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Polarized Fluorescence of Guests in MBBA

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Polarized fluorescence of organic molecules were studied utilizing a homogeneously aligned nematic liquid crystal as an orienting matrix. The polarized fluorescence ratios were largest for those guests which were the most linear and, therefore, could be aligned to the greatest extent by the matrix. The polarization of the electronic transitions of the fluorescent guests were determined.

INTRODUCTION

The use of aligned, nematic liquid crystals as orienting matrices for studying the anisotropy of the optical properties of dissolved solutes is well documented. The cooperative alignment of the solute in the aligned liquid crystal solvent has been named the guest-host effect.[1] It has been shown that a liquid crystal host will orient a guest for periods longer than the fluorescence lifetime of the guest.[2] This technique was first employed by Zocher,[3] who measured the polarized fluorescence of various dyes. Sackmann[4] has measured the polarized absorption of guests in a "compensated nematic" aligned by a magnetic field and subsequently cooled to form an oriented organic glass. He found that the long molecular axes of the guest molecules align parallel to those of the host liquid crystal molecules. This was confirmed by Ceasar and Gray[5] who measured the polarized absorption of guests in a room-temperature nematic.

Sackmann has measured the polarized absorption[6] and polarized fluorescence[7] of guests in a "compensated" nematic and has shown that the technique is useful for obtaining the absolute orientation of the transition moments of oriented guests. Watanabe, *et el.*,[8] have measured the polarized absorption of dyes in N-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) and have reported that the transition moment for azobenzene does not coincide with its long molecular axis. The technique is also useful for detecting the

position of hidden bands of the guest.[9,10] Gale, *et al.*,[11] have measured the linear dichroism spectra of the manganese(III) salt and free base of porphyrin in MBBA. They have shown that the liquid crystal technique gives a higher degree of guest orientation than stretched polythene film techniques. Haase and Wedel[12] have recently reported the results of polarized absorption of guests in some room temperature nematics and have reported a reduction technique for measuring weak absorption bands. Aligned nematics have the viscosity of liquids and, therefore, are suitable solvents for measuring the polarized fluorescence of excimers[7] and exciplexes.[13] The polarized fluorescence of guests in aligned nematic liquid crystals has also been reported to be useful in display devices.[14] Several guests have been reported which can be utilized advantageously in display devices employing polarized absorption in liquid crystals.[15]

The order parameter (S) which is a representation of the alignment of the guest molecules in the nematic liquid crystal has been computed from the guest's polarized absorption[9,12,15-17] and polarized fluorescence spectra.[16]

In this study, the polarized fluorescence of various guests in the room temperature, nematic liquid crystal N-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) have been studied and the directions of the transition moments of the guests have been determined.

EXPERIMENTAL

The room temperature, nematic liquid crystal MBBA (T_{nematic} = 19°C to 42°C) was used as the orienting matrix. It was obtained from two sources. That obtained from Eastman Organics was used without further purification but that obtained from Pfaltz and Bauer was vacuum distilled prior to use. It has an absorption edge at 405 nm and therefore only guests having an absorption band above 405 nm could be employed in the fluorescence studies. The 3H-thiadiazolo[4,3-a]pyridines were purified samples obtained from Professor K. T. Potts. All other guests were obtained commercially and recrystallized prior to use. Concentrations of 0.07% to 0.15% (by weight) of guests in MBBA were employed. The lowest concentration of a guest producing a measurable fluorescent signal was always used. The studies were made in a sandwich cell consisting of two quartz disks separated by a Teflon spacer of either 0.015 mm or 0.050 mm thickness. The sandwich cell was thermostated by means of a constant temperature, circulating water bath. The homogeneous orientation of MBBA and its guest was obtained by treating the cell walls with N-methyl-3-aminopropyltrimethoxysilane (MAP) and then unidirectionally rubbing the cell walls prior to sample introduction.[18]

The spectrofluorimeter employed has been described elsewhere.[19] The

sandwich cell was placed in the spectrofluorimeter at an angle of approximately 45° with the exciting light. The surface fluorescence was measured at approximately 45° from the cell walls. The bandwidth of the exciting light (λ_{ex}) was made as small as possible to reduce light scattering. The sample was irradiated with unpolarized light and the fluorescence passed through an ultraviolet polarizing filter (Polacoat 105 UV). The filter was oriented in two mutually perpendicular positions.

