Influence of Environment on the Electronic Spectra of Donor-Acceptor-Substituted trans-Stilbenes in Solvent Mixtures*

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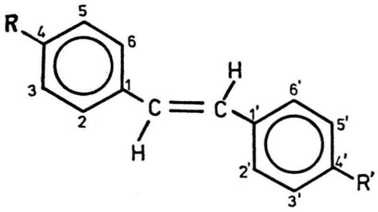
The effect of n-heptane and n-butanol mixtures upon the absorption and fluorescence spectra of donor-acceptor-substituted trans-stilbenes is investigated. The electronic-vibration spectra of these compounds depend upon the magnitude of the electric dipole moments in the ground and excited states, upon the relation between the mean lifetime τ_f^w and the time of dielectric relaxation τ_R, and upon the environment around the solute molecule.

1. Introduction

The vibronic absorption and fluorescence spectra of molecules with persistent electric dipole moments in binary solvents (nonpolar (I) + polar (II)) at room temperature indicate heterogeneous spatial structure of such solutions. Due to mutual orientational dipole-dipole interactions the solute molecules are surrounded mainly by the polar solvent molecules, which affects substantially the local (effective) dielectric constant. With increasing temperature however, the spatial distribution of the solvent molecules becomes more homogeneous. The electronic excitation of the solute is usually accompanied by a change in the electric dipole moment, which in turn causes a rebuilding of the solvent shell of the solute. This rebuilding is influenced by the rate of translational diffusion of the solvent molecules and by the mean lifetime of the solute. Multicomponent solutions of this type were the object of previous experimental and theoretical studies [1–17].



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In the present paper, the effect of binary solvents (n-heptane (I) + n-butanol (II)) upon the electronic spectra of strongly polar donator-acceptor-substituted trans-stilbenes **1** at 20 °C is investigated.

2. Experimental

The substances investigated were synthetized by Gloyna [18]. n-Heptane and n-butanol were of uvasol-quality. The absorption spectra were measured on a Beckman Model 25 spectrophotometer, the emission spectra with an instrument described previously [19].

3. Results and Discussion

The electric dipole moments in the ground (S_0) and excited (S_1) state, μ_g and μ_e respectively, increase with increasing electron-acceptor properties of R′, with the donor substituent ($-N(CH_3)_2$) remaining unchanged. The shift of the fluorescence band maxima ($\tilde{\nu}_F$) in binary solvents (n-heptane (I) + n-butanol (II)), amounting to 5000 and 6000 cm^{-1} for **1m** and **1l** respectively, results from high μ_e combined with a relatively long mean lifetime τ_f^w of these molecules in the excited state S_1 (Fig. 1 and Table 1). On the other hand, $\tilde{\nu}_F$ shifts significantly less for the remaining compounds, although μ_e is 2–3 times higher than μ_g. In this case, the mean lifetime, τ_f^w of the molecules is much shorter than 1 ns and comparable with the dielectric relaxation times τ_R of the solvent dipole orientation. In some cases the values of τ_f^w are substantially in-

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* Carried out under problem MR.I.5.

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Table 1.

Nr.	R	R′	μ_g	μ_e	τ_f^w (in 10^{-12} s) from [18, 22]			
			in Debye[a] from [20, 21]		n-heptane $\varepsilon_M = 1.918$[c]	benzene $\varepsilon_M = 2.27$	n-butanol $\varepsilon_M = 17.75$	dimethyl-formamide $\varepsilon_M = 36.7$
1m	NH_2	NO_2	6.5	20.7	—	2250	2360	—
1l	$N(CH_3)_2$	NO_2	7.2	23.1	—	2780	2680	—
1g	$N(CH_3)_2$	CN	6.95	22.3	130	—	900	—
1b	$N(CH_3)_2$	$Ph_2P(O)$[b]	7.5	20.1	160	—	370	—
1h	$N(CH_3)_2$	Br	5.6	15.2	180	—	280	—
1i	$N(CH_3)_2$	Cl	5.6	13.9	250	—	—	300
1j	$N(CH_3)_2$	F	5.4	13.4	400	—	—	420
1k	$N(CH_3)_2$	OCH_3	4.1	10.3	980	—	—	590

