Polycyclic Aromatic Hydrocarbon Solute Probes. Part VIII: Evaluation of Additional Naphthacene and Perylene Derivatives as Possible Solvent Polarity Probe Molecules

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Fluorescence emission spectra are reported for phenanthro[5,4,3,2efgh]perylen, dibenzo[cd,k]naphtho[8,1,2fghi]perylen, benzo[bp]perylen, dibenzo[e]h[perylen, and benzo[a]naphtho[8,1,2de]naphthacene dissolved in various organic solvents. Results of these measurements are used to screen PAHs for potential solvent polarity behavior. Of the five PAHs studied, only phenanthro[5,4,3,2efgh]perylen exhibited probe behavior, as evidenced by selective emission intensity enhancement of band I with increasing solvent polarity.

Index Headings: Fluorescence; Molecular structure.

INTRODUCTION

Fluorescence probe techniques are becoming increasingly popular for studying the surface micro-environment of chromatographic materials, surfactant micellization/adsorption, polymer-surfactant interactions, microemulsions, liquid crystals, and other molecularly ordered media. The method involves the use of a probe molecule (e.g., pyrene) that exhibits different fluorescence characteristics, depending upon the properties of the solubilizing media. The probe molecule selectively binds to a specific surface site or preferentially partitions into an organized structure. Appearance of new spectral bands, shifts in the emission wavelengths, or changes in the emission intensities provide an indication of the environment immediately surrounding the probe. When combined with lifetime measurements, probe techniques can provide additional information regarding diffusion coefficients in probe excimer formation, fluidity in lipid vesicles, and rates of intermolecular collisions in quenching experiments.

Earlier reports1–7 have been primarily concerned with determining the photophysical properties of dissolved polycyclic aromatic hydrocarbon (PAH), polycyclic aromatic sulfur heterocycle (PASH), and polycyclic aromatic nitrogen heterocycle (PANH) 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]perylen, ovalene, coronene, benzo[a]coronene, naphtho[2,3a]coronene, dibenzo[a,j]coronene, dinaphtho[8,1,2abc;2′,1′,8′klm]coronene, naphtho[8,1,2abc]coro-

nene, benzo[e]pyrene, dibenzo[def,p]chrysene, 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. Ratios of emission intensities serve as a measure of solvent polarity and structure.

Surprisingly, not all PAH, PASH, and PANH molecules behave in a similar fashion. Approximately one-half of the molecules studied thus far showed an enhancement effect. Various emission intensity ratios of perylene, dibenzo[bc,ef]coronene, benzo[a]pyrene, benzo[rq]naphtho[8,1,2bc]perylen, dibenzo[a,e]pyrene, anthracene, and several other PAHs remained essentially constant, irrespective of solvent polarity. For two additional pentaphene derivatives studied, dinaphtho[2,1,8,7def;′2,1′,8′,7′ijkl]pentaphene and benzo[rst]anthra[9,1,2de]pentaphene, the number of clearly resolvable bands varied from one solvent to another, thereby preventing assignment of a common set of emission bands. Fluorescence spectra of 1-azapyrene, 2-aza-pyrene, and 4-azapyrene contained many of the "pyrene-like" spectral features; however, emission intensity ratios failed to vary with solvent polarity.5 Our measurements further revealed that PASH molecules also behave differently than their PAH counterparts, perhaps because of either the reduced "double bond conjugation" or π → n transitions arising from the divalent sulfur atoms. Emission spectra of thianthrene, 1,6-dithiaperylene, 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.5

Thus far the enhancement phenomenon has not been satisfactorily explained. We have put forth several preliminary ideas based upon the number of Kekulé structures,6 point groups and symmetry elements,4 dissimilarities between a given molecule's excitation and emission spectra, and the relative length of the center aromatic row in the case of the coronene derivatives.4,5 The observations were far from definitive, as the spectral database included only 28 PAH molecules, and many of the molecular formulas were represented by only a single family member. To expand our spectral data file, we have measured the fluorescence emission behavior of dibenzo[e,ghi]perylen (DBP), benzo[b]perylen (BP), benzo[a]naphtho[8,1,2cd]naphthacene (BNN), dibenzo[cd,k]naphtho[8,1,2fghi]perylen (DNBP), and phenanthro[5,4,3,2efghi]perylen (PP; also called diben-
zo[cd,fg]anthracene) dissolved in various organic nonelectrolyte solvents. Molecular structures of the 5 PAHs (compounds AC–AG) are depicted in Fig. 1. Results of these measurements are used to classify the five solutes as either probe or nonprobe molecules, depending upon whether the emission intensity varies systematically with solvent polarity.

MATERIALS AND METHODS

Four of the PAHs were synthesized and purified by procedures described in the chemical literature. The remaining solute, PP, was isolated from a hydrocracker deposit material. 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 dilute to allow exclusion of both primary and secondary inner filtering artifacts. Solvents were of HPLC, spectroquality or AR grade, purchased commercially from Aldrich or Fisher Scientific.

Fluorescence spectra were recorded at ambient room temperature on Shimadzu RF-5000U (UNT) and at 25°C on Perkin-Elmer MPF-66 (Chevron) spectrophotometers. Solutions were excited at 330 nm (DBP), 312 nm (BP), 411 nm (BNN), 321 nm (DBNP), and 365 nm (PP). In the case of PP and DBP, the spectra obtained represent the average of at least nine scans. All fluorescence spectra were solvent blank corrected. Emission and excitation slit widths were 3 nm and 15 nm, respectively.

