The Effect of ω-Substituted Acceptors in 4-Dimethylamino-trans-Styrenes on the Polarity in the Ground and Excited Singlet State *

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The electric dipole moment in the ground (μ_g) and in the first excited singlet state (μ_e) of ω-substituted acceptors in 4-dimethylamino-trans-styrenes ($Z = P(S)Ph_2$, $P(O)Ph_2$, SO_2CH_3) were determined by solvatochromic and thermochromic methods. The obtained values of μ_e and μ_g and the values for $Z = CN$ and $Z = NO_2$ known from the literature [2] fulfill the linear relation between the dipole moments (μ_e or μ_g) and the Hammett constants σ_p of the substituents. On increasing the electron-acceptor power of Z, μ_e grows faster than μ_g.

1. Introduction

In our first paper [1] we investigated the effect of p-substituted donors ($R = N(CH_3)_2$, OCH_3, CH_3, H, Cl, Br, CN) on the polarity of trans-styryl-methyl-sulfones in the first excited singlet state (S_1). It was found that the electric dipole moment (μ_e) in the first excited singlet state increases with increasing electron-donor power of R, and that the dipole moment μ_e is linearly related to the Hammett constant of R.

The present paper reports on experimental investigations of the effect of ω-substituted acceptors in 4-dimethylamino-trans-styrenes on the polarity in the ground and first excited singlet states. Hitherto, only for two different acceptors (Z) CN and NO_2 the dipole moments in the ground (μ_g) and excited (μ_e) state are known [2, 3]. In order to investigate the behaviour of μ_e and μ_g for different Hammett constants σ_p, it is necessary to determine the dipole moments for other acceptors (Z) with different σ_p.

2. Basic Equations of Dipole Moment Analysis

The following equations can be derived, based on the theory [4, 5] of the absorption and fluorescence band shifts, $\tilde{\nu}_A$ (in m^{-1}) and $\tilde{\nu}_F$ (in m^{-1}), respectively, in solvents with different permittivities, ε, and refractive indices, n, when the dipole moments in the ground (μ_g) and in the excited (μ_e) state are parallel (this condition is fulfilled in the case of the compounds investigated) and when $(2\alpha/a^3)(1/4\pi\varepsilon_0) = 1$:

$$\tilde{\nu}_A - \tilde{\nu}_F = m_1 f(\varepsilon, n) + \text{const}, \tag{1}$$

$$\tilde{\nu}_A + \tilde{\nu}_F = -m_2 [f(\varepsilon, n) + 2g(n)] + \text{const}, \tag{2}$$

where

$$f(\varepsilon, n) = \frac{2n^2+1}{n^2+2}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right], \tag{3}$$

$$g(n) = \frac{3}{2}\,\frac{n^4-1}{(n^2+2)^2}, \tag{4}$$

and

$$m_1 = \frac{[\mu_e - \mu_g]^2}{\beta a^3}, \quad m_2 = \frac{\mu_e^2 - \mu_g^2}{\beta a^3}, \tag{5), (6}$$

where $\beta = 2\pi\varepsilon_0 hc$ is a universal constant amounting to $1.105110440 \times 10^{-35}\ C^2$, h the Planck constant, c the light velocity in vacuum, α and a the polarizability and Onsager interaction radius of the solute, respectively, and $\varepsilon_0 = 8.854187817 \times 10^{-12}$ F/m the permittivity of vacuum. The parameters m_1 and m_2 can be determined from the absorption and fluorescence shifts ((1) and (2)), and the values of μ_g and μ_e can be obtained from (5) and (6):

$$\mu_g = \frac{m_2 - m_1}{2}\left[\frac{\beta a^3}{m_1}\right]^{1/2}, \tag{7}$$

$$\mu_e = \frac{m_1 + m_2}{2}\left[\frac{\beta a^3}{m_1}\right]^{1/2}. \tag{8}$$

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Table 1. Dipole moments from solvent shifts (S) and temperature shifts (T) for ω-Z-substituted 4-dimethylamino-trans-styrene.

