Deactivation of the S_1-State of ω-Substituted 4-Dimethylamino-trans-Styrenes in Alkane Solutions

A. Kawski[1], I. Gryczyński[1,2], K. Nowaczyk[1,2], P. Bojarski[1], and J. Lichacz[1]

Z. Naturforsch. **46a,** 1043–1048 (1991); received July 18, 1991

Deactivation of three ω-substituted acceptors in 4-dimethylamino-trans-styrenes ($P(S)Ph_2$ (**1a**), $P(O)Ph_2$ (**2a**) and SO_2CH_3 (**3a**)), dissolved in n-paraffins (from $n=5$ to $n=16$) at 293 K, was investigated. *Trans-cis* isomerization and intersystem crossing are the main processes responsible for radiationless deactivation of the S_1 excited state. High fluorescence anisotropy, r, observed in low-viscous n-paraffins, is due to strong fluorescence quenching resulting in the considerable shortening of the lifetime τ of these molecules. The fluorescence depolarization which occurs when lowering the viscosity, η, of the solution is caused by Brownian rotations and conformational changes due to fast adiabatic twisting of the planar trans-S_1 form around the double bond, leading to the formation of the perp.-S_1 structure with perpendicularly oriented parts of the molecule, and to the concomitant change in the transition moment direction. Linear dependence of $\tau^2/(r_0/r-1)$ on $\eta\cdot\tau$ in the whole viscosity range was only observed for molecule **3a**.

1. Introduction

Substituted trans-styrenes were frequently the object of photophysical and photochemical investigations [1–11]. Monochromatic irradiation in the long-wave absorption region with sufficiently high light intensity leads to intensive formation of *cis* isomers. In the case of donor-acceptor-substituted trans-styrenes such photochemical *trans-cis* isomerization proceeds to a very large extent in the absence of chemical side reactions [8,12]. These compounds may therefore serve as good models for the investigation of the competition between photophysical (radiative and radiationless) and photochemical (twisting around the ethylene bond) deactivation of the excited state. As has been found for styrenes, the deactivation is due to both triplet and singlet mechanisms [13], obviously depending on the electronic structure of the ground and excited states. The different electric dipole moments of the ω-substituted 4-dimethylamino-trans-styrenes **1a**–**3a** (see Fig. 1) in the ground and excited state give a measure of donor acceptor interactions [10,11]. Substituent Z in **1a**–**3a** is a strong acceptor of electrons and it should therefore be expected that its specific effect upon deactivation processes is negligible.

The present paper reports a study on the deactivation processes occurring in three different ω-substituted Z acceptors ($P(S)Ph_2$, $P(O)Ph_2$, SO_2CH_3) in 4-dimethylamino-trans-styrenes solved in a series of n-alkanes (from $n=5$ to $n=16$) at 293 K. According to the process

$$\text{tr-}S_0 + h\nu \rightarrow \text{tr-}S_1, \tag{1}$$

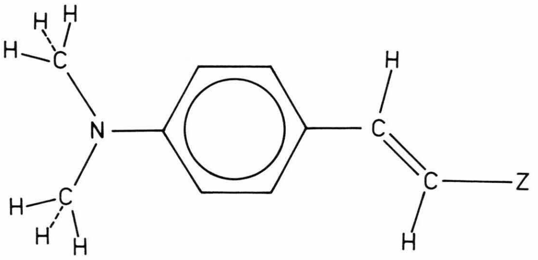
the deactivation of the trans-styrene excited state is described by [14,15]

$$\text{tr-}S_1 \xrightarrow{k_F} \text{tr-}S_0 + h\nu', \tag{2}$$

$$\text{tr-}S_1 \xrightarrow{k_{tp}} \text{perp.-}S_1, \tag{3}$$

$$\text{tr-}S_1 \xrightarrow{k_{ISC}} \text{tr-}T_1, \tag{4}$$

$$\text{perp.-}S_1 \xrightarrow{k_{iso}} \alpha\,\text{tr-}S_0 + (1-\alpha)\,\text{cis-}S_0, \tag{5}$$



