

Anisotropic Fluorescence of Donor-Acceptor-Substituted trans-Stilbenes in Solvents of Different Polarities and Low Viscosity*

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The fluorescence anisotropy (FA) and mean lifetime τ_F of substituted trans-stilbenes was investigated at 293 K in the nonpolar and polar low viscosity solvents n-heptane, toluene, acetonitrile, dimethylformamide and n-propanol. In most cases, the fluorescence was found to be strongly anisotropic due to a very short lifetime of the donor-acceptor-substituted trans-stilbenes.

1. Introduction

Trans-stilbene and its donor-acceptor-substituted derivatives exhibit not only photochemical trans-cis isomerization [1–3], but also particularly interesting fluorescent properties [4–7]. In para-position, the transition moment lies along their major axis [8, 9]. The rotational relaxation time in low-viscous solvents is comparable to the mean lifetime of the first singlet excited state, which accounts for high fluorescence anisotropy (FA)*** observed for a series of substances in solvents with low viscosities [10, 11].

Here we present some further interesting results concerning the FA and mean fluorescence lifetime τ_F for eleven stilbene 1 derivatives in low-viscous nonpolar (n-heptane and toluene) and polar (acetonitrile, dimethylformamide DMF and n-propanol) solvents.

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*** For plane polarized exciting light,

$$r = \frac{J_{\parallel} - J_{\perp}}{J_{\parallel} + 2J_{\perp}} = \frac{2P}{3 - P},$$

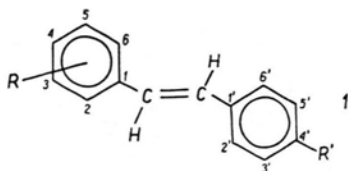
where J_{\parallel} and J_{\perp} are the components of the emitted intensity, parallel and perpendicular to the exciting light, respectively. P is the degree of polarization of light.

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Table 1. The fluorescence mean lifetimes τ_F (in 10^{-12} s)^a, fluorescence anisotropies r and polarization degrees P for trans-stilbene 1 in different solvents at 293 K.

Nr.	R ^c	n-Heptane			Toluene			Acetonitrile			Dimethylformamide			n-Propanol		
		τ_F	r	P	τ_F	r	P	τ_F	r	P	τ_F	r	P	τ_F	r	P
1a	H	40	0,1689	0,2336	40	0,2018	0,2750	50	0,2241	0,3023	50	0,2627	0,3483	100	0,3030	0,3947
1b	4-NMe ₂	160	0,1726	0,2383	150	0,1859	0,2551	410	0,0747	0,1080	500	0,1209	0,1709	370	0,1620	0,2248
1c	3-NMe ₂	6060	0,0151	0,0224	9200	0,0024	0,0036	8550	0,0015	0,0023	10730	0,0026	0,0039	9700	0,0172	0,0256
1d	4-OCH ₃	80	0,1865	0,2559	70	0,2812	0,3608	100	0,2866	0,3760	70	0,3053	0,3973	200	0,3278	0,4224
1e	3-OCH ₃	470	0,0462	0,0677	500	0,0717	0,1038	490	0,0471	0,0691	570	0,0808	0,1165	500	0,1751	0,2415
1f	2-OCH ₃	140	0,0764	0,1103	150	0,1294	0,1823	60	0,1570	0,2184	120	0,2025	0,2758	400	0,2788	0,3671
1g	4-NMe ₂	130	0,1320	0,1858	100	0,1284	0,1810	600	0,0318	0,0470	760	0,0517	0,0756	870	0,1410	0,1976
1h	4-NMe ₂	180	0,0666	0,0966	120	0,0940	0,1347	130	0,0812	0,1171	200	0,1406	0,1970	270	0,1763	0,2430
1i	4-NMe ₂	250	0,0570	0,0831	170	0,0875	0,1257	220	0,0592	0,0862	300	0,0859	0,1235	—	—	—
1j	4-NMe ₂	400	0,0275	0,0407	350	0,0514	0,0752	280	0,0430	0,0632	420	0,0686	0,0995	—	—	—
1k	4-NMe ₂	980	0,0158	0,0235	800	0,0266	0,0394	510	0,0321	0,0474	590	0,0529	0,0773	—	—	—

^a Compare to the literature data and the accuracy of measurements in [6]; ^b $P = 3r/(r + 2)$; ^c Me=CH₃, Ph=C₆H₅; ^d Pa·s = 1 kg m⁻¹ s⁻¹.