Compound	Z	Hammett constant σ_p [14]	Method, Solvent	Onager radius a (10^{-10} m)	m_1 ($10^2\ m^{-1}$)	m_2	μ_g (10^{-30} Cm)*	μ_e
1a	$P(S)Ph_2$	0.49	S different	6	1400	3800	16	34
			T ethylacetate, 1,2-dichloroethane		1350	3900	17	35
2a	$P(O)Ph_2$	0.53	S different	6	2100	5100	16	38
			T ethylacetate, 1,2-dichloroethane		2200	5100	15	38
3a	SO_2CH_3	0.73	S different from [1]	6	1550	5100	22	41
			T ethylacetate, 1,2-dichloroethane		1600	5000	21	40
4a	CN	0.71	Electrochromic absorption from [2]				23	47
5a	NO_2	0.81	Electrochromic absorption from [2]				26	60
			Electrochromic fluorescence polarization from [3]				26	60

* The conversion factor for the dipole moment: $\frac{[\mu]_{SI}}{Cm} = 3.33564 \times 10^{-30} \frac{[\mu]_{cgs}}{D}$, where D is the symbol for Debye and $1\ D = 10^{-18}$ esu cm.

The value of the Onsager radius, *a*, occurring in (7) and (8) can be estimated for the molecules investigated based on the molecular geometry. According to Lippert [6], for an ellipsoid of revolution, $a = 0.8\ b$ can be used, where *b* refers to the long molecular axis. Table 1 summarizes the values of *a* obtained from the molecular geometry using the Dreiding model for the compounds examined.

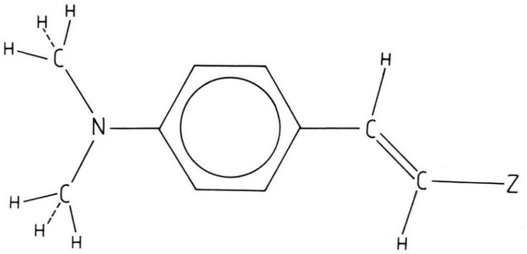

Fig. 1. Structural formula of ω-substituted 4-dimethylamino-trans-styrene (for Z see Table 1).

3. Experimental

The substances investigated are (see Figure 1):

4-dimethylamino-ω-diphenylthiophosphinyl-trans-styrene (**1a**),
4-dimethylamino-ω-diphenylphosphinyl-trans-styrene (**2a**),
4-dimethylamino-ω-methylsulfonyl-trans-styrene (**3a**).

The polar and nonpolar solvents used were spectroscopically pure.

The electric dipole moments in the ground, μ_g, and singlet excited state, μ_e, of **1a**, **2a**, **3a**, were determined by: 1) solvatochromic (different solvents) and 2) thermochromic (in ethylacetate and 1,2-dichloroethane) methods. In the first one, the absorption ($\tilde{\nu}_A$) and fluorescence ($\tilde{\nu}_F$) band shifts were measured for the above three compounds in nine different solvents.

Absorption spectra were measured by means of an M-40 (C. Zeiss, Jena) spectrophotometer, and the

