The Effect of Substituents on the Polarity in the First Excited Singlet State of Some trans-Styryl-Methyl-Sulfones *

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The effect of substituents R (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 is investigated. Linear relations are found between the dipole moment in the excited state, μ_e, and the Hammett constant, σ_p^+, and also between μ_e and the dipole moment in the ground state, μ_g. On increasing the electron-donor power of R, μ_e grows faster than μ_g.

1. Introduction

In substituted trans-β-styryl-methyl-sulfones a distinct electronic interaction occurs via the central ethylene bond linking the sulfonyl group with the substituent R. This has been evidenced by quantum-mechanical calculations [1], IR and ^{13}C-NMR measurements [2, 3], and investigations of the electric dipole moments in the ground state [4]. It has been found that the dipole moment increases with increasing electron-donor power of R, and that the dipole moment in the ground state is linearly related to the Hammett constant, σ_p^+, of R. As has been shown by quantum-mechanical calculations [1, 5], the presence of the sulfonyl group results in a substantial increase of the polarity of styrenes, this effect being markedly stronger in the excited than in the ground state. In the ground state, the effect due to the presence of the sulfonyl group is independent of the p-substitution. The increase in the dipole moment in the excited state is diminished to an extent corresponding to its increased value for the respective styrene.

The present paper reports on experimental investigations of the effect of substituents R on the polarity of trans-styryl-methyl-sulfones in the first excited singlet state (S_1).

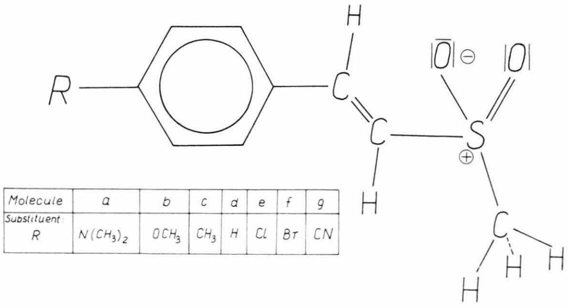
2. Experimental

2.1. Methods

Absorption spectra were measured with an M-40 (Zeiss, Jena) spectrophotometer, and the fluorescence spectra were recorded by the method decribed previously [6]. The styryl-methyl-sulfones (Fig. 1) were prepared by Wegener and Courault [7]. The polar and non-polar solvents used were spectroscopically pure. All measurements were carried out at 25 °C.

2.2. Basic Equations of the Analysis of Dipole Moments in the Excited State

The following equations can be derived based on the theory [8, 9] of the absorption and fluorescence band shifts, $\tilde{\nu}_A$, (in cm^{-1}) and $\tilde{\nu}_F$ (in cm^{-1}), respectively, in different solvents when the dipole moments in the ground (μ_g) and in the excited state (μ_e) are parallel (this condition is fulfilled in the case of the



Molecule	a	b	c	d	e	f	g
Substituent: R	$N(CH_3)_2$	OCH_3	CH_3	H	Cl	Br	CN

Fig. 1. Structural formulas of trans-styryl-methyl-sulfones.

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compounds investigated), and when $\alpha/a^3 \approx \frac{1}{2}$:

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

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

where

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

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

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

and

$$m_2 = \frac{\mu_e^2 - \mu_g^2}{\beta\, a^3}, \tag{6}$$

where $\beta = 2\pi\varepsilon_0 hc$ is a universal constant and amounts to $1.105110440 \times 10^{-35}$ C^2. ε and n are the permittivity and the refractive index of the solvent, respectively, a is the Onsager interaction radius and α the polarizability of the solute.

The parameters m_1 and m_2 are determined from (1) and (2), and for a known value of μ_g (based on dielectric investigations), μ_e can be found from (5) and (6):

$$\mu_e = \mu_g \frac{m_1 + m_2}{m_2 - m_1}, \tag{7}$$

and a from (5) or (6).

In the case of non-fluorescent molecules, μ_e can be determined from the absorption band shifts. The following formula expressing the band shift relative to a non-polar solvent is obtained for solvents with different polarities and similar refractive indices [10]:

$$\delta\tilde{\nu}_A = \tilde{\nu}_A^{\text{nonpol}} - \tilde{\nu}_A^{\text{pol}} = m_3\, f(\varepsilon, n), \tag{8}$$

where

$$m_3 = \frac{\mu_g(\mu_e - \mu_g)}{\beta\, a^3} \quad (\text{when } \boldsymbol{\mu}_g \parallel \boldsymbol{\mu}_e), \tag{9}$$

and the function $f(\varepsilon, n)$, being a measure of the solvent orientational polarity, is given by (3).

