Some Luminescence Properties of the Laser Dye Stilbene 3

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Absorption and emission spectra of stilbene 3 (Na-bis-ortho-stilbene-sulphonate) were measured and discussed on the basis of quantum-chemical calculations. The decay of the polarized fluorescence was investigated, yielding information about the rotational behaviour of stilbene 3 in solutions.

1. Introduction

Dye laser materials should be resistent to photodecomposition and should have a high quantum yield and good thermal stability. In the blue-violet lasing region, scintillator and coumarin dyes are often used. A new class of laser dyes in this spectral region are the bis-styryl compounds [1, 2, 3]. Stilbene 3 (Na-bis-ortho-stilbene sulphonate) in particular is a highly efficient photostable dye, soluble in water and alcohols. Strong absorption in the wavelength region of 300—380 nm makes this dye suitable for excitation which N_2-pulse and Ar-cw lasers.

With this dye, we obtained tunable laser action generating single spikes of less than 450 ps fwhm duration in ethylene glycol-methanol solutions excited with a subnanosecond compact TEA N_2 laser [4] of only 10 μJ pulse energy but 200 Hz repetition rate. It should be emphasized that no laser action could be obtained under these conditions for rhodamine 6G or 4-methylumbelliferone solutions. These favourable properties of stilbene 2 motivated us to study its spectral characteristics along with the decay and polarization of its fluorescence, as well as to perform some relevant quantum-chemical calculations for this molecule.

2. Quantum-Chemical Calculations

We applied the PPP method with the Mataga-Nishimoto integral approximation. In the CI calculations, all those configurations which are symmetry allowed in the first singlet excited state, were included. The geometrical model shown in Fig. 1 was used. The stilbene-like parts were taken to be planar with bond lengths 0.14 nm and 0.148 nm in the benzene rings and between the ethylene carbon atoms and benzene rings, respectively. We assumed the length of the ethylenic bonds to be 0.135 nm and all angles 120°. For a justification of these assumptions see Ref. [5]. In contrast to [3], the trans-configuration of the whole molecule was assumed because of the repelling interaction between the two sulphonate groups, which carry a negative charge on their oxygen atoms.

The length of the central bond between the two stilbene-like parts was assumed to be 0.15 nm, and two values for the twisting angle Θ around this

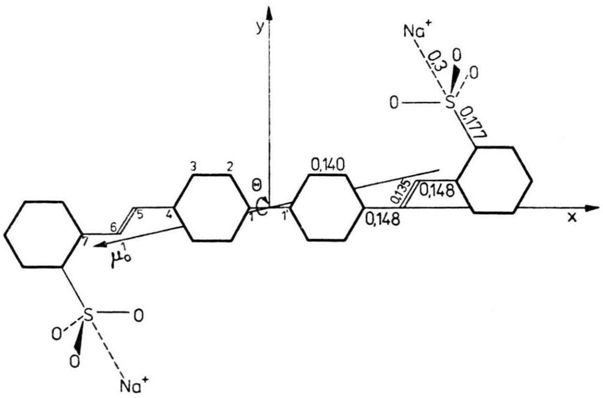

Fig. 1. Geometrical model of stilbene 3 with $\Theta = 0°$. Bond lengths are given in nm.

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bond were considered: 45° for the ground state conformation and 0° for the first excited state, by analogy with biphenyl [6]. Geometry-dependent resonance integrals β_{rs} between carbon atoms were used as follows:

$$\beta_{\mathrm{rs}}(\Theta) = \beta_0 \cos\Theta ,$$

$$\beta_{\mathrm{rs}}(R_{\mathrm{rs}}) = \beta_0 \exp(-18.62\, R_{\mathrm{rs}}) + 2.597 ,$$

with R_{rs} in nm. Provision was made for the inclusion of pΠ-dΠ interactions within the tetrahedrally hybridized sulphonate group (see for example [7]): d_{z^2} and $\mathrm{d}_{x^2-y^2}$ orbitals are especially suitable for Π interactions, which were therefore included in the PPP calculations taking the sulphur atom to be located in the stilbene plane.