[a] 1 Debye $= 3.33 \times 10^{-30}$ A · s · m; [b] Ph $= C_6H_5$; [c] ε_M — measured dielectric constant.

fluenced by the solvent (e.g. **1g**, **1k**), and the equilibrium between the solute in the excited state and the environment is not attained, the fluorescence then starting from an intermediate state between the Franck-Condon and the equilibrated state.

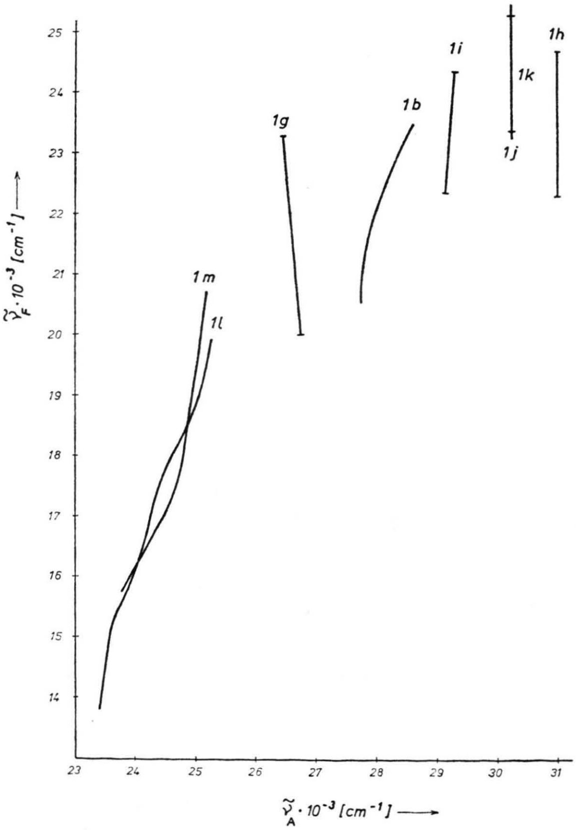

Fig. 1. Fluorescence shifts $\tilde{\nu}_F$ vs, absorption shifts $\tilde{\nu}_A$ of donor-acceptor-substituted trans-stilbenes **1** (see Table 1) in n-heptane — n-butanol mixtures at 20 °C for different mole fractions X.

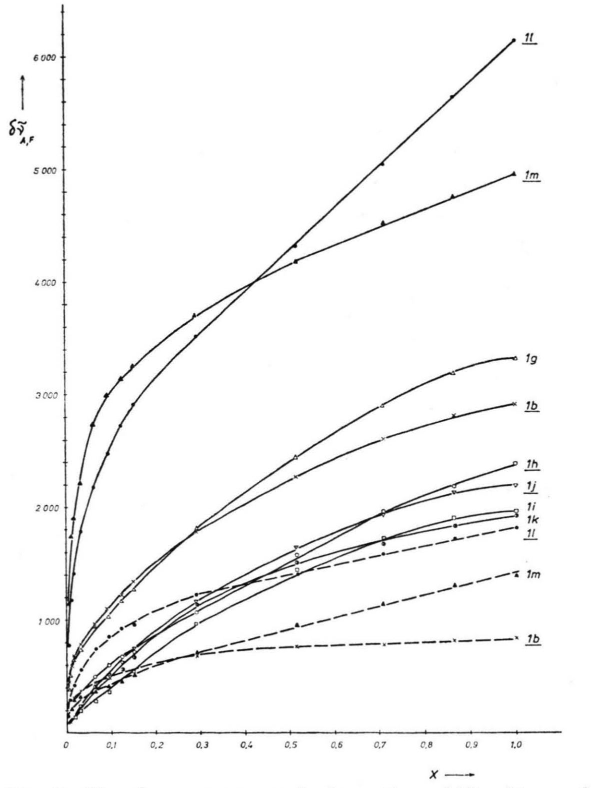

Fig. 2. The fluorescence- and absorption shifts $\delta\tilde{\nu}_{A,F}$ of donor-acceptor-substituted trans-stilbenes **1** (see Table 1) in n-heptane — n-butanol mixtures for different mole fractions X.