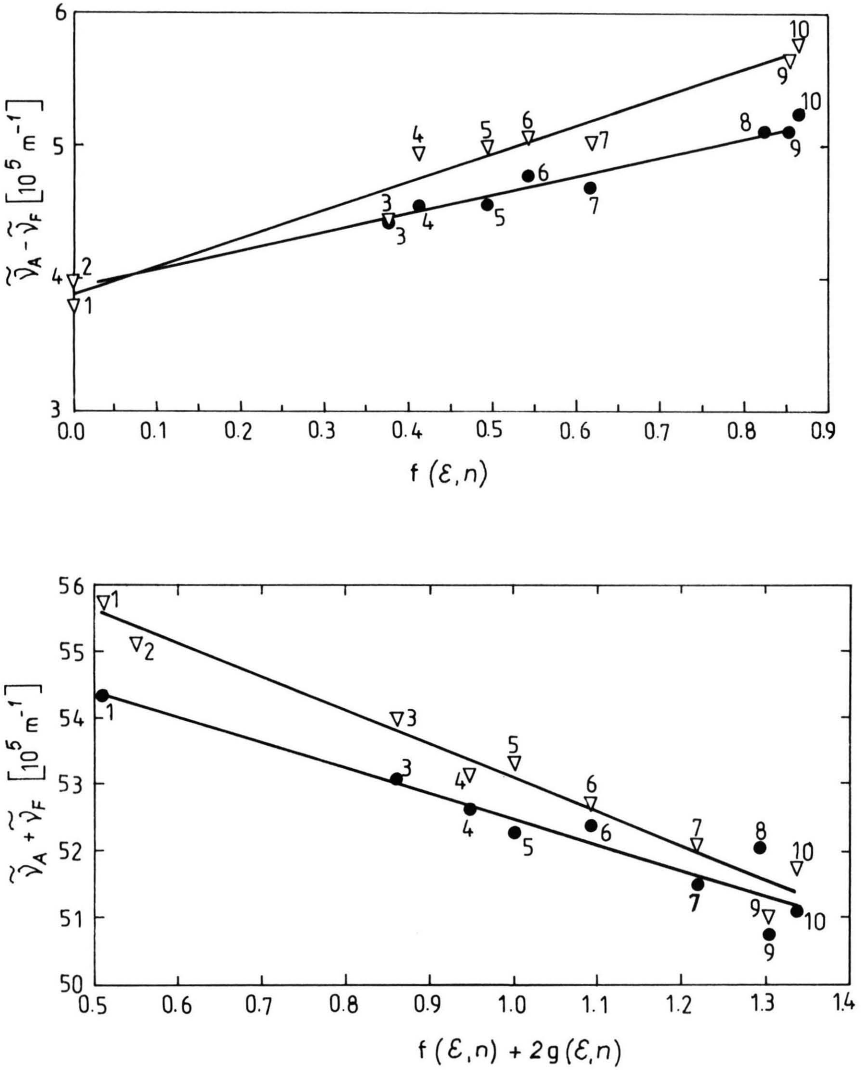

Fig. 2. Solvent shifts of the difference, $\tilde{\nu}_A - \tilde{\nu}_F$, and the sum, $\tilde{\nu}_A + \tilde{\nu}_F$, frequencies of the absorption and fluorescence bands according to (1) and (2), respectively, for **1a** (●) and **2a** (▽): 1 – n-hexane, 2 – cyclopentane, 3 – diethylether, 4 – butylacetate, 5 – ethylacetate, 6 – tetrahydrofuran, 7 – dichloroethane, 8 – ethanol, 9 – methanol, 10 – acetonitrile.

