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Estimation of Excited State Dipole Moments of Exalite Dyes by Solvatochromic Shift Studies

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The solvent effect in a series of polar and non-polar solvents of varying dielectric constants and refractive indices has been investigated by studying electronic spectra (S_1 band) of a series of exalite laser dyes at room temperature (25 ± 1°C). These data are used to determine the magnitude (μ_e) and direction (θ) of the electric dipole moments in the first electronically excited state. The results indicate that the observed band systems in these compounds may be attributed to $\pi^* \leftarrow \pi$ transition.

key words: electric dipole moments, exalite dye

Laser dyes have several applications such as anticoagulants, fluorescence indicator and possess anthelmintic and optical brightness properties [1]. Exalite laser dyes pumped by XeCl-excimer [2], Ar+ [3], Nd:YAG [4] lasers provide tunable lasers in the visible to ultraviolet range which are of considerable interest from dermatology to molecular spectroscopy [5] as well as in single crystal analysis [6]. Narrow line width operation is an important requirement for tunable laser that can be achieved in high performance dye-doped polymers and dye-doped exalite 377(E-377) sol-gel material, which may impair the laser spectral output and performance [5]. Exalite 428 (E-428) is used in generating circularly polarised light in glassy liquid crystal films and to study their thermotropic properties, thermal transition temperature and reflection wavelengths of glass forming liquid crystal, which will not change on E-428 dopingx [7]. The laser and fluorescence properties of doped and undoped silica samples in sol-gel (E-351 dye used to dope sol-gel silica) are studied. The fluorescence and the laser emission spectra of E-351-doped silica sample have a peak at 352 nm and the FWHM of fluorescence is ten times broader than spectral width of laser spectrum [8].

No experimental data on the excited state dipole moments of exalites seems to have been reported so far. Dipole moments of short-lived species are of considerable interest because, just as for molecules, they provide important information on the electronic structure and geometry. A prior knowledge of the dipole moments of electronically excited species is often useful in the design of non-linear optical materials and the elucidation of the nature of excited states as well as the course of any photochemical transformation. Further, experimental data on excited states are also useful in the parameterization of semi-empirical quantum chemical procedures for their states. Excited state dipole moments of substituted coumarins are studied by different methods by Sheng *et al.* [9], Giri *et al.* [10], Cyril *et al.* [1] and Samanta *et al.* [11].

The present work is a first report on the experimental determination of the excited state dipole moments of exalite (Exalite-389, E-392A, E-398 and E-428) dyes which are used extensively as laser dyes in the UV range. The study of UV absorption and fluorescence spectral studies and the effect of polar and non-polar solvents has been undertaken in order to determine their electric dipole moments in their first electronically excited states [12]. These parameters so determined also give insight into the electron distribution, reactivity, photochemical reaction, etc. of the solute molecule in its first electronically excited states. In addition to the determination of the dipole moments in the excited states, it is possible from these studies to determine the shape parameters, which are important and give information about the shape of the cavity in which the solute molecule is supposed to lie [13]. However in the present investigation the determination of excited state dipole moment (μ_e) and direction (θ) is carried out.

Exalite 389, 392A, 398, and 428 were obtained from Exciton Chemical Co., USA and were used without further purification. Electronic absorption spectra were recorded on a Hitachi 150-20 UV-vis spectrophotometer. Fluorescence spectra were recorded on Hitachi F2000 spectrofluorometer. The refractive indices of various dilute solutions for sodium D line were determined using Abbe's refractometer. The dielectric constants of the dilute solutions were measured in a suitably fabricated cell of usually small capacitance where the accurate determination of small changes in the capacitance would be possible. The small capacitance can be measured with the help of FT 6421 LCR data bridge at 10 kHz frequency. The dielectric sample holder consists of two concentric brass cylinders kept in position with small strips (to achieve electric isolation) and their leads

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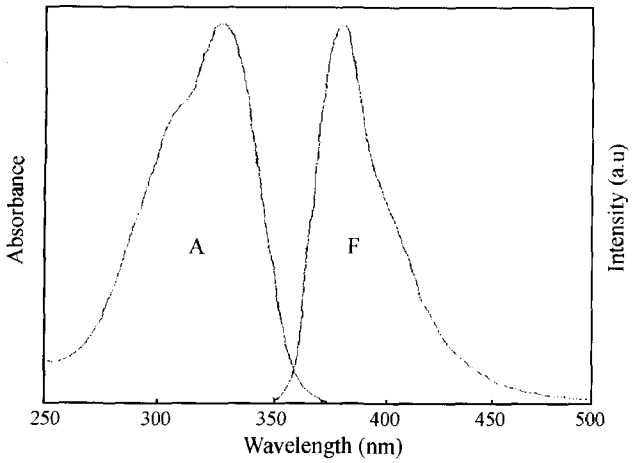

Figure 1.

are coated with gold. This assembly is kept in a glass beaker, so that the dilute solution can be filled into the cell. The capacitance of the empty cell is of the order of picofarads.

