Effect of Substituents on the Viscosity Dependence of Fluorescence and on the S_1-T_1 Energy Gap of Donor-Acceptor Substituted Trans-Stilbenes

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The dependence of fluorescence quantum yields and S_1-lifetimes of donor-acceptor substituted trans-stilbenes on temperature was measured in the temperature range from 298 to 100 K, using solutions of stilbenes in 3-methylpentane (3-MP). Measurements of fluorescence and phosphorescence spectra show that the triplet energy is almost independent of the acceptor. The S_1-energy and the S_1-T_1 energy gap decrease with increasing acceptor strength. For all compounds intersystem crossing (ISC) $S_1 \rightarrow T_1$ is negligible.

Key words: Stilbenes, Fluorescence, Phosphorescence, Singlet-Triplet Energy Gap, Rate Constants.

1. Introduction

Trans-stilbene and the donor-acceptor substituted trans-stilbenes show a strong viscosity dependence of the prompt $S_1 \rightarrow S_0$ fluorescence [1, 2, 3] owing to the twisting of the molecule around the ethylenic bond in S_1 that leads to a nonradiative deactivation of the first excited singlet state. In solutions of low viscosity, this twisting is the dominant deactivation channel of S_1. The ability of the molecules to twist around the ethylenic bond decreases with increasing solvent viscosity, and consequently the fluorescence quantum yield Φ increases.

The increased ability of twisting around the ethylenic bond with increasing dipole moment in S_1 is another property of donor-acceptor substituted stilbenes. With increasing electron acceptor strength and with the same donor substituent the charge separation in S_0 and in S_1 is enhanced.

Therefore both the dipole moments of the ground state μ_g and the excited state μ_e increase with increasing acceptor strength. The difference $\Delta\mu = (\mu_e - \mu_g)$ shows a linear dependence on the acceptor strength as well [4]. For a given solvent, these properties lead to a red shift of the (0-0) origin of the steady state fluorescence with increasing acceptor strength.

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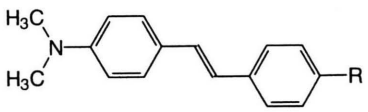

Table I. Hammet constants and dipole moments of Trans-4-dimethylamino-4'-(R)-stilbene from [4]. 1 Debye ≅ 3.34 · 10^{-30} A s m. E_{S_1} was determined as the point of intersection of the normalized corrected excitation and fluorescence spectra of solutions in 3-MP.

	Short names in this paper			
	DCS	DBrS	DClS	DFS
acceptor group R	CN	Br	Cl	F
Hammet constant	0.66	0.23	0.22	0.06
dipole moment in S_1 [D]	22.3	15.2	13.9	13.4
dipole moment in S_0 [D]	7.0	5.6	5.6	5.4
E_{S_1} [cm^{-1}]	24880	26530	26630	27320

In this investigation the following four donor-acceptor substituted stilbenes are examined: Trans-4-dimethylamino-4'-(R)-stilbene. (R) stands for the acceptor groups CN, Br, Cl, and F. The structural formula of the molecules is shown above. In Table 1 the short names used in this investigation and some properties of the stilbenes are summarized.

The present paper has three main objectives:

(i) Investigation of the viscosity dependence of the S_1 lifetimes and quantum yields of prompt $S_1 \rightarrow S_0$ fluorescence. This is of interest regarding the usefullness of stilbenes as a sensor of microviscosity of their

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environment[1]. Quantum yields and time dependences of the prompt $S_1 \rightarrow S_0$ fluorescence were measured in the temperature range from 298 to 100 K using the glass forming solvent 3-MP. It is possible to evaluate quantitative values of the radiative rate constant of fluorescence k_f and of the rate constant of the twisting around the ethylenic bond k_t. k_t is assumed as the only temperature dependent rate constant.

(ii) Examination of the rate constant k_{ISC} of ISC from S_1 to T_1 in comparison to k_f. In particular for DBrS an enhancement of ISC can be expected due to the internal heavy atom effect.

