene remained essentially constant, irrespective of solvent polarity. For two additional pentaphene derivatives studied, dinaphtho[2,1,8,7defg;2',1',8',7'ijkl]pentaphene and benz[*rst*]anthra[9,1,2cde]pentaphene, the number of clearly resolvable emission bands varied from one solvent to another, thereby preventing assignment of a common set of bands. Our measurements⁵ have further revealed that PASH molecules behave differently than their PAH counterparts, perhaps because of the reduced "double bond conjugation" arising from the sulfur atoms. Emission spectra of thianthrene, 1,6-dithiapyrene, 1,7-dithiaperylene, and 3,10-dithiaperylene contained relatively few bands. Significant band broadening and poor spectral resolution were noted in many of the more polar solvents examined.

To date, the enhancement phenomenon has not been satisfactorily explained. We have put forth, however, several preliminary observations based on the number of Kekulé structures,⁵ on point groups and symmetry elements,⁴ on dissimilarities between a given molecule's excitation and emission spectra,⁴ and on the relative length of the center aromatic row in the case of the coronene derivatives.^{4,5} To expand our spectral file, we have measured the fluorescence emission behavior of anthranthrene (also called dibenzo[def,mno]chrysene), dibenzo[def,p]chrysene, and benzo[*rst*]pentaphene dissolved in various organic solvents. These three PAHs, along with benzo[a]pyrene, benzo[e]pyrene, benzo[ghi]perylene, and dibenzo[a,e]pyrene, which were studied previously,^{1,3} all contain the pyrene moiety, as is shown in Fig. 1. For purposes of this paper, the seven PAHs will be classified as 5- and 6-ring pyrene derivatives despite the fact that their IUPAC names may be derived from some other parent compound. Results of these measurements will be used to classify anthranthrene, dibenzo[def,p]chrysene, and benzo[*rst*]pentaphene as either a solvent polarity probe or a nonprobe molecule, depending upon whether the observed emission intensity ratios vary systematically with solvent polarity.

MATERIALS AND EXPERIMENTAL METHODS

Anthranthrene, dibenzo[def,p]chrysene, and benzo[*rst*]pentaphene were synthesized and purified by procedures described in the literature.^{6,7} 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 made sufficiently low to allow exclusion of both primary and secondary inner filtering artifacts. Sol-

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FIG. 1. Molecular structures of PAH compounds: (A) dibenzo[def,p]chrysene; (B) anthranthrene; (C) benzo[rst]pentaphene; (D) benzo[e]pyrene; (E) benzo[a]pyrene; (F) benzo[ghi]perylene; and (G) dibenzo[a,e]pyrene. Solid circles denote one pyrene moiety contained within the molecule. Note: benzo[ghi]perylene and anthranthrene possess more than one pyrene substructural unit.

vents were of HPLC, spectroquality or AR grade, purchased commercially from Aldrich.

Fluorescence spectra were recorded on a Shimadzu RF-5000U spectrofluorometer at ambient room temperature. Solutions were excited at 306 nm (anthranthrene), 310 nm (dibenzo[def,p]chrysene), and 307 nm (benzo[rst]pentaphene) in 1-cm² quartz cuvettes. Excitation and emission slit width settings were 15 nm and 1.5 nm, respectively. All fluorescence spectra were solvent blank corrected and verified by repetitive measurements.

RESULTS AND DISCUSSION

The weakly allowed vibronic transitions in the fluorescence emission of dibenzo[def,p]chrysene (DBCh), benzo[rst]pentaphene (BPP), and anthranthrene are depicted in Figs. 2–4, respectively. Careful examination of the various spectra reveals that intensity ratios of dibenzo[def,p]chrysene and benzo[rst]pentaphene depend

FIG. 2. Fluorescence emission spectra of dibenzo[def,p]chrysene dissolved in [A (—)] *n*-hexadecane, [B (—)] butyl acetate, [C (—)] dichloromethane, and [D (—)] dimethyl sulfoxide. In butyl acetate the major emission peaks occur at 419, 432, 444, and 472 nm.

FIG. 3. Fluorescence emission spectra of benzo[rst]pentaphene dissolved in [A (—)] *n*-hexadecane, [B (—)] dichloromethane, [C (—)] butyl acetate, and [D (—)] dimethyl sulfoxide. In butyl acetate the major emission peaks occur at 432, 446, 459, and 490 nm.

upon solvent polarity. Pronounced enhancement of the I band intensity relative to band II is observed in the more polar solvents. Intensity ratios for DBCh (I/II) and BPP (I/II) range from approximately DBCh $\approx$ 1.01 and BPP $\approx$ 2.29 in the nonpolar solvent cyclohexane to DBCh $\approx$ 2.06 and BPP $\approx$ 3.48 in dimethyl sulfoxide, which was the most polar solvent studied. During the course of these measurements it was noted that vibronic band II of DBCh was observable only as a shoulder in *N,N*-dimethylformamide and dimethyl sulfoxide. Attempts to improve the resolution by employing a smaller 1.5-nm emission slit width proved futile and served only to decrease the measured emission intensity to the point where it was extremely difficult to locate the peak maximum. The emission intensity for anthranthrene remained essentially constant, irrespective of solvent polarity. A constant ratio of emission intensity renders this latter PAH unsuitable as a solvent polarity probe molecule.