The UV absorption spectra (for S_1 band) of the exalite dyes were recorded in cyclohexane, benzene, ethylether, dimethyl formamide, aniline, acetonitrile, butanol, methylcyclohexane, acetone and dioxane solvents (spectroscopic grade). Typical absorption and fluorescence spectra for E389 in cyclohexane are given in Figure 1. The absorption and fluorescence data are presented in Table 1. The permanent dipole moments in the excited state (μ_e) and the radius of the cavity in which the solute molecule is supposed to lie are obtained as follows [14] : the change in the permanent dipole moment for a series of solvents of different static dielectric constant (ε) but similar refractive index (n) is related to the observed energy shift $\Delta\nu_{a\text{-}b}$ between solvents a and b by

$$-\Delta\nu_{a\text{-}b}=(\mu_e^* \Delta\mu_{g\text{-}e}/hca_g^3)\{\Delta[f(\varepsilon)-f(n^2)]_{a\text{-}b}\} + (\mu_e^2-\mu_g^2/hca_g^3)\Delta f(n^2)_{a\text{-}b} \quad (1)$$

where μ_g is the permanent dipole moment in the ground state, h is Planck's constant, c is velocity of light, a_g is radius of the cavity in which solute molecule is supposed to lie and $f(\varepsilon)$ and $f(n^2)$ are polarity and polarizability functions defined as

$f(\varepsilon)=2(\varepsilon-1)/(2\varepsilon+1)$ and $f(n^2)=2(n^2-1)/(2n^2+1)$, respectively.

Another method [15] to determine μ_e expresses the equation (1) in the form

$$X/C_1+Y/C_2=1 \quad (2)$$

which is an equation of a straight line with intercept on either axes. By plotting the graph between $X(=\Delta[f(\varepsilon)-f(n^2)]_{a\text{-}b}/-\Delta\nu_{a\text{-}b})$ and $Y(=\Delta f(n^2)_{a\text{-}b}/-\Delta\nu_{a\text{-}b})$, the intercepts $C_1(=hca_g^3/\mu_e^*\Delta\mu_{g\text{-}e})$ and $C2(=hca_g^3/\mu_e^2-\mu_g^2)$ on the X and Y axes respectively are determined. The magnitude (μ_e) and direction (θ) are obtained by using the measured values of the static permittivities and refractive indices of solvents and various dilute solutions of the dyes (in benzene) at 10 kHz. Guggenheim's [16,17] modified equations:

$$\mu_g=0.0128[3/(\varepsilon_1+2)^2\times M^2/d_1\times T\times\Delta]^{1/2} \quad (3)$$

where $\Delta=\Delta'-\Delta''=[(\varepsilon_{12}-\varepsilon_1)/W_2]_{w2\to0}-[(n_{12}^2-n_1^2)/W_2]_{w2\to0}$

and $$\mu_g=0.0128\{3/(\varepsilon_1+2)^2\times M^2/d_1\times T \times 0.97[(\varepsilon_{12}-\varepsilon_1)/W_2]_{w2\to0}\}^{1/2} \quad (4)$$

are used to determine excited state dipole moments (μ_e). These are accurate up to second decimal place. The estimated errors in the present study, in the determination of ε and n are of the order of 5% and 1% respectively, and the values of μ are accurate within 10%. Here n, d, M, W and T denote refractive index, density, molecular weight, weight fraction and absolute temperature respectively. The suffixes 1, 2 and 12 refer to the solvent, solute and solution, respectively.

The dielectric constants, refractive indices and ground state dipole moments of all the four dyes are presented in Table 2. The values of X, Y, C_1 and C_2 are given in Table 3. The magnitude and orientation of the dipole moment for the excited state along with the corresponding ground state dipole moment values are given in Table 4. It is observed that the excited state dipole moment values are fairy higher well beyond the possible

Table 1. Electronic absorption and fluorescence spectral data (cm^{-1}) of the dyes in different solvents

Solvents	E-389			E-392A			E-398			E-428		
	ν_{max}	$\Delta\nu$	ν_{fmax}	ν_{max}	$\Delta\nu$	ν_{fmax}	ν_{max}	$\Delta\nu$	ν_{fmax}	ν_{max}	$\Delta\nu$	ν_{fmax}
Cyclohexane	30102	Ref	26041	30211	Ref	26028	29498	Ref	25316	27777	Ref	24681
Benzene	30026	76	25839	30084	127	25707	29585	-87	25157	27686	91	23392
Ethylether	30075	27	25974	30138	73	25906	29446	52	25380	28011	-234	24600
DMF	29891	211	25773	29785	426	25707	29069	429	25062	27530	249	23310
Aniline	29550	152	*	29550	661	*	28868	630	*	27412	365	*
Acetonitrile	30093	9	25839	30156	55	25853	25924	-26	25252			23518
Butanol	30030	72	25806	30147	64	25839	29558	-60	25284	27675	102	23640
Methyl-cyclohexane	30102	4	26178	30266	-55	25974	29515	-17	25413	27781	-4	23612
Acetone	30087	15	25906	30120	91	25839	29516	-18	25252	--	--	23529
Dioxane	30012	90	25974	30102	109	25906	29472	26	25316	27761	16	24630