It should be mentioned that stilbene 3 is a dianion and Na^+ does not form ion pairs with it, as indicated by the the high conductivity of stilbene 3 water and glycerol solutions. Nevertheless it is important to take the interaction of these charges into account. If this interaction is neglected, much too low excitation energies are obtained. The strong influence of the position of positive charges with respect to the sulphur atom can be interpreted as a field effect operating differently in the ground and excited states. This difference is connected with a slight charge shift from the oxygen atoms to sulphur and carbon atoms in the first excited state, although the charge of the whole sulphonate group remains constant. The results presented in this work were calculated with two positive charges placed about 0.3 nm from the sulphur atoms, in line with the C–S bonds. Table 1 contains the parameters used in our calculations. For comparison, calculations using the same parametrization were performed for Na-ortho-stilbene-sulphonate and other stilbenes [8]. The results of our calculations concerning the energies and transition moments are shown in Table 2.

Table 1. Parameters for the PPP calculations.

Π-atom X	$I_{\mathrm{p}}(\mathrm{X})$[a]	N_Π[b]	γ_{XX}[c]	K_{CX}[d]	r_{CX} [nm]
$-\mathrm{C}<$	9.84	1	10.53	1.0	see text
$-\mathrm{O}$	17.70	1	15.23	1.1	0.144
$-\mathrm{S}-$	1.60	1	1.80	0.7	0.177

[a] valence state ionization potential in eV (for the $\mathrm{CH_3}$ radical the value for the carbon atom is assumed).
[b] number of Π electrons per atomic orbital.
[c] one center two electron integral in eV.
[d] factor for $\beta_{\mathrm{CX}} = \beta_0\, K_{\mathrm{CX}}$ with $\beta_0 = 2.318$ eV.

Table 2. Calculated properties of the ground and first excited singlet states of stilbene 3, Na-ortho-stilbene sulphonate and stilbene.

Stilbene 3 twisting angle			Na-ortho-stilbene sulphonate	Stilbene
Θ	0°	45°		
$\Delta E/f$[a]	30.11/2.25	31.57/2.21	32.83/1.04	33.65/1.14
$\lvert\vec{\mu}_0{}^1\rvert$[b]	2.63	2.54	1.71	1.71
$\sphericalangle(\mu_0{}^1, x)$[e]	167	166	165	167
$\sphericalangle(\mu_0{}^1, y)$	103	103	105	103
$\sphericalangle(\mu_0{}^1, z)$	90	85	90	90
$Q(\text{-SO}_3)$[c]	−1.00	−1.00	−1.03	—
$Q^*(\text{-SO}_3)$	−1.00	−1.00	−0.99	—
$P_{1,1'}$[a]	0.28	0.20	—	—
$P^*_{1,1'}$	0.40	0.30	—	—
$P_{6,7}$	0.30	0.30	0.31	0.37
$P^*_{6,7}$	0.38	0.40	0.53	0.58
$P_{5,6}$	0.90	0.90	0.90	0.86
$P^*_{5,6}$	0.77	0.75	0.58	0.50

[a] S_0-S_1 transition energy [10^3 cm^{-1}]/oscillator strength.
[b] transition moment [Debye].
[c] charge of sulphonate group.
[d] bond orders in the ground and excited (*) state (for numbering of atoms see Figure 1).
[e] for the coordinate system *xyz* cf. Figure 1.

Some interesting features of stilbene 3 are evident from the results presented in Table 2. Thus, if we were treating stilbene 3 like a dimer of two non-overlapping Na-ortho-stilbene-sulphonate monomers M, we should obtain a doubled value of the transition moment to the excited state

$$^1\Psi^* = \frac{1}{\sqrt{2}}\left(\Psi_{\mathrm{M1}}\Psi^*_{\mathrm{M2}} - \Psi^*_{\mathrm{M1}}\Psi_{\mathrm{M2}}\right),$$

because of the tail to tail arrangement of the two monomer transition dipoles [9].

The somewhat lower value actually obtained is connected with the overlap of the two monomer electronic wavefunctions. It should be mentioned that the first excited state is characterized by a HOMO → LUMO orbital transition and leads to a more quinoidal structure, as in the case of stilbene. The changes of bond orders confirm this conclusion. An especially interesting feature of stilbene 3 is the strengthening of the central bond 1–1 in the excited state.

This supports the assumed analogy with biphenyl.

3. Absorption and Emission Spectra

A sample of stilbene 3, received from Dr. R. Raue, was used without further purification in the solvents ethylene glycol, glycerol (5% aqueous), water and methanol. Special care was taken to avoid any fluorescence of the solvente themselves. At the concentration 2×10^{-5} M the optical density did not exceed 0.2. In the absorption spectra of stilbene 3 in water and ethylene glycol (Fig. 2.) one observes a pronounced shift between these two absorption curves. The absorption spectra measured in water and methanol are practically the same, as is also the case for glycerol and ethylene glycol. The observed solvent shift cannot be explained by different dielectric influences. The only parameter of the solvents apparently correlated with the shift is the viscosity, but we cannot provide any explanation of this phenomenon.