(iii) Examination of the influence of different substituents on the S_1-T_1 energy gap by measuring the spectra of fluorescence and phosphorescence and the determination of the triplet lifetime τ_T.

2. Experimental

Sample Preparation

All compounds were purified by recrystallization. The purity of the compounds was checked by Gloyna[2]. 3-MP (Aldrich) was used, because its temperature dependence of viscosity $\eta(T)$ and refraction index $n(T)$ is well known [5, 6] in the temperature range of interest (298 - 100 K). For all measurements 1 cm quarz-cells were used. Absorption and fluorescence measurements were performed with non-degassed solutions without further purification of the solvent. For the phosphorescence measurements the solvent was destilled and chromatographically purified before sample preparation. Samples were carefully degassed by several pump and freeze cycles.

Absorption

Spectra were recorded with a Lambda 19 (Perkin Elmer) spectrometer.

Fluorescence

Steady state fluorescence spectra were recorded with a commercial fluorescence-spectrometer (Al-

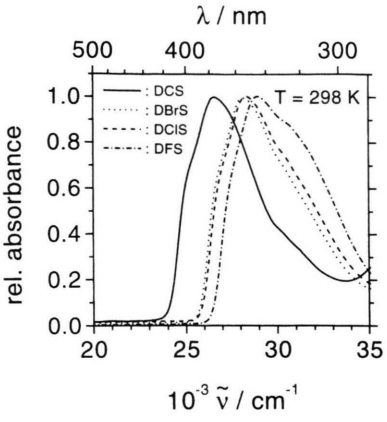

Fig. 1. Normalized absorption spectra of stilbenes in 3-MP at T = 298 K.

phascan, Photon Technology International). Samples were excited at the maximum of the strong $S_0 \rightarrow S_1$ absorption band (see Fig. 1) using a 75 W Xe-lamp and single monochromators both for wavelength separation of the excitation light (bandwith ≅ 4 nm) and the fluorescence light (spectral resolution 3 ≅ nm). The samples were cooled inside an Oxford-cryostat (DN 1704). The temperature was measured and controlled by an autotuning temperature controller (Oxford ITC4) with an accuracy of ± 2 K. The luminescence was detected by a photomultiplier (TP1527, Hamamatsu) and measured with the photon-counting technique. Polarization effects were eliminated by exciting the sample with vertically polarized light and detecting the luminescence with a second polarizer at the magic angle 54.7° relative to the polarization direction of the excitation light beam. Fluorescence quantum yields Φ were determined by the equation

$$\Phi^{sa}(T) = \Phi^{st} \frac{\int_{\lambda=0}^{\infty} I^{sa}(\lambda)\,d\lambda}{\int_{\lambda=0}^{\infty} I^{st}(\lambda)\,d\lambda} \frac{1 - 10^{A^{st}}}{1 - 10^{A^{sa}(T)}} \left(\frac{n^{sa}(T)}{n^{st}}\right)^2, \quad (1)$$

see [7]. $I(\lambda)$ is the corrected intensity of the fluorescence at wavelength λ. The temperature dependence of the refractive index n was taken from [6]. $A = \varepsilon(\lambda)cd$ is the absorbance. Assuming that the concentration c is the only temperature dependent factor, the temperature dependence of the absorbance of the sample was calculated using the temperature dependence of the density $\rho(T)$ of 3-MP from [5]. The absorbance at the excitation wavelength was always

[1] Furthermore, since the transition moments of absorption and emission moments are polarized along the long axis of the molecule, stilbenes are also appropriate as sensors for the degree of order in ordered systems like nematics.

[2] We are thankful to Dr. D. Gloyna, TU Berlin, FB Lebensmittelwissenschaft und Biotechnologie for preparation and purification of the stilbenes.

