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

A. Kawski, M. Alicka, and D. Gloyna **

Luminescence Research Group, Institute of Physics, University of Gdańsk, Gdańsk, Poland

Z. Naturforsch. **36a**, 1259–1260 (1981); received August 28, 1981

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.

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

Nr.	R[c]	R'[c]	n-Heptane $\eta = 0{,}397$ 10^{-3} Pa·s[d] $\varepsilon = 1{,}92$			Toluene $\eta = 0{,}552$ 10^{-3} Pa·s $\varepsilon = 2{,}38$			Acetonitrile $\eta = 0{,}34$ 10^{-3} Pa·s $\varepsilon = 36{,}7$			Dimethylformamide $\eta = 0{,}802$ 10^{-3} Pa·s $\varepsilon = 36{,}7$			n-Propanol $\eta = 2{,}2$ 10^{-3} Pa·s $\varepsilon = 19{,}7$		
			τ_F	r	P	τ_F	r	P	τ_F	r	P	τ_F	r	P	τ_F	r	P
1a	H	$Ph_2P(O)$	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	$Ph_2P(O)$	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	$Ph_2P(O)$	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	$Ph_2P(O)$	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	$Ph_2P(O)$	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	$Ph_2P(O)$	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	CN	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	Br	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	Cl	250	0,0570	0,0831	170	0,0875	0,1257	220	0,0592	0,0862	300	0,0859	0,1235	—	0,1652	0,2289
1j	4-NMe_2	F	400	0,0275	0,0407	350	0,0514	0,0752	280	0,0430	0,0632	420	0,0686	0,0995	—	0,1269	0,1789
1k	4-NMe_2	OCH_3	980	0,0158	0,0235	800	0,0266	0,0394	510	0,0321	0,0474	590	0,0529	0,0773	—	0,1034	0,1475

[a] Compare to the literature data and the accuracy of measurements in [6]; [b] $P = 3r/(r+2)$; [c] Me=CH_3, Ph=C_6H_5; [d] Pa·s = 1 kg m^{-1} s^{-1}.

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* Carried out under the research problem MR.I.5.

** Wissenschaftsbereich Organische Chemie, Sektion Chemie der Humboldt-Universität Berlin, GDR-104.

*** 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.

Reprint requests to Prof. Dr. Alfons Kawski, Instytut Fizyki, Uniwersytet Gdański, Wita Stwosza 57, 80-952 Gdańsk, Poland.

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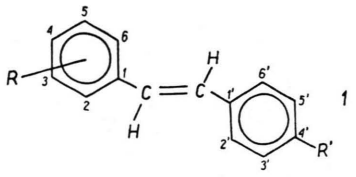

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2. Experimental

Fluorescence Anisotropies (FA) were measured by automatic photoelectric recording, using an elastooptical 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 **1c**, 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.

We thank Professor A. Schmillen (University of Giessen) for his valuable remarks.

[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. Heckner, 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).

Verantwortlich für den Inhalt: A. Klemm
Satz und Druck: Konrad Triltsch, Würzburg