The calculated electronic transition energies and relative oscillator strengths are also compared with the experimental spectra in Figure 2. For charge-sulphur atom separations within the range of 0.22 to 0.35 nm, the three absorption bands agree qualitatively with the calculated allowed electronic transitions. The agreement for these transitions is best at about 0.3 nm. The other properties did not change significantly within this range.

The emission spectra were measured in glycerol, in ethylene glycol and in a 1 : 1 water-ethylene glycol mixture at different temperatures and excitation wavelengths. A "Spectrim" (CTi-Cyrogenics) sample cooler was used to attain the low temperatures. Some of the emission spectra obtained are also shown in Figure 2. It is evident that the absorption and emission spectral overlap is small. A characteristic feature of the emission spectra is the pronounced vibrational structure contrasting with the structureless absorption profiles. This phenomenon may be understood in terms of the angular orientation of the two stilbene-sulphonate moieties connected by a biphenyl-like bond. There is a strong analogy to the case of biphenyl [10]. As is well known, this molecule is planar in its first excited state but twisted in the ground state by 42° [11].

The emission spectra of stilbene 3 in glycerol for different temperatures and excitation wavelengths are shown in Figure 3. At 340 K the emission spectra are red-shifted, practically independent of the excitation wavelength and broader than the spectra measured at 80 K. At this lower temperature the

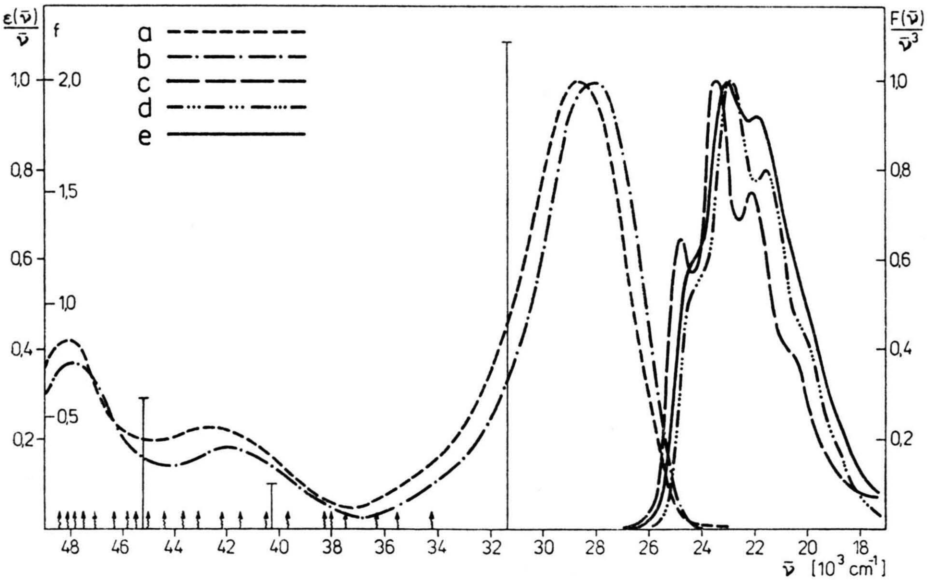

Fig. 2. Normalized absorption and emission spectra of stilbene 3 under various conditions. Absorption spectra for (a) water and methanol, and (b) ethylene glycol and glycerol solutions at 293 K. Fluorescence spectra for (c) 1 : 1 mixed water and ethylene glycol solutions at (d) 20 K and (e) 293 K. Excitation wavelength: 365 nm. The vertical bars represent the calculated transition energies and oscillator strengths *f* for a charge-sulphur atom separation of 0.2 nm. The arrows indicate transitions forbidden for the plane geometry, slightly allowed for the twisted one.

