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 $\tau_f^w$ and the time of dielectric relaxation $\tau_R$, 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. Multi-component solutions of this type were the object of previous experimental and theoretical studies [1—17].

In the present paper, the effect of binary solvents (n-heptane (I) + n-butanol (II)) upon the electronic spectra of strongly polar donor-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, $\mu_g$ and $\mu_e$ 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 ($\lambda_F$) in binary solvents (n-heptane (I) + n-butanol (II)), amounting to 5000 and 6000 cm$^{-1}$ for 1m and 11 respectively, results from high $\mu_e$ combined with a relatively long mean lifetime $\tau_f^w$ of these molecules in the excited state $S_1$ (Fig. 1 and Table 1). On the other hand, $\lambda_F$ shifts significantly less for the remaining compounds, although $\mu_e$ is 2—3 times higher than $\mu_g$. In this case, the mean lifetime, $\tau_f^w$ of the molecules is much shorter than 1 ns and comparable with the dielectric relaxation times $\tau_R$ of the solvent dipole orientation. In some cases the values of $\tau_f^w$ are substantially in-
Table 1.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>R</th>
<th>R'</th>
<th>$\mu_g$</th>
<th>$\mu_e$</th>
<th>$\tau_F$ (in $10^{-12}$ s) from [18, 22]</th>
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</thead>
<tbody>
<tr>
<td>1m</td>
<td>NH$_3$</td>
<td>NO$_2$</td>
<td>6.5</td>
<td>20.7</td>
<td>—</td>
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<tr>
<td>1l</td>
<td>N(CH$_3$)$_2$</td>
<td>NO$_2$</td>
<td>7.2</td>
<td>23.1</td>
<td>2250</td>
</tr>
<tr>
<td>1g</td>
<td>N(CH$_3$)$_2$</td>
<td>CN</td>
<td>6.95</td>
<td>22.3</td>
<td>2780</td>
</tr>
<tr>
<td>1b</td>
<td>N(CH$_3$)$_2$</td>
<td>Ph$_2$P(O)$_b$</td>
<td>7.5</td>
<td>20.1</td>
<td>130</td>
</tr>
<tr>
<td>1h</td>
<td>N(CH$_3$)$_2$</td>
<td>Br</td>
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<td>15.2</td>
<td>160</td>
</tr>
<tr>
<td>1i</td>
<td>N(CH$_3$)$_2$</td>
<td>Cl</td>
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<td>13.9</td>
<td>180</td>
</tr>
<tr>
<td>1j</td>
<td>N(CH$_3$)$_2$</td>
<td>F</td>
<td>5.4</td>
<td>13.4</td>
<td>250</td>
</tr>
<tr>
<td>1k</td>
<td>N(CH$_3$)$_2$</td>
<td>OCH$_3$</td>
<td>4.1</td>
<td>10.3</td>
<td>400</td>
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$\mu_g$ in Debye from [20, 21]

<table>
<thead>
<tr>
<th></th>
<th>n-heptane</th>
<th>benzene</th>
<th>n-butanol</th>
<th>dimethylformamide</th>
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<tbody>
<tr>
<td>$\epsilon_M$</td>
<td>1.918</td>
<td>2.27</td>
<td>17.75</td>
<td>36.7</td>
</tr>
</tbody>
</table>

$\epsilon_M$ — measured dielectric constant.

Fig. 1. Fluorescence shifts $\delta F$ vs. absorption shifts $\delta A$ of donor-acceptor-substituted trans-stilbenes 1 (see Table 1) in n-heptane — n-butanol mixtures at 20 °C for different mole fractions X.

In order to determine quantitatively the local dielectric constant $\langle \epsilon \rangle$, the well-known equation

$$\delta F_{A,F} = A_F \langle \epsilon \rangle - A_F^{II} \langle \epsilon \rangle = C_{A,F} f(\langle \epsilon \rangle, n) [12]$$

* The constants $C_{A,F}$ are associated with $\mu_g$, $\mu_e$, and the Onsager radius $a$. $n = n_1 = n_2$ is the refraction index of the solvent mixture,

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

Fig. 2. The fluorescence- and absorption shifts $\delta F_{A,F}$ of donor-acceptor-substituted trans-stilbenes 1 (see Table 1) in n-heptane — n-butanol mixtures for different mole fractions X.
which connects the relative shifts of the absorption and fluorescence bands in mixed solvents with $\langle \varepsilon \rangle$, can be applied, but only with molecules 1m and 11 where total equilibrium between the solute molecule and the environment is attained.

Figure 2 shows the relative shifts $\delta \varepsilon_A, F$ for the compounds under examination as functions of the molar ratio $X$ of n-butanol in n-heptane. Marked shifts $\delta \varepsilon_A$ were observed only for 1m, 11 and 1b, but they were substantially smaller than $\delta \varepsilon_F$. 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 $\varepsilon_M$ and the local dielectric constant in the ground ($\varepsilon_1^A$) — and excited ($\varepsilon_1^F$) state. A substantial change of $\varepsilon_1^F$, compared to $\varepsilon_1^A$, 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.

Knowing $\varepsilon_1^{A,F}$ one can find the filling-up degree of the solvent shell with the polar solvent molecules.