2. Experimental

Fluorescence Anisotropies (FA) were measured by automatic photoelectric recording, using an elasto-optical quartz light modulator with frequency modulation of 52.4 kHz and a quartz Arago compensator [12]. Mean fluorescence lifetimes, τ_F , were obtained with a modified Bauer fluorimeter [13]. The accuracy of the τ_F measurement was ± 10 ps.

3. Results and Discussion

In Table 1 the obtained values of τ_F and FA are given. The viscosities of the nonpolar solvents n-heptane and toluene differ only slightly from those of the polar solvents DMF and acetonitrile, in contrast to the relatively large viscosity of n-propanol. The effect of the viscosity upon the FA is obvious (e.g. **1a**, **1d**, **1e** with τ_F equal in different solvents). The magnitude of the FA, however, is strongly related to the mean molecular fluorescence lifetime τ_F . In the case of very short τ_F (e.g. **1a**, **1b**, **1d**, **1f**, **1h**), high FA can be observed despite low solvent viscosities. For molecules **1e**, however, τ_F is very long, and hence the FA becomes very low. The FA of molecules with equal τ_F in different

solvents having equal viscosities and different dielectric constants (e.g. **1a**, **1d** and **1e**, in n-heptane and acetonitrile) reveals a distinct effect of ϵ upon the FA, the FA increases with growing ϵ , contrary to the phenomenon observed previously [14]. It is difficult to determine unequivocally the effect of ϵ upon the FA for the remaining 1 substances, as the influence of such quantities as τ_F and η is substantial.

As shown in Table 1, in the polar solvents DMF and acetonitrile, τ_F is not monotonic function of the acceptor activity of the R' substituent, in contrast to the nonpolar solvent case (n-heptane and toluene [6]). In both polar solvents, τ_F attains a minimum value for the substituted halogenoderivatives **1h** and **1i** in the series **1g**, **1b**, **1h–1k**, which has already been observed qualitatively for the series of substances mentioned above, both in non-polar and polar solvents, by measuring the FA, i.e. by an independent method (compare the values of τ_F and r in Table 1).

Compound **1b** is an exception, it having a too large ratio r/τ_F . This can be accounted for, comparing the remaining substances of the series **1g**, **1b**, **1h–1k**, by the fact that **1b** exhibits a slower rotational motion in these solvents. Molecule **1b** with its large tetrahedral diphenylphosphinyl group serving as an acceptor, differs most strongly from the other substances of this series, due to its geometry.

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- [1] H. Görner and D. Schulte-Frohlinde, J. Phys. Chem. **82**, 2653 (1978); Ber. Bunsenges. physik. Chem. **81**, 712 (1977).
- [2] D. J. S. Birch and J. B. Birks, Chem. Phys. Letters **38**, 432 (1976).
- [3] J. B. Birks, Chem. Phys. Letters **38**, 437 (1976).
- [4] M. Alicka, R. K. Bauer, and A. Kawski, Z. Naturforsch. **35a**, 896 (1980).
- [5] I. Gryczyński, D. Gloyna, and A. Kawski, Z. Naturforsch. **35a**, 777 (1980).
- [6] D. Gloyna, A. Kawski, and I. Gryczyński, Z. Naturforsch. **35a**, 1192, 1411 (1980).
- [7] D. Gloyna, I. Gryczyński, and A. Kawski, Z. Naturforsch. **36a**, 626 (1981).
- [8] A. Kawski, I. Gryczyński, Ch. Jung, and K.-H. Hecker, Z. Naturforsch. **32a**, 420 (1977).
- [9] W. Liptay, Dipole Moments and Polarizabilities of Molecules in Excited Electronic States, in Excited States Vol. 1, Acad. Press, London 1974, p. 129–229.
- [10] W. Liptay, H. J. Schumann, and F. Petzke, Chem. Phys. Letters **39**, 427 (1976).
- [11] A. Kawski and M. Alicka, Z. Naturforsch. **34a**, 1371 (1969); **35a**, 775 (1980).
- [12] A. Kawski, Z. Kojro, and M. Alicka, Z. Naturforsch. **35a**, 1197 (1980).
- [13] R. K. Bauer and K. J. Rudik, Acta Phys. Polon. **35**, 259 (1969).
- [14] A. Kawski, J. Kukielski, and J. Kamiński, Z. Naturforsch. **33a**, 1228 (1978).