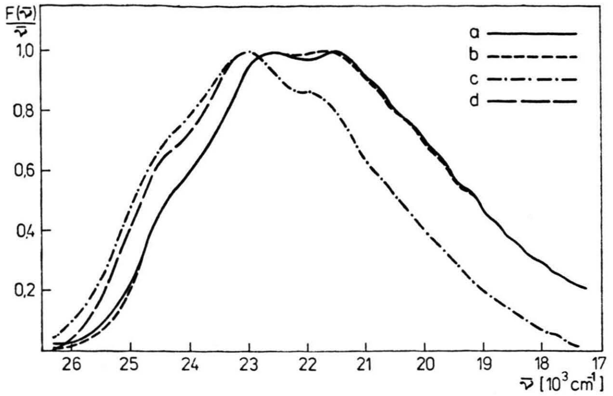

Fig. 3. Fluorescence spectra of stilbene 3 in glycerol at 340 K (a, b) and 80 K (d, d). Excitation wavelengths were 313 nm (a, c) and 365 nm (b, d).

emission excited at 313 nm is broader at the blue edge and less structured in comparison with the emission excited at 365 nm. Besides the observed spectral shift, the temperature change also leads to a change in the relative emission intensities of the vibrational bands. Such a change in the structure of the emission spectra, superimposed upon the spectral shift, indicates that the latter cannot be explained only on the basis of the Onsager-Böttcher theory [12]. We would like to interpret the temperature induced change of the vibrational structure in the following way: the C–C stretching potential in the ground state reaches its minimum at a considerably shorter C–C bond length for the twisted geometry compared with the non-twisted one (repulsion between the ortho-hydrogens [10]. In the excited state, due to the strengthening of the biphenyl-like C–C Π-bond which compensates the repulsion between hydrogen atoms, the twisting potential becomes more flat, and therefore the dependence of the C–C stretching potential minimum on the twisting angle should be small.

At 340 K the relaxation along the twisting angle coordinate enables the vertical emissive transition from the minimum of the twisting potential curve. This relaxation is hindered at 80 K and the transition to the ground state takes place from higher twisting levels to different values of the C–C stretching coordinate in the ground state, i.e., to other vibrational levels. From the above considerations it follows that different vibrational intensities are possible at different temperatures. This model also accounts for the bathochromic shift accompanying the temperature increase.

The excitation wavelength dependence of the emission profile at the blue edge supports the concept of Van Metter and Knox [13]. Basing their treatment on the idea of inhomogeneous broadening introduced by Mazurenko [14], they dealt quantitatively with the excitation wavelength dependence of spectra. According to their theory, such a dependence of the emission spectra should occur if the average lifetime τ_s of the fluctuations in the environment of the solute molecule is longer than the mean fluorescence lifetime τ_f. At 80 K one can safely estimate that τ_s must be orders of magnitude longer than τ_f. This is not so at 340 K, where the inequality $\tau_s \gg \tau_f$ no longer holds and the excitation wavelength dependence of the emission spectra practically disappears.

4. Decay and Polarization of Emission

Due to Brownian rotations of the dye molecule together with its solvation shell, the parallel and perpendicular polarized components of the fluorescence intensity do not decay monoexponentially and their mean decay times are different. As was first shown by Jabłoński [15], the decay of these components is governed by the equations:

$$I^{\parallel}(t) = \frac{I_0}{3}\,(1 + 2\,r_0\,e^{-\varphi t})\,e^{-t/\tau}\,,$$

$$I^{\perp}(t) = \frac{I_0}{3}\,(1 - r_0\,e^{-\varphi t})\,e^{-t/\tau}\,, \tag{1}$$

if one assumes that both the molecular emission and the emission anisotropy (EA) $r(t)$, decay monoexponentially. In Eq. (1), r_0 denotes the limiting EA, i.e. the value observed when the rotational depolarization is negligible, φ is the reciprocal of the rotational correlation time and τ is the mean lifetime of the excited state.

The assumption of the monoexponential decay of the EA, $r(t) = r_0\,\exp(-\varphi t)$ is justified if the dye molecule with its solvation shell rotates isotropically, i.e. if it is effectively spherical or if the absorption and/or emission dipole moment is parallel with the symmetry axis of an effective ellipsoid of revolution. Based upon Eq. (1), Jabłoński derived expressions for the mean decay times of the polarized fluorescence components. If these decay times $\tau^{\parallel}$ and $\tau^{\perp}$ are measured as a function of temperature T and/or viscosity η together with the mean EA $\langle r \rangle$, one is able to calculate the value of r_0 and

$\varphi = kT/\eta\, V$ and finally the effective volume of the dye with its solvation shell V [16]. The decay times of the polarized components and the EA of the fluorescence of stilbene 3 dissolved in glycerol-methanol mixtures were measured by means of a phase-fluorometer and compensation polarimeter, respectively. The viscosity of these mixtures was measured using the Hoeppler viscometer.