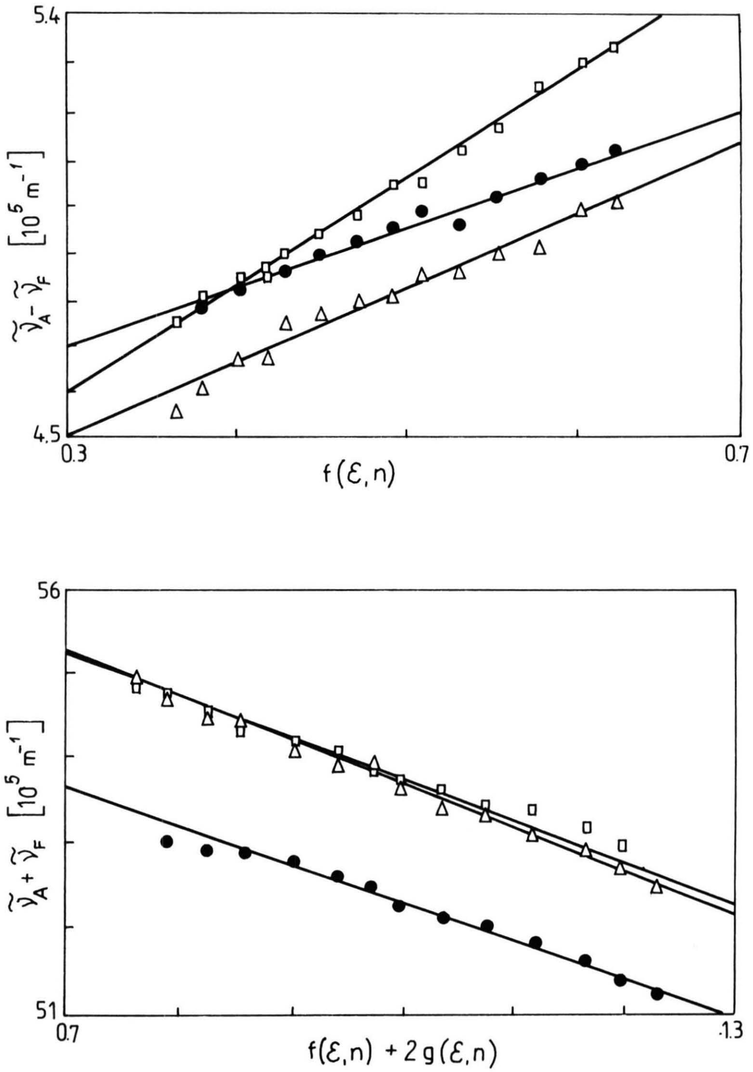

Fig. 3. Temperature shifts of the difference, $\tilde{\nu}_A - \tilde{\nu}_F$, and the sum, $\tilde{\nu}_A + \tilde{\nu}_F$, frequencies of the absorption and fluorescene bands, according to (1) and (2), respectively, for **1a** (●), **2a** (□) and **3a** (△) in ethyl acetate from $T = 433$ K ($\varepsilon = 3.91$, $n = 1.290$) to $T = 293$ K ($\varepsilon = 6.09$, $n = 1.372$) and in 1,2-dichloroethane from 393 K ($\varepsilon = 6.56$, $n = 1.386$) to $T = 293$ K ($\varepsilon = 10.46$, $n = 1.444$).