Molecule	1a	2a	3a
Substituent Z	$Ph_2P(=S)-$	$Ph_2P(=O)-$	$CH_3-S(=O)_2-$

Fig. 1. Structural formula of ω-substituted 4-dimethylamino-trans-styrenes:
4-dimethylamino-ω-diphenylthiophosphinyl-trans-styrene (**1a**)
4-dimethylamino-ω-diphenylphosphinyl-trans-styrene (**2a**)
4-dimethylamino-ω-methylsulphonyl-trans-styrene (**3a**)

---

[1] Luminescence Research Group, Institute of Experimental Physics, University of Gdańsk, 80-952 Gdańsk, Poland.
[2] Center for Fluorescence Spectroscopy, Department of Biological Chemistry, University of Maryland, 660 West Redwood Street, Baltimore MD 21201, USA.
Reprint requests to Prof. Dr. Alfons Kawski, University of Gdańsk, Institute of Experimental Physics, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland.

0932-0784 / 91 / 1200-1043 \$ 01.30/0. – Please order a reprint rather than making your own copy.

where k_F, k_{tp}, k_{ISC}, and k_{iso} are the rate constants of radiative, adiabatic twisting, intersystem crossing and trans-cis isomerization, respectively.

The quantum yield of process (2) is given by

$$\Phi_F = k_F (k_F + k_d)^{-1}, \tag{6}$$

where

$$k_d = k_{tp} + k_{ISC} \tag{7}$$

is the global rate of radiationless deactivation and

$$(k_F + k_d)^{-1} = \tau \tag{8}$$

is the mean lifetime of the excited state. Based on (6) and (8) we obtain

$$k_F = \frac{\Phi_F}{\tau}, \tag{9}$$

$$k_d = \frac{1}{\tau} - \frac{\Phi_F}{\tau}. \tag{10}$$

2. Experimental

The alkane solvents were spectroscopically pure. The viscosities η of the saturated hydrocarbons C_nH_{2n+2} were calculated using the Adamczewski and Calderwood formula [16]

$$\eta = 2.54 \times 10^{-5} \exp(-0.0235\, n) \cdot \exp[(416\sqrt{n} - 230)/T] \tag{11}$$

(in Pa · s), valid for $n = 1$ to $n = 64$ at temperatures ranging from 88 to 574 K. In [17] we demonstrated good accordance with the values calculated using (11).

The absorption spectra were obtained on a Zeiss model M-40 spectrophotometer and the fluorescence spectra were recorded by means of a fully corrected spectrofluorimeter designed and built in our laboratory[1].

The fluorescence quantum yields, Φ_F, were measured using a quinine sulfate standard ($\Phi_F^s = 0.55$) and the relation [18]

$$\Phi_F = \Phi_F^s \frac{\int_0^\infty I_F(\nu)\, d\nu}{\int_0^\infty I_F^s(\nu)\, d\nu} \frac{(1-10^{-D^s})}{(1-10^{-D^s})} \left(\frac{n}{n^s}\right)^2, \tag{12}$$

where D is the optical density and n the refractive index. The integrals represent the surfaces under the fluorescence spectra. The samples and the reference solution were excited with $\lambda_{exc} = 348$ nm. All measurements were carried out at 293 K, using rotation-free "magic angle" conditions.

The fluorescence anisotropy, r, was measured by the single photon counting technique as in [19, 20], and the mean fluorescence lifetimes, τ, by means of a 10 GHz frequency-domain fluorometer [21].

The phase-(τ_p) and modulation-(τ_m) lifetimes were measured for selected frequencies ranging from 4 to 10 GHz. The cavity-dumped output of a synchronously pumped pyridine 2 dye laser was used to generate a laser pulse train with a pulse width of about 5 ps, which was next doubled to 348 nm. This source is intrinsically modulated up to many gigahertz and used for direct excitation of the samples. τ_p and τ_m were measured under rotation-free magic angle polarized conditions. The emission was isolated with a 3-75 Corning cut-off glass filter. In general we found $\tau_p = \tau_m$, indicating homogeneous intensity decays.

3. Results and Discussion

3.1 Deactivation of the S_1-State

The long-wave absorption bands of substituted styrenes **1a, 2a** and **3a** stem from two electronic transitions [13, 22]. In unsubstituted styrene these transitions were found at 40 300 cm^{-1} (high intensity) and 35 400 cm^{-1} (lower intensity) [23]. This marked separation between the $S_0 - S_1$ and $S_0 - S_2$ transitions disappears upon the introduction of electron-effective substituents in positions ω and p, causing the $S_0 - S_2$ transition to be strongly shifted to longer wavelength [13, 22, 24]. As evidenced by the calculations, the more intense band for **1a, 2a** and **3a** is located at longer wavelength [22, 24].

