Thermochromic Shifts of Absorption and Fluorescence Spectra and Excited State Dipole Moment of PRODAN*

A. Kawski, B. Kukliński, and P. Bojarski

Institute of Experimental Physics, University of Gdańsk, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland

Reprint requests to Prof. A.K.; ul. Gen. W. Sikorskiego 11, PL-84-200 Wejherowo, Poland

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Using the thermochromic shift method of absorption and fluorescence spectra, the dipole moments in the ground, μ_g, and excited, μ_e, state are simultaneously determined for PRODAN in ethyl acetate. The obtained values for μ_g and μ_e are compared with those previously determined by the solvatochromic method for two different Onsager radii, and a satisfactory agreement has been obtained.

Key words: Thermochromic Shifts; Solvatochromic Shift; Dipole Moments in the ground and excited states; PRODAN.

1. Introduction

PRODAN (Fig. 1) belongs to the category of solvent – sensitive probes due to the fact that the aromatic naphthalene ring is attached to two groups: an electron donor and an electron acceptor which contribute to a distinct increase in the electric dipole moment $\Delta\mu = \mu_e - \mu_g$ (μ_e and μ_g is the dipole moment in the excited and ground state, respectively) as a result of excitation to the lowest excited singlet state. The change of the PRODAN dipole moment was studied by several authors [1–4]. Different values of μ_e have been reported. In [4] a profound discussion concerning the methods used has been given and the values of μ_g and μ_e have been determined by the "solvent perturbation" method applying solvents of different permittivities ε and refractive indexes n.

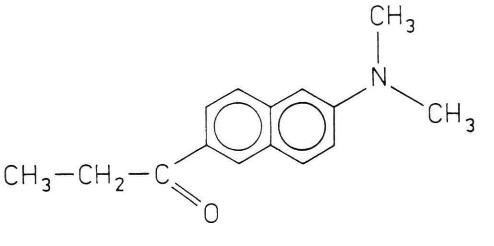

Fig. 1. Structural formula of 6-propionyl-2-(dimethylamino)naphthalene (PRODAN).

In the current study the "thermochromic shift" method is used. This method exploits the effect of temperature on the location of the absorption and fluorescence bands of a given luminescent compound in a selected polar solvent. At higher temperatures a specific interaction between the luminescent molecule and solvent molecules as well as interactions among solvent molecules are eliminated. This method allows for a very accurate determination of μ_g and μ_e.

2. Basic Equations for the Analysis of Dipole Moments

The following equations are based on the quantum mechanical perturbation theory [5, 6] of the absorption ($\tilde{\nu}_A$) and fluorescence ($\tilde{\nu}_F$) band shifts (in wavenumbers) in solvents of different permittivities ε and refractive indexes n provided that the dipole moments μ_g and μ_e are parallel and $\alpha/a^3 = 1/2$ (α denotes the polarizability, whereas a is the Onsager radius of the solute) [7]:

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

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

where

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

is the solvent polarity parameter [8] and

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

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* 6-propionyl-2-(dimethylamino)naphthalene.

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

$$m_2 = \frac{2\,(\mu_e^2 - \mu_g^2)}{h\,c\,a^3}\,. \tag{6}$$

μ_g and μ_e are the dipole moments in the ground and excited state, respectively, h is Plancks constant, and c is the velocity of light in the vacuum. The parameters m_1 and m_2 can be determined from the absorption and fluorescence band shifts given by (1) and (2), and the values of μ_g and μ_e from the following relations obtained from (5) and (6) [7, 9]:

$$\mu_g = \frac{m_2 - m_1}{2} \cdot \left(\frac{h\,c\,a^3}{2\,m_1}\right)^{1/2}, \tag{7}$$

$$\mu_e = \frac{m_1 + m_2}{2} \cdot \left(\frac{h\,c\,a^3}{2\,m_1}\right)^{1/2}, \tag{8}$$

$$\mu_e = \frac{m_1 + m_2}{m_2 - m_1} \cdot \mu_g\,, \quad (m_2 > m_1)\,. \tag{9}$$

3. Experimental

3.1. Methods

The absorption and fluorescence spectra between 296 and 351 K were measured with the apparatus described in [10, 11], using a home constructed high pressure cell [7, 12]. The cell, made of stainless steel with quartz windows, was heated electrically, controlled by a thermo-element placed directly in the cell, using the temperature controller (type UNIPAN 650) with an accuracy of ±0.2 K.

The measurements between 251 and 296 K were performed using a thermally isolated metal cell with quartz optics cooled down by Peltier elements. These elements were supplied by a power amplifier controlled by the mentioned temperature controller.