*no fluorescence

Table 2. Dielectric constants and refractive indices of the laser dyes in benzene at 25± 1°C (d_1=0.864, ε_1=2.278, n_1=1.4970)

Dye	Mole.wt (M_2)	Wt.fraction. ($W_2\times 10^3$)	Dielectric const (ε_{12})	$\frac{\varepsilon_{12}-\varepsilon_1}{W_2}$	Refractive index(n_{12})	$\frac{n_{12}^2-n_1^2}{W_2}$	Intercepts			Calculated μ_g in D	
							Δ'	Δ''	Δ	Eqn(3)	Eqn(4)
E-389	463	1.1560	2.2871	7.8460	1.4979	2.3316	7.6613	2.3996	5.2617	4.7504	5.6455
		2.3041	2.2966	8.1162	1.4985	1.9501					
		3.4602	2.3073	8.4735	1.4990	1.7317					
		6.8965	2.3403	9.0354	1.4993	0.9992					
		9.1743	2.3654	9.5255	1.4999	0.9473					
E-392A	583	1.1560	2.2859	6.8685	1.4973	0.7767	7.0899	0.7812	6.3087	5.8369	6.0942
		2.3041	2.2930	6.5184	1.4975	0.6515					
		3.4602	2.2990	6.0690	1.4978	0.6924					
		6.8965	2.3148	5.3458	1.4983	0.5646					
		9.1743	2.3217	4.7622	1.4985	0.4897					
E398	867	1.1560	2.2848	5.8823	1.4972	0.5190	6.1648	0.5133	5.6514	6.7369	6.9299
		2.1942	2.2905	5.6467	1.4974	0.5459					
		3.2300	2.2961	5.1083	1.4976	0.5563					
		6.8965	2.3070	4.2093	1.4983	0.6080					
		9.1734	2.3115	3.6515	1.4989	0.6204					
E428	1012	1.1560	2.2813	2.8374	1.4973	0.8897	2.9331	0.8894	2.0437	4.3769	5.1643
		2.3041	2.2840	2.6171	1.4977	0.9098					
		3.4602	2.2806	2.4806	1.4981	0.9521					
		6.8965	2.2918	2.0155	1.4992	0.9558					
		11.4416	2.2953	1.5120	1.5008	0.9956					

Table 3. Values of X and Y, intercepts and molecular radius (a_g) of dyes

Solvents	E-389		E-392A		E-398		E-428	
	$X\times 10^4$	$Y\times 10^4$	$X\times 10^4$	$Y\times 10^4$	$X\times 10^4$	$Y\times 10^4$	$X\times 10^4$	$Y\times 10^4$
Benzene	1.1210	6.2118	0.6708	3.7173	-0.9793	-5.4426	0.9362	5.1879
Ethylether	124.6500	-19.3666	46.1068	-7.1630	64.7269	-10.0554	14.3837	2.2346
DMF	26.1398	0.1256	12.9471	0.0622	12.856	0.0617	22.1506	0.1064
Aniline	19.6026	6.1210	4.5077	1.4075	4.7295	1.4768	8.1639	2.5490
Acetonitrile	681.5110	-64.7880	111.5200	-10.6018	-235.9000	22.4269	–	–
Butanol	73.7416	-2.5527	82.9590	-2.8715	-88.4900	3.0632	52.0529	-1.8019
Methyl-cyclohexane	3.2500	-5.2500	-0.8666	1.3400	-0.7647	1.1823	-3.2500	5.0225
Acetone	380.5666	-31.3840	62.7307	-5.1732	-317.3800	26.1536	–	–
Dioxane	4.8333	-0.2977	3.9908	-0.2458	16.7307	-1.0307	27.1875	-1.6750
Intercepts :								
C_1	22.1016×10^4		13.6027×10^4		16.6051×10^4		27.7644×10^4	
C_2	1.7745×10^4		1.3729×10^4		1.2360×10^4		4.1745×10^4	
Molecular Radius (a_g) :	4.7706 Å		5.2579 Å		6.0271 Å		6.1462 Å	

Table 4. Ground state and excited state dipole moments

Compound	Eqn.No	μ_g in D	μ_e in D	θ (in °)
E-389	3	4.75	12.00	76°
	4	5.65	12.39	73°
E-392A	3	5.84	15.63	81°
	4	6.09	15.73	81°
E-398	3	6.74	19.93	81°
	4	6.93	19.99	80°
E-428	3	4.38	11.39	87°
	4	5.16	11.71	80°

errors when compared to the values obtained using Guggenheim's equation for the ground state. The orientation (θ) in all the cases lies the first quadrant and does not vary except for the case of E-389 and E-428. The very method of calculation (vector addition of group moment) has its own limitation of not accounting for the possible inductive/hydrogen bonding effect in these systems. Under the circumstances if it is assumed that these values would not improve much when bonding effects are also taken into account, the presently observed dipole moment values remain high [18].

In the present study the excited state dipole moment values are certainly greater than the ground state values. Based on these observations, it may be presumed that the observed transition belongs to $\pi^* \leftarrow \pi$.

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