3. Results and Discussion

From our seven substituted trans-β-styryl-methyl-sulfones (a, b, c, d, e, f, g), only compound a exhibits measurable fluorescence. The absorption and fluorescence spectra were measured for this compound in different solvents, and the parameters m_1 and m_2 were determined according to (1) and (2) from the slopes of straight lines. Hence, based on (7) and (5) or (6), the values of μ_e and a were obtained. The Onsager radius, $a = 6.2 \times 10^{-10}$ m thus determined, differs only slightly from the value calculated from the molecular geometry (see Table 1). For molecule a also μ_e was determined based on the Czekalla effect consisting in the fluorescence polarization in an external electric field *. The value 43.0×10^{-30} C m obtained is in good agreement with that determined when considering the effect of solvent on the absorption and fluorescence spectra.

The value of the parameter m_3 determined from the absorption band shift and amounting to 1.8×10^5 m^{-1} is in good agreement with that calculated from the formula $m_3 = \frac{1}{2}(m_2 - m_1) = 1.78 \times 10^5$ m^{-1} (see [11]). This indicates that μ_e can successfully be determined for the remaining non-fluorescent compounds investigated based on relative absorption band shifts (from (8) and (9)). The value of the Onsager radius occurring in (9) was obtained from the molecular geometry for an ellipsoid of revolution. According to Lippert [12], the relation $a \approx 0.8b$ can in this case be used, where b refers to the long molecular axis. Table 1 summarizes the parameters m_1, m_2 and m_3 determined for all the molecular investigated (a – g), and the values of a estimated from the molecular geometry. Table 1 shows also the values of μ_g known from the literature [4], and μ_e obtained in the present paper. Also the Hammett constant, σ_p^+, of the substituents R [13, 14] have been given for the trans-β-styryl-methyl-sulfones investigated. As can be inferred from the experimental results (Table 1 and Fig. 2), the increase in the electron-donor power of R is accompanied by an increase in the electric dipole moment in the excited state, similarly as in the case of the ground state, the former effect being, however, markedly stronger. This is in accordance with the quantum-mechanical calculations [1, 5] which indicate that the presence of the sulfonyl group results in a marked increase in the polarity of styrenes in the excited state. There exists a linear relation between the dipole moments (μ_g or μ_e) and the constants σ_p^+ of the substituents (Figure 2). The better correlation between μ_e and electrophilic substituent constant σ_p^+, as compared to σ_p, is an evidence of the intense electronic interaction, in particular in the excited state. The poor location of com-

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* The results will be reported in a separate paper.

Table 1. Fluorescence and absorption shift parameters, dipole moments and Hammett constants for different substituents of trans-styryl-methyl-sulfones.

Molecule	Substituent R	a	m_1	m_2	m_3	μ_g (from [4])	μ_e	σ_p^+ ** (from [13, 14])
		(10^{-10} m)	(10^2 m^{-1})			(10^{-30} C m) *		
a	$N(CH_3)_2$	6.0	1540	5100	1800	23.3	43.5	−1.7
b	OCH_3	5.8			750	18.3	27.1	−0.778
c	CH_3	4.9			750	17.3	22.9	−0.311
d	H	4.5			825	16.0	21.2	0
e	Cl	4.7			590	13.5	18.5	0.114
f	Br	4.8			650	13.1	19.2	0.150
g	CN	5.0			500	12.0	17.7	0.659

* The conversion factor for the dipole moment:

$$\frac{[\mu_{SI}]}{\text{C m}} = 3.33564 \times 10^{-30} \frac{[\mu]_{cgs}}{\text{D}},$$

where D is the symbol for debye and 1 D = 10^{-18} esu cm.