Figures 2 and 3 show the absorption, fluorescence and emission anisotropy spectra in these bands for **2a** and **3a**. By the excitation in the 0–0 transition (360 nm), limiting fluorescence anisotropies of 0.377, 0.365 and 0.375 were obtained for **1a, 2a** and **3a**, respectively, in glycerol at 273 K, indicating the coincidence of the absorption and emission transition moments. Table 1 summarizes the values of Φ_F and τ measured for **1a, 2a** and **3a** in alkanes with different viscosities. The values for **1a** are by an order of magnitude lower than those measured for **2a** and **3a**. For all compounds (**1a**–**3a**), an increase in quantum yields, Φ_F, and mean lifetimes, τ, was observed with growing viscosity η.

Table 1. Fluorescence quantum yields Φ_F, mean lifetimes τ (in 10^{-12} s), deactivation rate constants of fluorescence k_F (in $10^8\ s^{-1}$) and radiationless deactivation rate constants $k_d = k_{tp} + k_{Isc}$ (in $10^{12}\ s^{-1}$) for **1a**, **2a** and **3a** in *n*-paraffins of different viscosities at 293 K.

No.	Solvent (C_nH_{2n+2})	η (10^{-3} Pa · s)*	**1a**				**2a**				**3a**			
			Φ_F	τ**	k_F	k_d	Φ_F	τ**	k_F	k_d	Φ_F	τ**	k_F	k_d
1	pentane	0.247	0.00033	3	1.10	0.3332	0.0041	4	10.25	0.2489	0.0059	18	3.28	0.0552
2	hexane	0.326	0.00039	6	0.65	0.1666	0.0046	7	6.57	0.1422	0.0059	19	3.11	0.0523
3	heptane	0.420	0.00040	7	0.57	0.1428	0.0052	8	6.50	0.1244	0.0068	23	2.96	0.0432
4	octane	0.532	0.00051	8	0.64	0.1249	0.0056	9	6.20	0.1105	0.0072	25	2.88	0.0397
5	nonane	0.665	0.00064	9	0.71	0.1110	0.0069	10	6.90	0.0993	0.0072	25	2.88	0.0397
6	decane	0.818	0.00070	9	0.78	0.1110	0.0073	10	7.30	0.0993	0.0080	26	3.08	0.0382
7	undecane	0.993	0.00074	10	0.74	0.0999	0.0080	11	7.27	0.0902	0.0086	26	3.31	0.0381
8	dodecane	1.120	0.00076	10	0.76	0.0999	0.0084	12	7.00	0.0826	0.0087	26	3.35	0.0381
9	tridecane	1.426	0.00079	11	0.72	0.0908	0.0092	12	7.67	0.0826	0.0090	26	3.46	0.0381
10	tetradecane	1.700	0.00089	12	0.74	0.0833	0.0098	14	7.00	0.0707	0.0094	26	3.62	0.0381
11	pentadecane	1.996	0.00099	13	0.76	0.0768	0.0100	15	7.67	0.0660	0.0101	27	3.70	0.0367
12	hexadecane	2.330	0.00120	18	0.66	0.0555	0.0110	20	5.50	0.0495	0.0110	29	3.79	0.0341

* $1\ \mathrm{cP} = 10^{-3}\ \frac{\mathrm{kg}}{\mathrm{m \cdot s}} = 10^{-3}\ \mathrm{Pa \cdot s}$.

** τ was measured with an accuracy of ± 1 ps, which resulted in the highest errors in k_F calculated from (9) for **1a** and **2a** in pentane: 33% and 25%, respectively.