The fluorescence intensities were measured with the polarizing filter oriented paralled ($I_{||}$) and perpendicular ($I_{\perp}$) to the long molecular axes of the molecules. The fluorescence polarization is defined as the ratio of the two relative intensities:

$$P = \frac{I_{||}}{I_{\perp}}$$

It is important to correct for the wavelength dependence of the monochromator to different polarizations of light. This is due primarily to the grating's efficiency, which results in unequal reflection of parallel and perpendicular polarized light. To correct for the inherent polarization of the instrument, a modified method of Sackmann's[7,9] was developed and used for each compound studied. The polarized fluorescence ratio obtained for the guest in isotropic MBBA was used as the normalization factor. The polarized fluorescence ratio was measured at several temperatures, including temperatures above the nematic–isotropic transition of MBBA, without moving the sandwich cell for any of the measurements. In the isotropic liquid phase, the host can no longer orient the guest. Any polarization produced must be due to the inherent polarization of the instrument. The nematic–isotropic transition of MBBA (42°C) was lowered to approximately 37°C when approximately 0.1% (by weight) of guest was dissolved in MBBA.

$$P_{\text{isotropic}} = \frac{I_{||\text{isotropic}}}{I_{\perp\text{isotropic}}}$$

The corrected polarization is then defined as

$$P_{\text{corrected}} = \frac{P}{P_{\text{isotropic}}}$$

Similar results were obtained when the exciting light was polarized. In addition, changing the exciting wavelength in the guest's absorption band had no effect on $P_{\text{corrected}}$.

Some of the fluorescent guests studied (perylene, tetracene, and 1,8-diphenyl-octatetraene) have several vibrational components associated with their fluorescence spectrum. Only the largest peak was monitored in such

cases because the smaller peaks were less sensitive to polarization measurements. The errors that are listed for the polarized fluorescence ratio of each guest are statistical errors and are not meant to be absolute errors.

RESULTS AND DISCUSSION

The polarized fluorescence ratio of a guest in MBBA is highest at 19°C because of the solvent properties of MBBA. This is illustrated for 4-dimethylamino-4′-nitro stilbene in Table I. At 19°C, the MBBA host has its maximum order as a liquid crystal and is able to align the guest appreciably. As the temperature is raised, the liquid crystal host loses some of its order and, therefore, some of its ability to align the guest. The polarized fluorescence of the guest subsequently decreases with an increase in temperature. At 37°C, MBBA passes into the isotropic liquid phase, and can no longer align the guest. The polarized fluorescence ratio of the guest equals unity at this temperature. A value of unity indicates that the fluorescence intensities are equal along the long and short molecular axes of the guest. The previously determined polarized fluorescence ratios could again be determined upon slow cooling below the nematic–isotropic transition temperature. These results are similar to those reported by other workers[16] for 4-dimethylamino-4′-nitro stilbene in MBBA. The results of the polarized fluorescence of the various guests studied are presented in Table II. The band shapes of the fluorescence spectra of the guests in MBBA resembled those obtained in isotropic solvents with some expected solvent shifts. The transition moment is directed parallel or perpendicular to the long axis of the rod, only for those symmetric, rod-shaped guests studied in this work possessing C_{2v} or D_{2h} symmetry. The polarized fluorescence ratio obtained for these guests is, within experimental error, an absolute polarization. For these molecules, the

TABLE I

Polarized fluorescence of 4-dimethylamino-4′-nitro stilbene in MBBA as a function of temperature

Temperature-°C (±0.1°C)	$P_{\text{corrected}}$ (±0.03)
19.0	2.63
25.0	2.56
30.0	2.32
35.0	2.27
40.0	1.00
45.0	1.00
50.0	1.00

	Point group	λ_{ex} (nm)	λ_{fl} (nm)	$P_{corrected}$ at 19°C	Direction of the transition moment relative to the long molecular axis of the guest: This study	Rigid glass studies	Theoretical studies	Liq. cr. studies
4-Dimethylamino-4'-nitro stilbene	C_s	450	585	2.63 ± 0.03	∥		∥ (20)	∥ (16)
Acridine orange (free base)	C_{2v}	425	525	1.41 ± 0.02	∥			
Acridine orange (monocation)	C_{2v}	490	540	1.44 ± 0.03	∥			
1-Amino anthraquionone	C_s	460	565	1.41 ± 0.02	∥			
Perylene	D_{2h}	420	482	1.35 ± 0.02	∥	∥ (21)	∥ (22)	
Tetracene	D_{2h}	440	490	0.75 ± 0.03	⊥	⊥ (21)	⊥ (23)	⊥ (16, (6), (7)
Rubrene	C_{2h}	500	558	1.39 ± 0.02	∥			
1,8-Diphenyl-1,3,5,7-octa-tatraene	C_{2h}	415	520	2.78 ± 0.03	∥	∥ (24)		
Brilliant sulphoflavin	C_s	420	510	1.16 ± 0.02	∥			
Acridine yellow (monocation)	C_{2v}	430	497	1.37 ± 0.02	∥			
9-Amino acridine	C_{2v}	415	474	1.05 ± 0.01		⊥ (25)		
Benzoflavin	C_{2v}	430	500	1.85 ± 0.03	∥			
6-Chloro-3-(5-chloro-2-pyridyl-imino)-3H [1,2,4]-thiadiazolo[,3-a] pyridine	C_s	420	500	1.19 ± 0.02	∥			
6-Bromo-3-(5-bromo-2-pyridyl-imino)-3H[1,2,4]-thiadiazolo[4,3-a] pyridine	C_s	420	498	1.17 ± 0.02	∥			
6-Bromo-3-(2-pyridyl-imino)-3H[1,2,4]-thiadiazolo[4,3-a] pyridine	C_s	420	500	1.20 ± 0.02	∥			
Auramine 0	C_{2v}	425	496	1.72 ± 0.03	∥	∥ (26)		