3.2. Determination of Permittivities ε and Refractive Indexes n at Different Temperatures

From the numerous solvents studied in [12, 13], ethyl acetate was selected for our study. The values of ε and n over the temperature range studied were determined from the empirical formulas [12]

$$\varepsilon(T) = \varepsilon_0(T_0) - \alpha\,(T - T_0) - \beta\,(T - T_0)^2 - \gamma\,(T - T_0)^3, \tag{10}$$

$$n(T) = n_0(T_0) - a\,(T - T_0) - b\,(T - T_0)^2, \tag{11}$$

where the parameters α, β, γ as well as a and b are given in Table 1. For n and ε determined by this method the parameters $f(\varepsilon, n)$ and $f(\varepsilon, n) + 2g(n)$ appearing in (1) and (2) were calculated.

The changes in these parameters with temperature T are presented in Figs. 2 and 3.

3.3. Thermochromic Shifts of Absorption and Fluorescence Spectra of PRODAN in Ethyl Acetate

Figures 4 and 5 show the effect of temperature on the PRODAN fluorescence intensity in ethyl acetate for temperature ranging from 251 to 351 K. Strong quenching of PRODAN fluorescence is observed for increasing temperature. This fact did not allow to increase the temperature above 351 K. For this reason, in order to broaden the scale of $f(\varepsilon, n)$ (cp. Fig. 6), we decided to measure the absorption and fluorescence band shift for temperature decreasing from 296 to 251 K.

In both cases (Figs. 4 and 5) a blue shift of the fluorescence band is observed with increase in temperature which is caused by the decreasing permittivity ε. This shift is stronger than that of the absorption band.

Using the dependencies of $f(\varepsilon, n)$ and $f(\varepsilon, n) + 2g(n)$ on temperature T given in Figs. 2 and 3 we obtain

$$f(\varepsilon, n) = -0.00104\,T + 0.7982\,, \tag{12}$$

$$f(\varepsilon, n) + 2g(n) = -0.00155\,T + 1.45082\,. \tag{13}$$

After introducing (12) and (13) in (1) and (2), we have

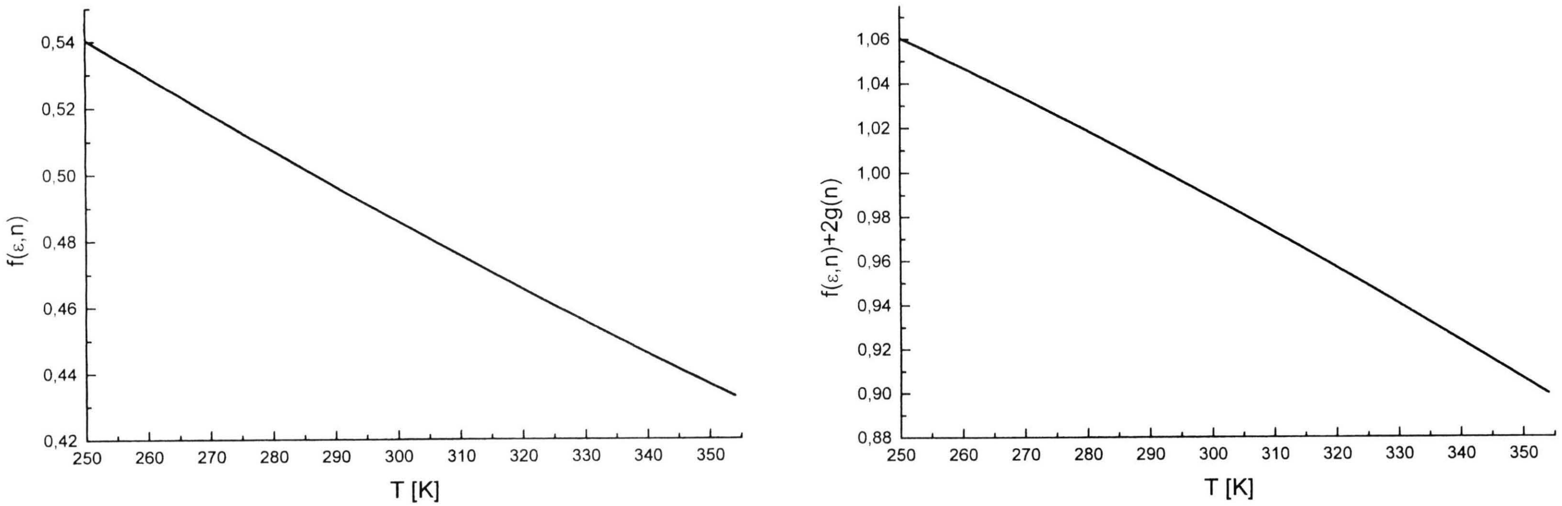
$$\tilde{\nu}_A - \tilde{\nu}_F = m_1\,[0.7982 - 0.00104\,T] + \text{const}, \tag{14}$$

$$\tilde{\nu}_A + \tilde{\nu}_F = -m_2\,[1.45082 - 0.00155\,T] + \text{const}, \tag{15}$$