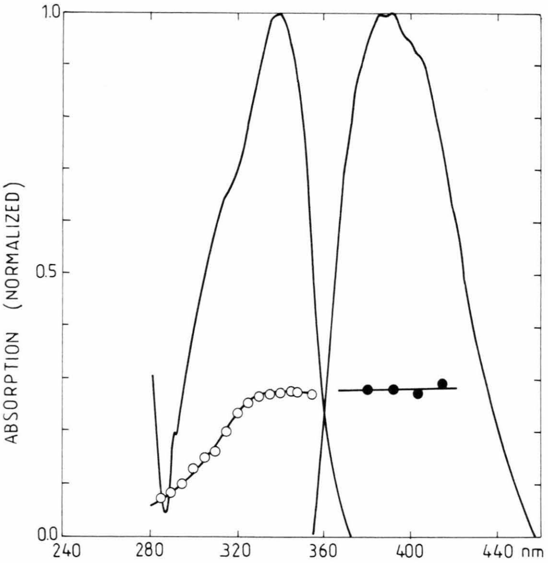


Fig. 2. Absorption, fluorescence and emission anisotropy spectra of **2a**.

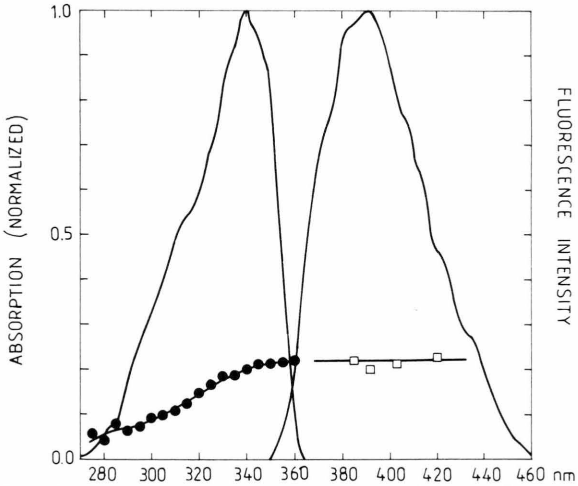


Fig. 3. Absorption, fluorescence and emission anisotropy spectra of **3a**.

The values of k_F and k_d (Table 1) calculated according to (9) and (10) clearly show that, unlike the unquenched rate constant $k_F = 1/\tau_0$ (τ_0 is the radiative lifetime), radiationless deactivation strongly depends on the solvent viscosity. Moreover, deactivation of the excited S_1 state depends also on the energy spacing between the ground, S_0, lowest excited singlet, S_1, and lowest excited triplet, T_1, states. The energy difference between S_1 and T_1 is of fundamental significance for the rate of radiationless intersystem crossing (ISC) between these two levels. When comparing the molecules investigated it can readily be noticed that substituent *Z* in molecule **1a** is the heaviest (Figure 1). Thus, the reason for the strongest, nearly by an order of magnitude, quenching lies in the strengthened intersystem crossing (ISC) according to the schematic process (4). In the case of **1 a**, the energy difference $\Delta W(S_1 - T_1)$ is the smallest, amounting to 7130 cm^{-1}, whereas the respective values for the molecules **2 a** and **3 a** are 7770 cm^{-1} and 8170 cm^{-1} [24, 25]. It can therefore be concluded that the radiationless intercombination (ISC) between S_1 and T_1 affects the non-sensitized photochemical *trans-cis* isomerization of styrenes.

According to Förster and Hoffmann [26], it is the radiationless solvent-viscosity-dependent process that is responsible for the extremely low fluorescence quantum yield of molecules possessing some rotating groups (e.g. hindered rotations of phenyl groups or rotations around the ethylene bond). For low viscosities they obtained the expression

$$\Phi_F = 0.893 \frac{\tau}{\tau_0}\left(\frac{\eta}{\delta}\right)^{2/3} = \frac{0.893}{\tau_0}\left(\frac{\eta}{\delta'}\right)^{2/3}, \qquad (13)$$

where

$$\delta = \left(\frac{\beta d^2 \alpha^2 \tau^3}{192 \pi^2 r^6}\right)^{1/2}, \quad \delta' = \left(\frac{\beta d^2 \alpha^2}{192 \pi^2 r^6}\right)^{1/2} \qquad (14)$$

(r is the effective radius of one of the molecular segments, α is a constant potential depending on the character of the double bond in the fluorescent state and on the steric effect, $d = \varphi_0' - \varphi_0$ is the difference between coordinates corresponding to minima on the potential curves in the excited and ground state, and β is a constant coefficient) and Φ_F is independent of τ, that is

$$\Phi_F = C \eta^{2/3}. \qquad (15)$$

Figure 4 shows Φ_F versus $\eta^{2/3}$, as determined experimentally for **1 a**–**3 a** according to (15).