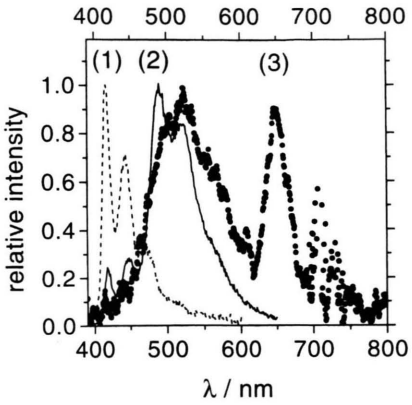

Fig. 2. Emission spectra of DCS in 3-MP at 110 K: (1) Absorbance at 380 nm: < 0.01; spectrally corrected spectrum of the prompt fluorescence. Only the fluorescence from monomers contributes to the spectrum of prompt fluorescence. (2) Absorbance at 380 nm: 0.1; the spectrum of the prompt fluorescence was measured after the sample was kept at 110 K for 2 hours. In addition to the spectrum of monomers a broad, weakly structured and red shifted fluorescence from microcrystals occurs. (3) Absorbance at 380 nm: 0.1; spectrally not corrected delayed luminescence. In addition to the spectrum of phosphorescence (see Fig. 3) the delayed annihilation fluorescence from microcrystals occurs.

lower than 0.1. The indices sa and st stand for sample and standard, respectively. As the fluorescence standard, quinine-sulfat in 0.1 N H_2SO_4 (Φ = 0.54 at 25°C, [8]) was used. The accuracy of the values of Φ at 298 K was estimated to be better than ±25%. The values at lower temperatures are based on the value determined at 298 K.

To avoid the formation of microcrystals, the measurements at sample temperatures below 180 K were performed with solutions with an absorbance smaller than 0.01. Figure 2 shows how the formation of microcrystals influences the spectra of prompt and delayed luminescence.

Fluorescence decay curves were measured using the time correlated single photon counting technique. The excitation light source was a frequency doubled dye laser (701, Coherent) synchroneously pumped by a frequency doubled mode locked Nd: YAG-laser (2 W, 76 MHz) (Antares 76 ML, Coherent). The repetition rate was reduced to 3,8 MHz by a cavity dumper 7200. The samples were excited by pulses of about 5 ps and 355 nm using pyridine 2 as the laser dye. The fluorescence light was dispersed by a subtractive double monochromator (Amko) and detected by a MCP-PMT R3809U (Hamamatsu). The all over instrumental response width using timing electronics from Tennelec and Ortec incl. an 8 k multi channel analyzer is 40 ps. The lifetimes were calculated by the software "Physfit" (Picoquant). Cooling of the sample and elimination of the polarization bias was performed as described above.

Phosphorescence

The excitation light source was a pulsed dye laser (Scanmate, Lambda Physik) pumped by an excimer laser (EMG 50, Lambda Physik) at 308 nm. All samples were excited at 350 nm with a repetition rate of 20 Hz and with an energy of ca. 1 mJ per pulse. The pulse halfwidth was ca. 15 ns. Laser dye was paratherphenyl in dioxane with peak efficiency at 343 nm. Because of the very weak phosphorescence signal, the absorbance of the samples was adjusted to 0.1 at the excitation wavelength. In order to prevent the formation of microcrystals (see Fig. 2), samples were cooled only to 180 K using a "closed cycle cryostat" (Cryo Genics). The prompt fluorescence was suppressed by a fast mechanical chopper with a deadtime of 6 µs between the laser pulse and the full opening of a slit of 2 mm in the luminescence light path. The phosphorescence was dispersed by a spectrograph (500IS/SM, spectral resolution ca. 4 nm) and detected with a nitrogen cooled CCD-camera (Photometrics). The wavelength calibration of the spectrograph was performed with the lines of a mercury lamp. Spectra of phosphorescence are not corrected regarding the spectral sensitivity of the detection system.

For the measurement of phoshorescence decay curves the luminescence light was guided through an interference filter (Schott, 590 nm, halfwidth ca. 20 nm) and detected with a photomultiplier (RCA-C-31034). The decay curves were recorded with a Nicolet 370 signal averager (10 MHz) with a channel dwell time of 1 µs.

3. Results and Discussion

Fluorescence

The absorption spectra in Fig. 1 and the fluorescence spectra in Fig. 3 show that the S_1 energy strongly correlates with the values of the Hammet-constant (see Table 1). However there is practically no difference in the vibrational structure.