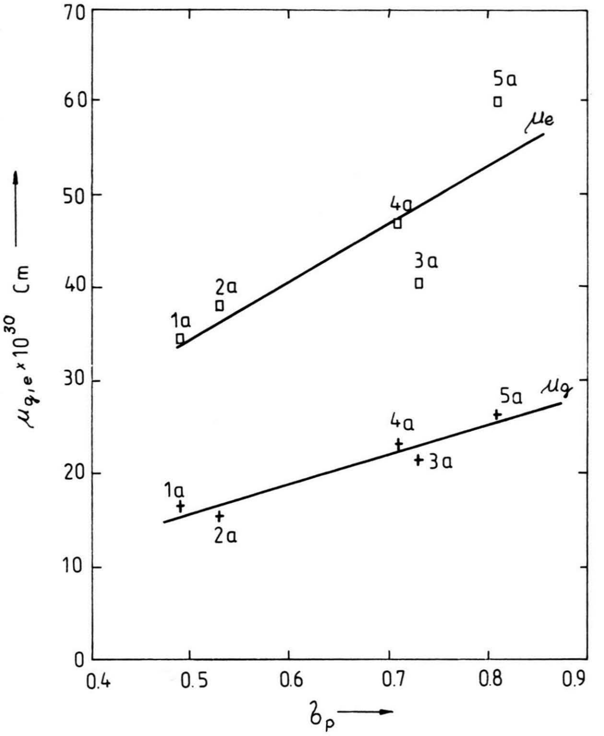

Fig. 4. Dependence of the dipole moments (μ_e, μ_g) on Hammett constants σ_p of the substituents Z given in Table 1. Regression coefficients for $\mu_e = a_1 \sigma_p + b_1$: $a_1 = 62.235 \times 10^{-30}$ Cm, $b_1 = 3.298 \times 10^{-30}$ Cm, correlation coefficient $r = 0.851$; and for $\mu_g = a_2 \sigma_p + b_2$: $a_2 = 31.118 \times 10^{-30}$ Cm, $b_2 = 0.149 \times 10^{-30}$ Cm, correlation coefficient $r = 0.965$.

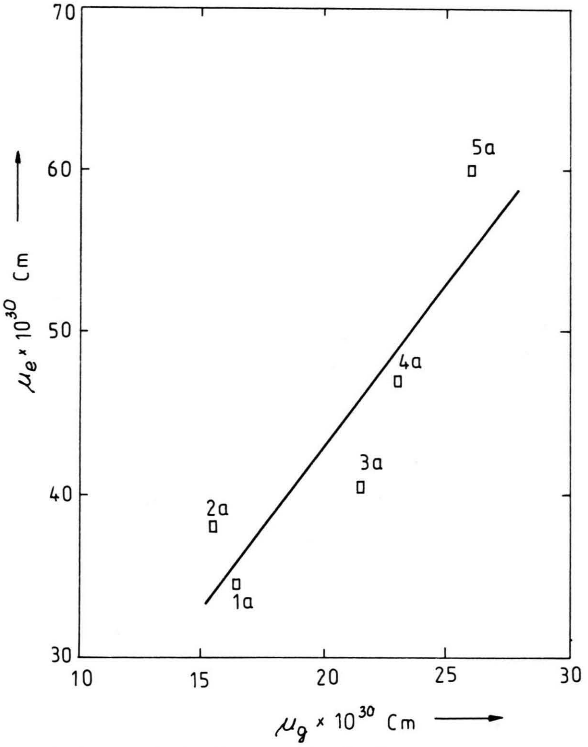

Fig. 5. Linear relation between the dipole moments μ_e and μ_g of ω-substituted acceptors in 4-dimethylamino-trans-styrenes (**1a**–**5a**): $\mu_e = 2.038\,\mu_g + 2.217$ ($r = 0.899$).

fluorescence spectra were recorded by the method described previously [7]. The measurements of the fluorescence spectra were fully automatic and computer-controlled. In the thermochromic method, a stainless steel cell was used which could be thermostated with an accuracy of 0.2 °C using silicon oil. High pressure due to heating prevented the solvents boiling in the temperature range investigated (for ethylacetate from 293 K to 433 K, and for 1,2-dichloroethane from 293 K to 393 K). The permittivity, ε, and refractive indices, *n*, were determined by the method given in [8]. The absorption and fluorescence spectra were measured stepwise at every 20 K interval. Figure 3 shows the dependence of $(\tilde{\nu}_A - \tilde{\nu}_F)$ and $(\tilde{\nu}_A + \tilde{\nu}_F)$ on $f(\varepsilon, n)$ and $f(\varepsilon, n) + 2g(n)$, respectively, for the same compounds **1a**, **2a**, **3a**. The parameters m_1 and m_2 determined according to (1) and (2) from the slopes of straight lines (Figs. 2 and 3) are given in Table 1. When comparing Figs. 2 and 3, marked deviations of the experimental points from linearity can be observed in the solvatochromic method (Figure 2). It is therefore very important to measure the absorption and fluorescence spectra at various high solution temperatures. The effect of the specific interactions on the dipole moments determined can in this way be eliminated.