Expression (13) yields a formula for τ which is similar to (15):

$$\tau = \Phi_F \cdot \tau_0 = K \cdot \eta^{2/3}, \qquad (16)$$

where $K = \dfrac{0.893}{\delta'^{2/3}}$ is a constant.

For molecules **1 a**–**3 a**, on account of inequality

$$1/\tau \gg \Phi_F/\tau,$$

(c.f. values in Table 1), and from (10) one obtains

$$\tau \simeq 1/k_d, \qquad (17)$$

i.e., the relation between the inverse radiationless deactivation rate constant and $\eta^{2/3}$ (formula (16)) shown in Figure 5.

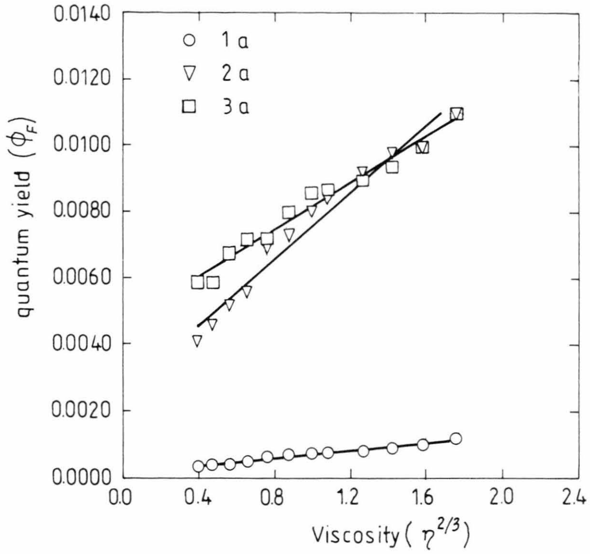


Fig. 4. Dependence of the quantum yield, Φ_F, on $\eta^{2/3}$ for **1 a**, **2 a** and **3 a**; correlation coefficients amount to 0.980, 0.985, and 0.986, respectively.

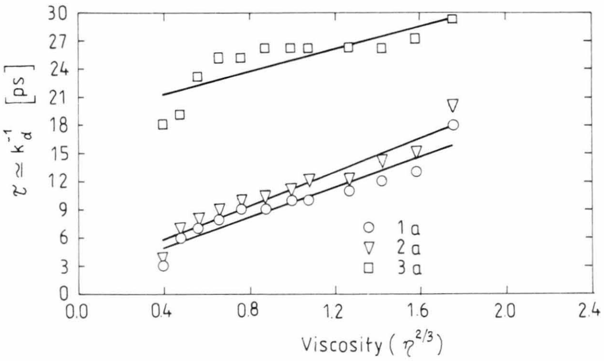


Fig. 5. Dependence of reciprocal rate constants, k_d^{-1}, on $\eta^{2/3}$ for **1 a**, **2 a** and **3 a**; correlation coefficients amount to 0.948, 0.959 and 0.833, respectively.

3.2 *Fluorescence Depolarization*

From among the three compounds examined, distinct rotational depolarization was observed for **3 a**, since the mean lifetime of this compound in *n*-paraffins, from pentane to hexadecane (Table 1), only changes by 1.6. In the case of **1 a** and **2 a**, five- and six-fold changes have been found, respectively. Therefore, the emission anisotropy for **1 a** and **2 a** in pentane (very low viscosity) is a high as 0.295 and 0.285, respectively, whereas for **3 a** it scarcely amounts to 0.164. It was only for **3 a** that the following linear relation, valid for prolate molecules in the whole viscosity

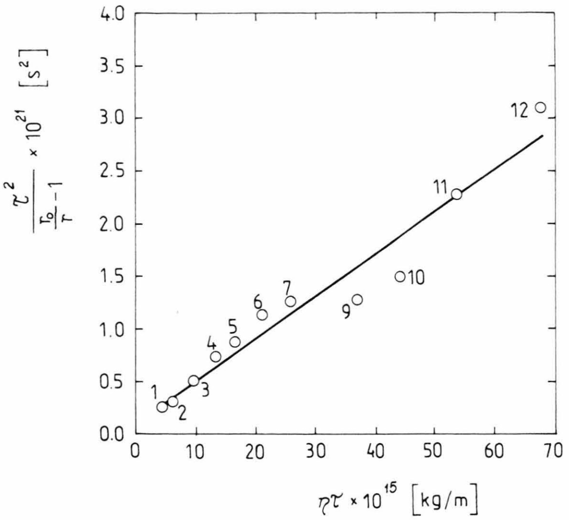


Fig. 6. Dependence of $\tau^2/(r_0/r-1)$ on $\eta\,\tau$ for **3a** in different *n*-paraffins (according to Table 2); correlation coefficient $r = 0.973$.