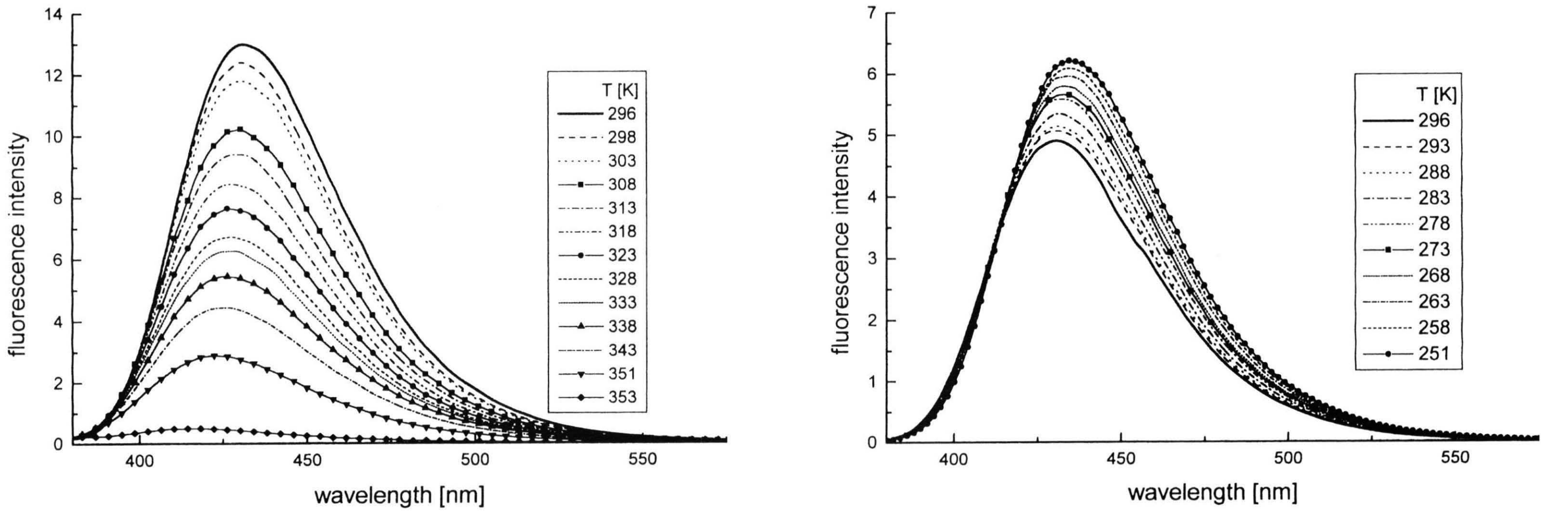
The above semiempirical equations (14) and (15) are valid only for luminescent molecules in ethyl acetate over the temperature range 251–351 K.

Solvent	$\varepsilon(T_0)$ $T_0 = 293$ K	$n(T_0)$ $T_0 = 293$ K	$\alpha \times 10^2$ [deg^{-1}]	$\beta \times 10^4$ [deg^{-2}]	$\gamma \times 10^6$ [deg^{-3}]	$a \times 10^4$ [deg^{-1}]	$b \times 10^6$ [deg^{-2}]
Ethyl acetate	6.09	1.372	2.155	−0.534	0.098	3.390	2.319

Table 1. Permittivity ε and refractive index n at $T_0 = 293$ K and parameters for ethyl acetate occurring in (10) and (11).



Figs. 2 and 3. Temperature dependence of functions $f(\varepsilon, n)$ (Fig. 2) and $f(\varepsilon, n) + 2g(n)$ (Fig. 3) for ethyl acetate.



Figs. 4 and 5. Influence of temperature on the fluorescence intensity for PRODAN in ethyl acetate from 296 K to 351 K (Fig. 4) and from 251 K to 296 K (Figure 5).

4. Ground – and Excited – State Dipole Moments of PRODAN

The slope parameters, m_1 and m_2, occurring in the general equations for the difference $\tilde{\nu}_A - \tilde{\nu}_F$ and the sum $\tilde{\nu}_A + \tilde{\nu}_F$ of the wavenumbers, respectively, are functions of the orientation polarization of the solvent, $f(\varepsilon, n)$, and the sum $f(\varepsilon, n) + 2g(n)$, respectively. Figures 6 and 7 show the thermochromic spectra shifts $\tilde{\nu}_A - \tilde{\nu}_F$ and $\tilde{\nu}_A + \tilde{\nu}_F$ versus the solvent polarity functions $f(\varepsilon, n)$, and $f(\varepsilon, n) + 2g(n)$, respectively.