FIG. 4. Fluorescence emission spectra of anthranthrene dissolved in [A (—)] *n*-hexadecane, [B (—)] butyl acetate, [C (—)] dimethyl sulfoxide, and [D (—)] dichloromethane. In butyl acetate the major emission peaks occur at 431, 457, and 488 nm.

TABLE I. Relative emission band intensities for pyrene (Py), dibenzo[def,p]chrysene (DBCh), and benzo[rst]pentaphene (BPp) in various organic solvents.

Solvent	Py ^a	DBCh		BPp ^d
		(I/II) ^b	(I/III) ^c	
Cyclohexane	0.58	1.01	1.01	2.29
2,2,4-Trimethylpentane	0.59	0.99	1.00	2.32
<i>n</i> -Hexadecane	0.60	1.10	1.07	2.30
Benzene	1.05	1.55	1.24	2.97
2-Propanol	1.09	1.62	1.27	3.14
Butyl acetate	1.35	1.80	1.40	3.21
Methanol	1.35	1.81	1.29	3.18
Dichloromethane	1.35	1.80	1.35	3.25
Acetonitrile	1.79	1.96	1.34	3.46
N,N-dimethylformamide	1.81	2.01	1.42	3.48
Dimethyl sulfoxide	1.95	2.06	1.48	3.48
Dynamic range ^e	1.37	1.07	0.48	1.19

^a Experimental Py values are from Dong and Winnik.⁸

^b Defined as I (at 418–422 nm)/II (at 432–435 nm). Band II is visible only as a shoulder in the more polar solvents such as N,N-dimethylformamide and dimethyl sulfoxide.

^c Defined as I (at 418–422 nm)/III (at 443–447 nm).

^d Defined as I (at 430–435 nm)/II (at 445–449 nm).

^e Defined as the difference between the largest and smallest PAH value.

Numerical DBCh and BPp values, together with literature Py values,⁸ are summarized in Table I for eleven nonelectrolyte organic solvents of varying polarity. Estimated uncertainties are believed to be on the order of ± 0.03 (or less) based upon replicate measurements for select solvents. As an example, measured values for butyl acetate were DBCh = 1.80, 1.82, 1.80, 1.77, and 1.79 over a five-day period. Inspection of Table I reveals that the rank ordering of solvents by polarity remains unchanged, at least to within experimental uncertainties associated with the 3 scales. For practical applications the Py and DBPp scales may be preferred from the point of view that observed enhancement is visually apparent, and the solvent polarity can be estimated by visually comparing the I and II band intensities. Furthermore, the dynamic range of the Py scale is slightly larger than those of the DBCh and BPp scales.

Classification of only dibenzo[def,p]chrysene and benzo[rst]pentaphene as solvent polarity probes does provide spectral information for three additional PAHs for inclusion in possible molecular structure–probe character correlations. Of the seven 5- and 6-ring pyrene de-

rivatives given in Fig. 1, only benzo[ghi]perylene, benzo[e]pyrene, dibenzo[def,p]chrysene, and benzo[rst]pentaphene were found to exhibit probe character. Three of these probe molecules (benzo[ghi]perylene, benzo[e]pyrene, and benzo[rst]pentaphene) belong to the C_{2v} point group. Symmetry elements present in the C_{2v} point group include a 2-fold major rotational axis and two vertical mirror planes. Interestingly, all three nonprobe molecules either have a mirror plane horizontal to the 2-fold rotation axis (anthracene, C_{2h} point group) or lack the 2-fold axis completely, as is the case with benzo[a]pyrene and dibenzo[a,e]pyrene, both of which have C_s symmetry. One further notes that all nonprobes had at least one added aromatic ring in the so-called “a” position, adopting the nomenclature common to pyrene derivatives, i.e., dibenzo[a,e]pyrene. For purposes of this discussion, the nonprobe anthracene is regarded as naphtho[1,8am]pyrene. Probe behavior is observed whenever a second aromatic ring is added in either the “i” or “l” positions. Unpublished fluorescence measurements⁹ indicate that dibenzo[h,rst]pentaphene (tribenzo[a,e,i]pyrene according to the pyrene nomenclature) also exhibits modest probe behavior, in accord with our preliminary observations regarding C_{2v} point group symmetry and substituent ring position. Although we are still unable to predict which polycyclic aromatic hydrocarbons will show probe character, our observations concerning common structural features in known PAH solute probes do suggest possible molecules for future studies.

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