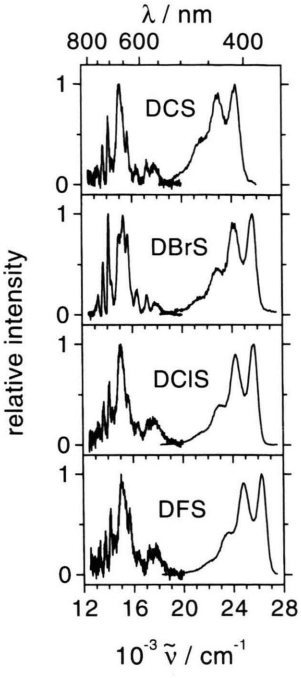

Fig. 3. Spectrally corrected spectra of prompt fluorescence and spectra of phosphorescence (not spectrally corrected) of solutions of stilbenes in 3-MP.

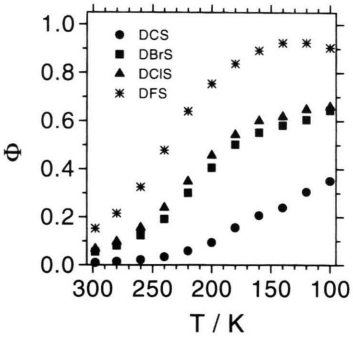

Fig. 4. Temperature dependence of fluorescence - quantum yields of stilbenes in solutions of 3-MP.

In Fig. 4 the temperature dependence of the fluorescence quantum yield Φ is shown. For a given temperature, Φ correlates with the Hammet-constant. All derivatives show a strong temperature dependence in the temperature range between 298 and 150 K, whereas for temperatures below 150 K the temperature dependence of Φ is relatively small, especially for DBrS, DClS and DFS, where Φ asymptotically reaches a constant value. With an activation energy E_g between the fluorescent and the twisted form of

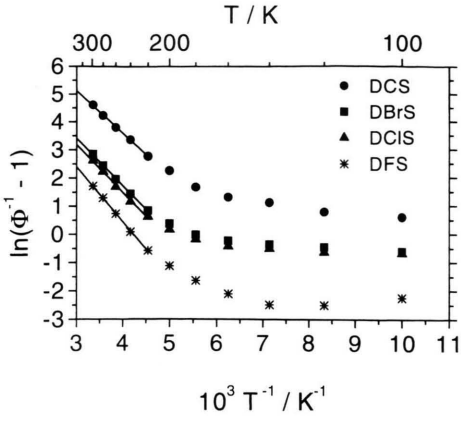

Fig. 5. F(T) plotted in the form of (3).

stilbenes in S_1 the corresponding rate constant k_t is assumed as a monoexponential:

$$k_t(T) = k_t^0 \exp\left(\frac{-E_g}{RT}\right). \tag{2}$$

The temperature dependence of Φ is determined by the equation

$$\Phi(T) = \frac{k_f}{k_f + k_t(T) + k_c}, \tag{3}$$

where k_f is the fluorescence rate constant, and k_c the rate constant describing one or more non-radiative deactivation processes – including intersystem crossing and internal conversion – of trans-stilbenes in S_1. k_f and k_c are assumed independent of temperature. From (2) and (3) follows

$$\ln\left(\Phi^{-1} - 1\right) = \frac{-E_g}{RT} + \ln\left(\frac{k_t^0}{k_f}\right) + \ln\left(\frac{k_c}{k_f}\right). \tag{4}$$

$\ln(\Phi^{-1} - 1)$ is shown in Fig. 5 as a function of T^{-1}. In Table 2 the mean values of k_f are given, which are determined from measurements of $\Phi(T)$ and the fluorescence lifetime $\tau_S(T)$ in the temperature range from 298 to 100 K. k_f was found to be virtually temperature independent for all compounds investigated. Values for E_g are obtained by fitting (4) to the values shown in Fig. 5 in the temperature range from 298 to 220 K. Values of k_c are estimated from (3) neglecting k_t and using the values of k_f and the fluorescence quantum yields at 100 K. Values of k_t^0 are then obtained from the measured fluorescence decay times τ_S at 298 K using the relation $1/\tau_S = k_t + k_f + k_c$.