The results of these measurements are presented in Table 3 and Figure 4. The quite accurate fit between calculated and measured values of τ''/τ and $\tau^{\perp}/\tau$ means that the assumption of an exponential decay of the EA is justified. We conclude therefore that stilbene 3 molecules, which are of a rather elongated shape, behave in solution like quasi-spherical* particles, which allows us to calculate the effective volume V. The calculated volumes depended on the solvent composition. Since the solvent shell may be considered to arise from solute-solvent interaction, its volume will reflect the magnitude and/or character of this interaction.

The values of the limiting EA are constant at $r_0 = 0.375$ within the limits of experimental error. For a linear oscillator with parallel absorption and emission transition moments, the maximum value of the EA is equal 0.4. The observed difference might be due to an angle δ between absorption and emission transition moments, for which the maximum value of the EA is $r_{\mathrm{f}} = 0.6 \cos^2 \delta - 0.2$.

The value of δ obtained from the quantum-chemical calculations (results in Table 2) is on the order of 1°, leading to $r_{\mathrm{f}} = 0.399$.

It is therefore evident that stilbene 3 in solution undergoes rapid librations which are independent of solvent composition. The average value of the mean decay time τ of total fluorescence is 1 ± 0.05 ns. This short lifetime is advantageous for laser action because, combined with the high

% of alcohol	T [K]	viscosity [cP]	$\langle r \rangle$	τ'' [ns]	τ [ns]	τ^1 [ns]	V [10^{-22} cm^3]	φ [10^7 s^{-1}]
100	313	0.46	0.069	0.94	1.04	1.11	22	430
100	293	0.60	0.092	0.85	0.95	1.04	22	300
80	293	1.57	0.165	0.86	0.98	1.10	20	130
60	293	5.02	0.258	0.89	1.01	1.13	16	50
40	293	32.2	0.328	0.94	0.98	1.06	10	14
20	293	82.2	0.358	0.97	1.02	1.05	10	5
10	293	164.1	0.363	1.01	1.02	1.09	8	3

Table 3. Parameters of thermal rotations of stilbene 3 molecules dissolved in glycerol-methanol mixtures.

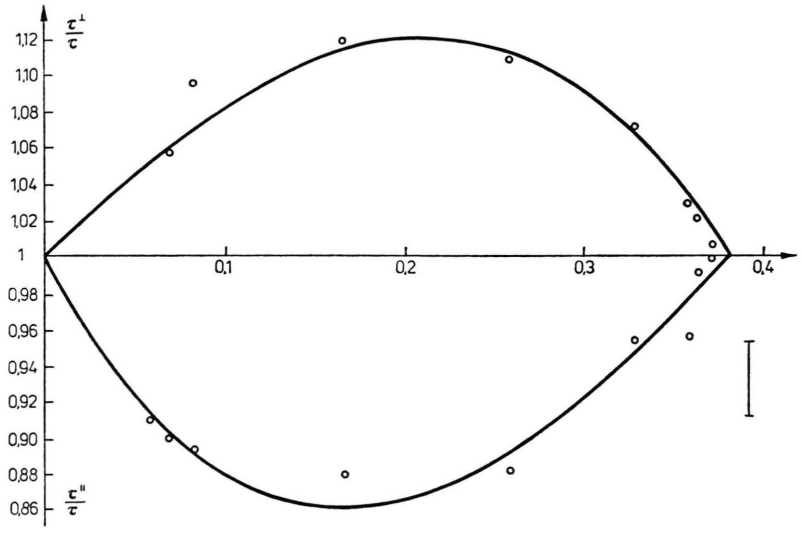

Fig. 4. Mean decay time ratios of polarized fluorescence components for stilbene 3 in mixed glycerol and methanol solvents versus EA. Solid line: values calculated for $r_0 = 0.375$.

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* In our case, for $V = 1.5 \times 10^{-21}$ cm^3 and taking the effective length of the stilbene 3 molecule as about 2 nm (Fig. 1) we estimate an axial ratio of about 1 : 4, assuming a rod-shaped solvation shell. In contrast to this, calculations for the prolate ellipsoid of revolution based on Perrin's formulae [17] lead to an axial ratio value of about 1 which indicates that the solvation shell is effectively spherical.

quantum efficiency of stilbene 3, it implies high radiative deactivation rates and low triplet formation efficiency.

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