RESULTS AND DISCUSSION

Representative fluorescence spectra of the various solutes dissolved in n-hexadecane, butyl acetate, dichloromethane, and dimethyl sulfoxide are given in Figs. 2–6. The four nonelectrolyte solvents were selected so as to encompass the entire range of solvent polarity, from the nonpolar n-hexadecane hydrocarbon to the moder-
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)\textsuperscript{11} and methanol (Py = 1.35)\textsuperscript{11} with solvents of comparable pyrene scale polarity, namely n-hexadecane (Py = 0.60)\textsuperscript{11} and butyl acetate (Py = 1.35),\textsuperscript{11} 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.\textsuperscript{12-16} 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.

Inspection of the five figures reveals that the PAH solutes can be divided into two categories—probe or non-probe molecules—depending upon whether the ratio of emission intensities changes with solvent polarity. For phenanthro[5,4,3,2-efg][b]pyrene, significant enhancement of the band I emission intensity relative to that of band II is observed with increasing solvent polarity. Calculated I/II intensity ratios range from PP = 2.12 for n-hexadecane to PP = 3.72 for dimethyl sulfoxide. Estimated uncertainties in the measured intensity ratio are believed to be on the order of ±0.05 (or less) on the basis of replicate measurements for select solvents. Dibenzo[e,ghi]pyrene initially appeared to show “probe-like” character. Upon closer examination of the fluorescence emission spectra, however, it was noted that several additional bands appeared whenever DBP was dissolved in n-hexadecane. To be consistent with our past classification scheme, we have labeled DBP as NA because we were unable to decide whether the probe-like character was truly attributable to enhancement of band I intensity or to abnormally large 435-nm and 455-nm bands caused by the “extra” band near 448 nm. In many respects the behavior of DBP in n-hexadecane resembles recently published low-temperature deuterocoronene-matrix pyrene,\textsuperscript{17} coronene,\textsuperscript{18} and hexabenzob[bc,ef,hi,kl,no,qr]- coronene\textsuperscript{18} spectra, where the rigid solvent matrix restricts solute motion to the point where overlapping bands are now resolved. Emission intensity ratios of BP, DBNP, and BNN remain nearly constant, irrespective of solvent polarity. Of the ten perylene derivatives studied thus far, only benzo[g,ghi]pyrene and phenanthro[5,4,3-efg][b]pyrene exhibit probe character.

As additional PAHs are studied, it is important to re-examine our preliminary observations regarding possible probe character vs. molecular structure correlations. Table I lists molecular formulas, point groups, number of π-electrons, and Kekulé structure counts for BP, DBP,
### TABLE 1. Summary of the fluorescence probe character vs. molecular structure for polycyclic aromatic hydrocarbons.

<table>
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<tr>
<th>Compound</th>
<th>Molecular formula</th>
<th>Probe</th>
<th>(x)-electrons</th>
<th>Point group</th>
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*Continuation of Table 1 from Ref. 5. PAH solutes are: (B) benzo[a]coronene; (C) naphtho[2,3a]coronene; (D) dibenzo[a,j]coronene; (O) benzo[g,h,i]perylene; (Q) naphtho[1,2,3,4ghi]perylene; (R) benzo[qr]naphtho[8,1,2bd]perylene; (S) dibenzo[cjd,m]perylene; (V) dibenzo[a,e]pyrene; and (Y) dinaphtho[1,2,5,6,7,8,9,10]pentaphene.

* Point groups are assigned on the basis of planar structures.

* 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.

PP, DBNP, and BNN. Also included in this tabulation are any previously studied PAHs having molecular formulas of C₂₅H₁₄, C₂₅H₁₄, C₂₅H₁₄, C₂₅H₁₄, C₂₅H₁₄, and C₂₅H₁₄. Careful examination of Table I reveals that there is no correlation between probe character and overall molecular symmetry, even if one considers just the perylene derivatives. For example, benzo[g,h,i]perylene, naphtho[1,2,3,4ghi]perylene, and phanthro[5,4,3,2e/fghi]perylene possess C₁₉ point group symmetry, having a major twofold rotation axis and two vertical mirror planes. Only benzo[g,h,i]perylene and phanthro[5,4,3,2e/fghi]perylene exhibit probe character, as evidenced by selective enhancement of band I intensity.

Table I contains four more exceptions to our preliminary observation that if solute probes exist in any given molecular formula family then they generally (not always) have a greater number of Kekulé structures than do nonprobe family members. Two of the exceptions pertain to the C₂₅H₁₄ molecular formula family. Benzo[rst]pentaphene (SC = 14) and dibenzo[def,p]chrysene (SC = 16) are solute probes, yet both possess fewer Kekulé resonance forms than does dibenzo[a,e]pyrene (SC = 17). The remaining exceptions occur in the C₂₅H₁₄ and C₂₅H₁₄ families, where phanthro[5,4,3,2e/fghi]perylene (SC = 30) and naphtho[2,3a]coronene (SC = 48) exhibit probe behavior, but not benzo[qr]naphtho[8,1,2bd]perylene (SC = 31) and dibenzo[cjd,m]naphtho[8,1,2ghi]perylene (SC = 49). Interestingly, these exceptions involve the nonprobe’s having an odd number of Kekulé structures. All solvent polarity probes, except benzo[e]pyrene (SC = 11) and dibenzo[a,j]coronene (SC = 57), had even Kekulé structure counts. Although four more exceptions have been found in the present study, we still believe that Kekulé structure count provides a useful criterion to initially screen PAHs for future studies. The only definitive method for determining whether a given PAH behaves as a solvent polarity probe still remains to actually measure its fluorescence properties in various organic solvents.

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