Table 2. Fluorescence anisotropies r, mean lifetimes τ and rotational relaxation times τ_R of **3a** in different *n*-paraffins at 293 K.

No.	Solvent	η (10^{-3} Pa · s)	τ (ps)	r	τ_R (ps)
1	pentane	0.247	18	0.1644	24.1
2	hexane	0.326	19	0.1725	31.4
3	heptane	0.420	23	0.1842	52.4
4	octane	0.532	25	0.2029	75.4
5	nonane	0.665	25	0.2187	91.9
6	decane	0.818	26	0.2345	117.7
7	undecane	0.993	26	0.2441	132.9
8	dodecane	1.120	26	–	–
9	tridecane	1.426	26	0.2451	134.6
10	tetradecane	1.700	26	0.2582	159.9
11	pentadecane	1.996	27	0.2840	240.7
12	hexadecane	2.330	29	0.2950	309.6

range [27–29], was observed:

$$\frac{\tau^2}{r_0/r-1} = \frac{I}{6kT} + \frac{V\eta\tau}{kT}. \tag{18}$$

In (18), apart from the already specified quantities, I is the moment of inertia and V is the volume of the luminescent molecule. When I is neglected ($I \simeq 0$) or highly viscous solutions are dealt with, (18) becomes the Perrin equation [30]. The more general equation (18) is valid for prolate molecules and is satisfied at both high and very low viscosities. On plotting the left-hand side of (18) versus $\eta \cdot \tau$ one obtains a straight line, from the slope of which volume V, and from the intercept on the ordinate axis the moment of inertia, I, can be found. Figure 6 shows the experimental results obtained for **3a** according to (18). The following values were obtained for **3a**: $I = 2.4 \times 10^{-42}$ kg m^2 and $V = 170 \times 10^{-30}$ m^3. The I value calculated for a free molecule based on its geometry amounts to 4.96×10^{-44} kg m^2, which is by two orders of magnitude smaller than that determined experimentally. The determined values of I and V in various solvents differ from those calculated for free molecules, which results from the solvatation effect.

An interesting quantity is the rotational relaxation time $\tau_R = 3\,\theta$, where $\theta = \dfrac{V\eta}{kT}$ is the rotational correlation time. One obtains τ_R from (18)

$$\tau_R = 3\,\tau\left(\frac{r}{r_0-r} - A\right), \tag{19}$$

where $A = \dfrac{I}{6kT} \cdot \dfrac{1}{\tau^2}$. The τ_R values calculated according to (19) for **3a** in *n*-paraffins with different viscosities have been summarized in Table 2. As readily seen, $\tau_R > \tau$, which accounts for the marked fluorescence anisotropy observed in the solvents investigated. Short lifetimes τ result from strong fluorescence quenching due to radiationless *trans-cis* deactivation and to intersystem crossing. As observed, much stronger quenching and, hence, still greater shortening of the mean lifetime occur for the remaining **1a** and **2a** molecules (Table 1). Markedly higher fluorescence anisotropy is therefore observed for **1a** and **2a** as compared to that of **3a** in the same viscosity range.

Depending on the size of mobile molecular segments, the conformational changes as well as Brownian rotations are considerably hindered due to the growing viscosity [31]. For low $\tau \cdot \tau_R^{-1}$ values (small contribution of depolarization due to Brownian rotations), marked fluorescence anisotropy is observed. Fluorescence depolarization may also result from rapid adiabatic twisting of the planar trans-S_1 form around the ethylene bond, markedly weakened by the donor-acceptor interaction. This finally leads to the perp.-S_1 form (schematic process (3)) with perpendicular orientation of both molecular fragments and to the change in the transition moment direction. Further deactivation gives rise to *cis*-styrene according to process (5) (photochemical *trans-cis* isomerization). Then, of course, one cannot expect the linear relation given by (18) to be obeyed, and this is the case for substances **1a** and **2a**.