Table 2. Experimentally determined parameters of solutions in 3-MP. E_{S-T} is the energy of the S_1-T_1 energy gap; E_g and k_t^0 are parameters of the rate constant k_t describing radiationless deactivation of S_1 by twisting around the ethylenic bond (see (2)); k_f is the rate constant of radiative decay of S_1, k_c is the sum of all nonradiative rate constants describing the nonradiative deactivation of S_1, k_f^m the measured rate constant of the fluorescence at T = 298 K, Φ the quantum yield of prompt fluorescence. The error of the value at 298 K is estimated to be ± 25%, the value at 100 K is based on the value at 298 K; $k_T^m$is the measured rate constant of the phosphorescence.

	E_{S-T} [cm^{-1}]	E_g [kJ/mol]	k_t^0 [10^{12} s^{-1}]	k_f [10^8 s^{-1}]	k_c [10^8 s^{-1}]	k_f^m [10^9 s^{-1}] T = 298 K	Φ T = 298 K	Φ T = 100 K	k_T^m [10^4 s^{-1}] T = 180 K
DCS	6580	12.6±0.5	2.9±0.5	1.80±0.20	3.36	18.2	0.010	0.35	7.14
DBrS	8230	13.9±0.5	1.9±0.5	4.25±0.20	2.35	7.6	0.055	0.64	16.66
DClS	8330	14.0±0.5	1.4±0.5	4.40±0.20	2.29	5.4	0.067	0.66	3.85
DFS	9020	16.1±0.5	1.9±0.5	5.73±0.20	0.61	3.4	0.150	0.90	4.17

The values of the different rate constants are listed in Table 2.

It follows from the measurements of the temperature dependence of the fluorescence quantum yields in Fig. 4 that the contribution of k_{ISC} to k_c is negligible, that is the relations $k_{ISC} \ll k_c$ and $k_{ISC} \ll k_f$ hold. This can be deduced from the quantum yields of DClS and DBrS: The spectroscopic and kinetic values of both molecules are almost identical (see Tables 1 and 2). However, from measurements of phosphorescence (see next section) it is confirmed that the relation k_{ISC} (DBrS) > k_{ISC} (DClS) holds. If the values of k_{ISC} of DBrS would have the same magnitude as the value of k_f, the fluorescence quantum yields of DBrS would deviate from the quantum yields of DClS at low temperatures. Contrary to this, $\Phi(T)$ for both molecules is close together and nearly parallel over the whole temperature range.

At low temperatures, where the fluorescence quantum yield reaches its maximum, also the twisting around the ethylenic bond as a deactivation process of S_1 is negligible. Therefore other non radiative deactivation processes are responsible for the deactivation of S_1. These deactivation processes correlate with the acceptor strength.

Phosphorescence

Spectra of phosphorescence are shown in Figure 3. Values of the triplet decay rate constants are listed in Table 2. From the phosphorescence spectra in Fig. 3 follows that – compared to the energy of S_1 – the energy of T_1 does practically not depend on the substituents. This result is in agreement with the results of Alder et al. [9], who measured oxygen-induced $S_0 \rightarrow T_1$ absorption spectra of donor acceptor substituted trans-stilbenes in $CHCl_3$[3]. They determined the triplet energies of donor acceptor substituted trans-stilbenes in the region 17150-17550 cm^{-1}. Taking into account the Stokes-shift between absorption and emission spectrum, these values are in satisfactory agreement with the value of the first emission band of the phosphorescence at ca. 18300 cm^{-1} determined in this investigation. Since the triplet energy is almost independent of the different substituents, the electronic distribution in S_1 and T_1 must differ drastically [9].