transition moment is paralleled to the long axis of the rod if $P_{\text{corrected}} > 1$. If $P_{\text{corrected}} < 1$, the transition moment is directed perpendicular to the long axis of the rod.[12] For the less symmetric molecules studied, the transition moment is not necessarily directed parallel or perpendicular to the long axis of the rod. The observed polarization ratio is then the ratio of the projections of the transition moments on the rod axis and is called a relative polarization. Although the entire transition moment is not directed parallel or perpendicular to the long axis of the rod, the largest projection is directed parallel to the long axis of the rod if $P_{\text{corrected}} > 1$. If $P_{\text{corrected}} < 1$, the largest projection is directed perpendicular to the long axis of the rod.[12]

4-Dimethylamino-4'-nitro stilbene and 1,8-diphenyl-1,3,5,7-octatetraene (DPOT) yielded the highest polarized fluorescence ratios of the guests studied. $P_{\text{isotropic}}$ for DPOT was obtained with a room temperature solution of DPOT in benzene because of the increase in isomerization of DPOT at higher temperatures in MBBA. The ratio obtained for 4-dimethylamino-4-nitro stilbene agrees with that reported by Bauer, *et al.*,[16] in the same liquid crystal host (data presented graphically and method of orientation not reported). These two guests are the most linear and, therefore, align to the greatest extent in the liquid crystal host. Bulky molecules on the other hand produce ratios that are closer to unity. Several guests have similar structures and yielded similar polarized fluorescence ratios. This indicates that the guest's alignment is dependent on its geometry.

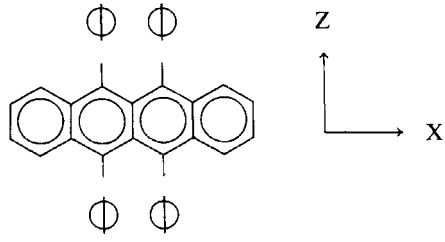
The absorption and fluorescence spectra of the free base of acridine orange and its monocation in MBBA agree with the published spectra[27] in isotropic solvents. Concentrations of 0.10% (by weight) of these guests in MBBA did not appear to give any dimer formation in the absorption spectra. However, dimer formation cannot be totally discounted for dyes of this nature. Komiyama and Mori[27] have reported concentration depolarization of the fluorescence of the acridine orange monocation in polyvinyl alcohol films at concentrations greater than 10^{-4} Molar, due to the formation of higher aggregates. The formation of higher aggregates in MBBA would reduce the polarized fluorescence ratio of the guest because of their inability to be aligned by MBBA.

9-Amino acridine gives an absolute polarized fluorescence ratio approaching unity. It has a structure similar to the free base of acridine orange and its monocation, 1-amino anthraquinone, and the monocation of acridine yellow (which all produced similar polarizations). Therefore, it is reasonable to assume that it is aligned to the same extent as these molecules and its polarized fluorescence ratio of unity is not due to a lack of alignment. It may be due to two bands, ^1L_a and ^1L_b, in the long wavelength region of 9-amino acridine that have opposite polarizations but overlap quite strongly. This has been observed for several mono- and disubstituted amino acridines[28] and the series

9X-acridine (X=H, Cl, Br).[29] However, Zanker and Wittwer[25] have classified all the absorption bands for 9-amino acridine in the 310 nm region as ^1L_b and in the 400 nm region as ^1L_a. 9-Amino acridine, like all other guests in this study, was excited within its longest absorption band region.

Our studies indicate that the electronic transition at longest wavelength for rubrene (9,10,11,12-tetraphenyltetracene) is polarized along its axis of highest molecular polarizability. Haase and Wedel[12] have reported that the axis of highest molecular polarizability for 9,10-diphenylanthracene is its Z axis and it aligns with its Z axis preferentially parallel to the optical axis of the nematic host. It is, therefore, reasonable to assume that rubrene also aligns with its Z axis preferentially parallel to the optical axis of the nematic host. The electronic transition at longest wavelength for rubrene must then be polarized along its Z axis. This is in agreement with a Z axis polarization of the electronic transition reported for 9,10-diphenylanthracene.[12] It is also in agreement with our results for tetracene. Our studies indicate that the electronic transition at longest wavelength for tetracene is polarized perpendicular to its long molecular axis or parallel to its Z axis. Other workers[6,16,17] have reported similar results for tetracene.

The 3H[1,2,4]-thiadiazolo-[4,3-a] pyridines yielded similar polarized fluorescence ratios of low magnitude. The fluorescence of these guests in isotropic solvents have been reported by Potts, Richtol and Armbruster.[30] They reported a steady decrease in resolution as the polarity of the solvent increased. Only a broad emission was observed from these guests in MBBA, similar to the resolution observed in alcohol.



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