Acknowledgements

The authors wish to thank Dr. habil. Wolfgang Wegener and Dr. Dieter Gloyna for the gift of the chemical compounds.

Professor A. Schmillen we should like to thank for his helpful remarks.

This work was carried out under Research Project BW/5-200-4-053-1 and performed partially at the Center for Fluorescence Spectroscopy, NSF DIR-8710401.

[1] D. A. R. Happer, Austral. J. Chem. **29**, 2607 (1976).
[2] L. Skulski and D. Augustynek, Bull. Acad. Polon. Sci., Ser. Sci. Chim. **24,** 903 (1976).
[3] K. Baily and D. Legault, Org. Magn. Reson. **16,** 47 (1981).
[4] D. J. Cowley, Helv. Chim. Acta **61,** 184 (1978).
[5] D. J. Cowley, J. Chem. Soc. Perkin Trans. **2,** 1576 (1975).
[6] G. Butt and R. D. Topsom, Spectrochim. Acta Part A **36,** 811 (1980).
[7] E. Lippert, W. Lüder, F. Moll, W. Nägele, H. Boss, H. Prigge, and J. Seibold-Blankenstein, Angew. Chem. **73,** 695 (1961).
[8] E. Lippert and W. Lüder, J. Phys. Chem. **66,** 2430 (1962).
[9] K.-G. Berndt and D. Gloyna, Acta Chim. Acad. Sci. Hung. **110,** 145 (1982).
[10] A. Kawski, A. Kubicki, amd J. Czajko, Z. Naturforsch. **44a,** 1163 (1989).
[11] A. Kawski, D. Gloyna, P. Bojarski, J. Czajko, and J. Gadomska-Lichacz, Z. Naturforsch. **45a,** 1230 (1990).
[12] D. Gloyna and K.-G. Berndt, Acta Phys. et Chem. (Szeged) **26,** 155 (1980).
[13] W. Wegener, Dissertation B, Humboldt-Universität zu Berlin, 1986.
[14] D. J. S. Birch and J. B. Birks, Chem. Phys. Letters **38,** 432 (1976).
[15] D. Gloyna, I. Gryczyński, and A. Kawski, Z. Naturforsch. **36a,** 626 (1981).
[16] I. Adamczewski and J. H. Calderwood, J. Phys. D: Appl. Phys. **8,** 1211 (1975); **9,** 2479 (1976).
[17] A. Kawski, Z. Kojro, P. Bojarski, and J. Lichacz, Z. Naturforsch. **45a,** 1357 (1990).
[18] D. Gloyna, A. Kawski, and I. Gryczyński, Z. Naturforsch. **35a,** 1192, 1411 (1980).
[19] C. Bojarski, A. Kawski, A. Kubicki, and G. Źurkowska, Z. Naturforsch. **43a,** 297 (1988).
[20] A. Kubicki, Experiment. Tech. Phys. **37,** 329 (1989).
[21] G. Laczko, I. Gryczyński, Z. Gryczyński, W. Wiczk, H. Malak, and J. R. Lakowicz, Rev. Sci. Instrum. **61,** 2331 (1990).
[22] J. Sauer, I. Grohmann, R. Stosser, and W. Wegener, J. prakt. Chem. **321,** 177 (1979).
[23] UV Atlas of Organic Compounds, Butterworths and Verlag Chemie, London and Weinheim, 1970.
[24] W. Wegener, L. Alder, D. Palm, and K. D. Schleinitz, Acta Phys. Polon. **A 59,** 659 (1981).
[25] D. Gloyna, K. G. Berndt, and W. Wegener, J. Prakt. Chem. **324,** 107 (1982).
[26] Th. Förster and G. Hoffmann, Z. Phys. Chem. N. F. **75,** 63 (1971).
[27] R. Alicki, M. Alicka, and A. Kawski, Z. Naturforsch. **36a,** 1158 (1981).
[28] R. Alicki and M. Alicka, Z. Naturforsch. **38a,** 835 (1983).
[29] A. Kawski, Z. Naturforsch. **38a,** 1040 (1983).
[30] F. Perrin, Ann. Phys. (Paris) **12,** 169 (1929).
[31] D. Gloyna, A. Kawski, and A. Kubicki, Chimia **41,** 154 (1987).