4. Results and Discussion

The value of μ_g for **3a** is known from the literature [9] and amounts to 23.3×10^{-30} Cm; therefore the values of μ_e and *a* can be determined for this compound. The Onsager radius, $a = 6.2 \times 10^{-10}$ m thus obtained [1] differs slightly only from that calculated from the molecular geometry (see Table 1). Table 1 summarizes also the values of μ_g and μ_e obtained with two different methods for the three compounds. The real fluorescence lifetimes τ_F for **2a** in methanol at 293 K amount to 80 ps [10]. However, the solvent relaxation time τ_R for alcohols ranges from 100 to

2200 ps at 293 K [11–13]. The value of τ_F estimated for **1a** from the oscillator strength is of similar order [10]. Hence, $\tau_F \leqq \tau_R$ and the emission occurs from the state which is not fully intermolecularly relaxed. Although the relaxation times τ_R of the solvents used in our experiments are not known, it can be assumed that complete excited state relaxation is not established due to very short lifetimes of the compounds examined (**1a**, **2a**, **3a**). The values of μ_g and μ_e obtained by both methods are in satisfactory agreement.

Table 1 shows also the values of μ_g and μ_e for **4a** and **5a** known from the literature [2, 3] and also the Hammett constants, σ_p, of the substituents Z [14] for all investigated compounds. As predicted, the dipole moments μ_g and μ_e increase with the enhancement of the electron-acceptor interactions of the Z substituents, expressed by the Hammett constants, σ_p. There exists a linear relation between the dipole moments (μ_e or μ_g) and the constants σ_p of the substituents (Figure 4). On increasing the electron-acceptor power of Z, μ_e grows faster than μ_g. A similar linear relation can be observed between the values of the dipole moments in the excited μ_e, and the ground μ_g state (Figure 5).

For similar donor-acceptor substituted systems, good linear correlation of μ_g and μ_e with the Hamett constants was found for different acceptors in the trans-stilbene series [15], as well as for various donors in the trans-styrene series [1]. For 4-dimethylamino-4′-diphenylphosphinyl-trans-stilbene, the phenyl analogue of **2a**, a comparable ratio of μ_e/μ_g was obtained.

[1] A. Kawski, A. Kubicki, and J. Czajko, Z. Naturforsch. **44a,** 1163 (1989).

[2] J. Czekalla and G. Wick, Z. Elektrochem. **65,** 727 (1961).

[3] J. Czekalla, W. Liptay, and K. O. Mayer, Ber. Busenges. Phys. Chem. **67,** 465 (1963).

[4] L. Bilot and A. Kawski, Z. Naturforsch. **17a,** 621 (1962); **18a,** 10, 256 (1963).

[5] A. Kawski, Acta Phys. Polon. **29,** 507 (1966).

[6] E. Lippert, Z. Elektrochem. **61,** 962 (1957).

[7] A. Kawski, J. Kamiński, and E. Kuteń, J. Phys. **B 4,** 609 (1971).

[8] J. Gryczyński and A. Kawski, Z. Naturforsch. **30a,** 287 (1975).

[9] W. Wegener, K. Hoffmann, K. D. Schleinitz, J. Meyer, and W. Regenstein, Z. Chem. **22,** 312 (1982).

[10] D. Gloyna, K. G. Berndt, and W. Wegener, J. prakt. Chem. **324,** 107 (1982).

[11] C. P. Smyth, in: Molecular Relaxation Processes, Chemical Society Symposium Aberystwyth 1965, Burlington House and Academic Press, London and New York 1966.

[12] S. K. Garg and G. P. Smyth, J. Phys. Chem. **69,** 1294 (1965).

[13] E. M. Kosower and D. Huppert, Chem. Phys. Lett. **96,** 433 (1983).

[14] O. Exner, in: Correlation Analysis in Chemistry (N. B. Chapman and J. Shorter, eds.), Plenum Press, New York 1978.

[15] J. Gryczyński, D. Gloyna, and A. Kawski, Z. Naturforsch. **35a,** 777 (1980).