In order to determine quantitatively the local dielectric constant $\langle\varepsilon_l\rangle$, the well-known equation $\delta\tilde{\nu}_{A,F} = \Delta\tilde{\nu}^{I}_{A,F} - \Delta\tilde{\nu}^{I+II}_{A,F} = C_{A,F} \cdot f(\langle\varepsilon_l\rangle, n)$ [12]*,

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* The constants $C_{A,F}$ are associated with μ_g, μ_e and the Onsager radius a. $n = n_I = n_{II}$ is the refraction index of the solvent mixture,

$$f(\langle\varepsilon_l\rangle, n) = \frac{2n^2+1}{n^2+2}\left(\frac{\langle\varepsilon_l\rangle - 1}{\langle\varepsilon_l\rangle + 2} - \frac{n^2-1}{n^2+2}\right).$$

which connects the relative shifts of the absorption and fluorescence bands in mixed solvents with $\langle \varepsilon_l \rangle$, can be applied, but only with molecules **1m** and **1l** where total equilibrium between the solute molecule and the environment is attained.

Figure 2 shows the relative shifts $\delta\tilde{\nu}_{A,F}$ for the compounds under examination as functions of the molar ratio X of n-butanol in n-heptane. Marked shifts $\delta\tilde{\nu}_A$ were observed only for **1m**, **1l** and **1b**, but they were substantially smaller than $\delta\tilde{\nu}_F$. For the remaining trans-stilbene derivatives, the shift of the broad absorption band was negligible, so that the maxima of the absorption bands could not be determined precisely in individual mixtures of n-heptane and n-butanol. Figure 3 shows exemplary plots of the measured ε_M and the local dielectric constant in the ground ($\varepsilon_l{}^A$) — and excited ($\varepsilon_l{}^F$) state. A substantial change of $\varepsilon_l{}^F$, compared to $\varepsilon_l{}^A$, can be observed, which is due to a significant change in the dipole moment $\Delta\mu = \mu_e - \mu_g$, during the $S_0 \rightarrow S_1$ transition.

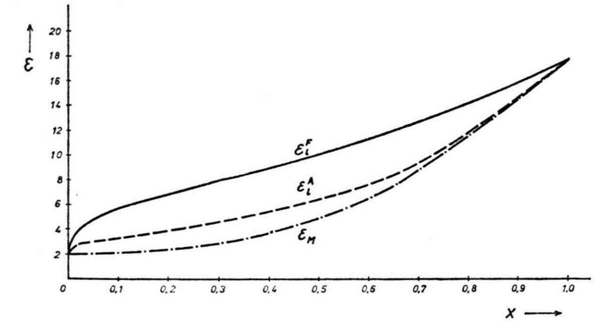

Fig. 3. Measured ε_M and effective dielectric constants in the ground $\varepsilon_l{}^A$ and excited $\varepsilon_l{}^F$ states of **1m** in n-heptane — n-butanol mixtures for different mole fractions X.

Knowing $\varepsilon_l^{A,F}$ one can find the filling-up degree of the solvent shell with the polar solvent molecules [12]. Apart from monomers, also associated molecules (dimers and tetramers) are formed in n-butanol [23, 24], therefore the estimation of the filling-up degree is improper in this case, as the geometric dimensions of the molecules of n-heptane and n-butanol consisting of monomers and associated molecules, differ remarkably.

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