The vibrational structure in the phosphorescence spectra is more pronounced than in the fluorescence spectra. Concerning the relative intensities of the vibrational modes, there are some differences between the four spectra. The differences between the phosphorescence of DBrS and the three other compounds are most obvious. For example, the emission in the region from 15000 to 16000 cm^{-1} is more structured and three bands with approximately the same amplitude can be separated, whereas for the three other compounds in this spectral range only one band dominates and the other two are only present as small shoulders. The relative intensity of the band at 14000 cm^{-1}, which for DBrS is greater than for the three other compounds, is another example. The differences between the phosphorescence spectra of DCS, DClS and DFS are smaller. The total intensities of the phosphorescence emissions of DCS, DClS and DFS are approximately of the same order of magnitude, whereas the total intensity of the phosphorescence of DBrS is significantly greater. We think that this results from the greater production of triplet-molecules due to more effective spin-orbit coupling

[3] In their investigation they examined stilbenes with other substituents than those examined in this investigation.

based on the heavy atom effect. This is consistent with the measured triplet lifetime ($\tau_T \cong 6$ µs) of DBrS, which is the shortest one. The relatively short triplet lifetimes are not caused by diffusion controlled quenching of the stilbene triplet by rests of oxygen or by impurities. This is proved by the measurements of the phosphorescence of DCS at 110 K and at 180 K: For both measurements the intensity of the phosphorescence does not change. If impurities would have quenched the triplet, the phosphorescence intensity at 110 K ($\eta \cong 1.7 \times 10^3$ mPa s) would be significantly greater than the intensity at 180 K ($\eta \cong 1.69$ mPa s).

Delayed Fluorescence

The very low intensity of the phosphorescence is one reason for the absence of a delayed fluorescence, that is caused by triplet-triplet annihilation[4]. This means that the triplet state is dominantly deactivated by one or more non radiationless processes, that is the relation $k_{nr}(T_1) \gg k_r(T_1)$ holds. $k_{nr}(T_1)$ symbolizes the sum of rate constants of the non radiative triplet decays and $k_r(T_1)$ is the rate constant of the radiative triplet decay. Moreover, the lack of intersystem crossing is not favourable for the detection of a delayed fluorescence.

4. Outlook

Fluorescence and phosphorescence emissions of the different donor-acceptor substituted stilbenes show a high similarity of the vibrational structure. This shows that the vibrational bands are dominated by vibrational modes of the stilbene framework. Contributions of vibrations of the different substituents play practically no role in the emission spectra in solution.

The relatively well structured bands of the phosphorescence open the possibility to perform a complete vibrational analysis of this emission. By measurements of IR- and Raman-spectra of the stilbenes we hope to attribute the different bands of the phosphorescence to vibrational modes. By that we could determine the (0-0) transition of the phosphorescence with higher accuracy. Experiments are on the way.

Acknowledgement

We are thankful to Dr. B. Nickel (MPI für Biophysikalische Chemie, Göttingen, Germany) for the possibility to measure the phosphorescence spectra in his laboratory and Dr. A. A. Ruth (University College Cork, Cork, Ireland) for critical reading of the manuscript and for valuable comments. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[4] The population of the triplet state T_1 leads to a delayed $S_1 \rightarrow S_0$ fluorescence (DF) of the "pyrene type", which is caused by the non-radiative annihilation of two triplet molecules (triplet-triplet annihilation, TTA) and the following generation of one molecule in S_1 (by internal conversion $S_n \rightarrow S_1$, IC) and one in S_0 [7]:

$$T_1 + T_1 \xrightarrow{TTA} S_n + S_0 \xrightarrow{IC} S_1 + S_0 \xrightarrow{DF} S_0 + S_0 + h\nu.$$

In viscous solutions TTA is a diffusion controlled reaction. The time dependence of the intensity of the delayed fluorescence in its stationary state is proportional to the relative diffusion coefficient D of the two molecules in T_1 and to the fluorescence quantum yield Φ, and proportional to the square of the triplet concentration c_T:

$$I_{DF}(t) \propto D\Phi c_T^2 \propto D\Phi\Phi_{ISC}^2 \exp(-2k_T^m t).$$

k_T^m is the measured rate constant of the phosphorescence decay.

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