** Electrophilic substituent constant (Hammett constant).

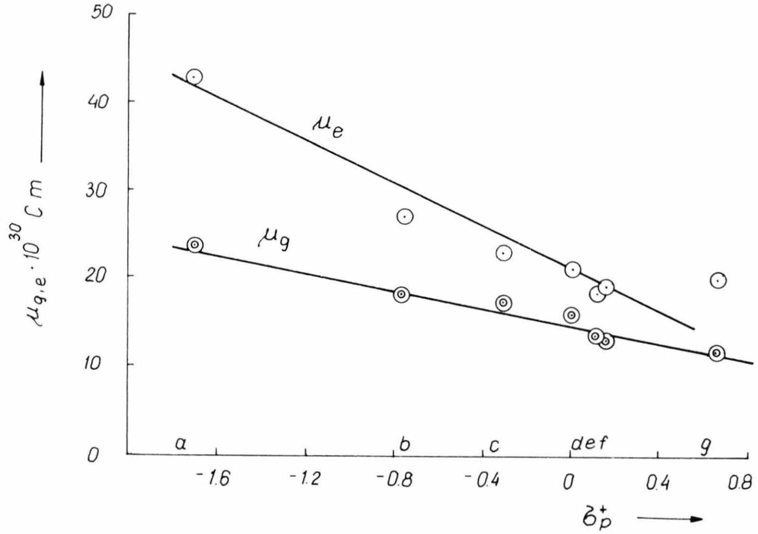

Fig. 2. Dependence of the dipole moments (μ_e, μ_g) on Hammett constants σ_p^+ of the substituents R given in Fig. 1 and Table 1. Regression coefficients for $\mu_e = a_1 \sigma_p^+ + b_1$: $a_1 = -11.186 \times 10^{-30}$ C m, $b_1 = 21.289 \times 10^{-30}$ C m, correlation coefficient $r = 0.960$; and for $\mu_g = a_2 \sigma_p^+ + b_2$: $a_2 = -4.927 \times 10^{-30}$ C m, $b_2 = 14.901 \times 10^{-30}$ C m, $r = 0.977$.

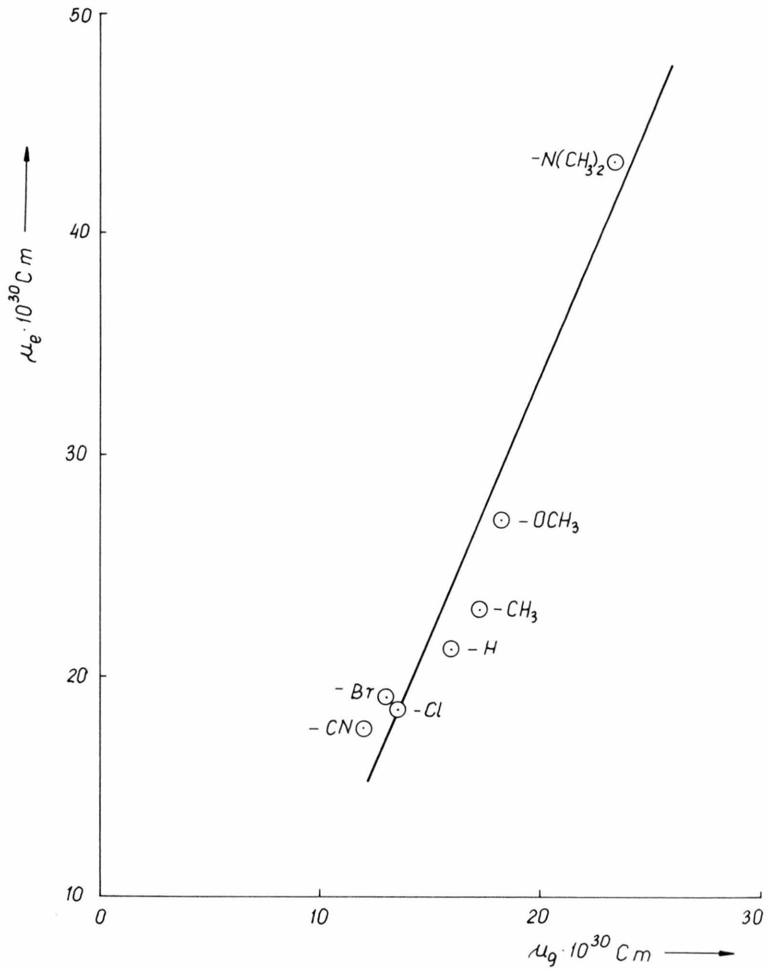

Fig. 3. Linear relation between the dipole moments μ_e and μ_g of substituted trans-styryl-methyl-sulfones: $\mu_e = 2.197\,\mu_g - 11.349$ ($r = 0.951$).

pound g (R = CN) in the excited state (see Fig. 2) can be accounted for by the fact that the substituents in positions 4 and ω do not participate to a greater extent in any distinct donor-acceptor interactions. A similar linear relation can be observed between the values of the dipole moments in the excited μ_e, and the ground state, μ_g (Figure 3).

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