The slopes of the fitted lines presented in Figs. 6 and 7 were found to be $m_1 = 2400$ cm^{-1} and $m_2 = 5200$ cm^{-1}, respectively. According to (5) and (6), the values of the dipole moments μ_g and μ_e depend not only on m_1 and m_2 but also on the Onsager interaction radius *a*. For PRODAN, $a = 4.2$ Å was assumed based on crystallographic data [1] and $a = 4.6$ Å based on the calculation of the spherical cave volume being a sum of all volumes of atoms [14]. In the present work, μ_g and μ_e are determined for both values of *a* and they are listed in Table 2. It is seen that the ratio $\mu_e/\mu_g = 2.7$ determined by the thermochromic method is smaller than that determined from the solvatochromic method ($\mu_e/\mu_g = 3.0$). The thermochromic method used here gives much less spread experimental data (cp. Figs. 2 and 3 from [4] and Figs. 6 and 7 from this work).

Figures 6 and 7 present also the dependencies of $\tilde{\nu}_A - \tilde{\nu}_F$ and $\tilde{\nu}_A + \tilde{\nu}_F$ on temperature *T* according to (14) and (15).

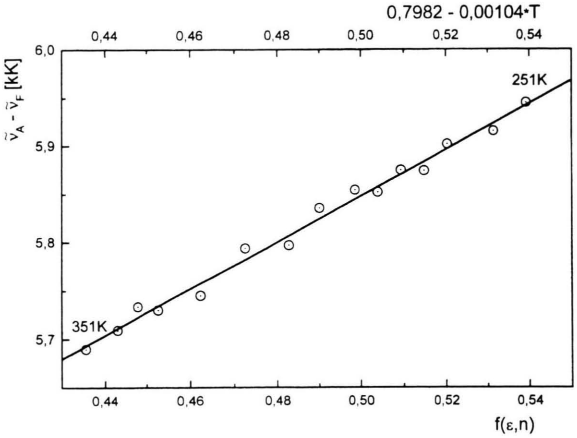


Fig. 6. Plots of $\tilde{\nu}_A - \tilde{\nu}_F$ versus $f(\varepsilon, n)$ for PRODAN in ethyl acetate at different temperatures *T*.

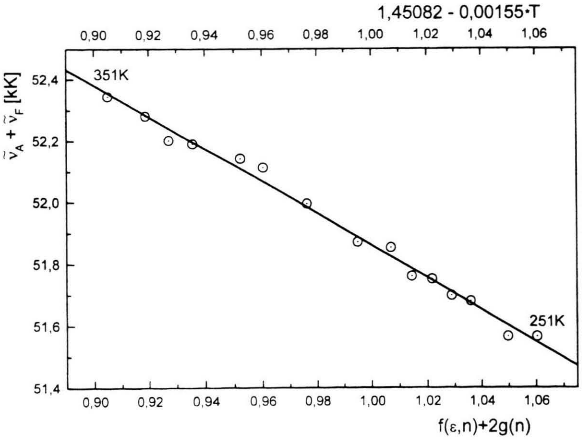


Fig. 7. Plots of $\tilde{\nu}_A + \tilde{\nu}_F$ versus $f(\varepsilon, n) + 2g(n)$ for PRODAN in ethyl acetate at different temperatures *T*.

Table 2. Dipole moments (in Debye) determined from thermochromic shifts and solvatochromic shifts for PRODAN.

Onsager radius *a* [Å]	Thermochromic shifts in Debye [D]			Solvatochromic shifts in Debye [D]		
	μ_g	μ_e	$\Delta\mu$	μ_g	μ_e	$\Delta\mu$
4.2	2.45	6.65	4.20	2.14	6.43	4.29
4.6	2.80	7.60	4.80	2.46	7.37	4.91

5. Conclusions

The values of dipole moments in the first excited singlet state μ_e determined based on the method of thermochromic shifts of absorption and fluorescence spectra for two somewhat different Onsager radii differ only slightly from those obtained from the solvatochromic method (Table 2). However, the dipole moments in the ground state μ_g differ more significantly. The structure of PRODAN leads to the conclusion that both moments, $\boldsymbol{\mu}_g$ and $\boldsymbol{\mu}_e$, are parallel and therefore can be simultaneously determined by the above mentioned methods for the estimated values of Onsager radii. For the known value of μ_g determined experimentally based on the dielectric studies it is possible to determine μ_e from (9) without knowing the Onsager radius. However, best to our knowledge, no such measurements are known for PRODAN. The experimental values of μ_g obtained by us (Table 2) may be only compared with the value of $\mu_g = 3.77$ D calculated by the CNDO/2 method [14], which is, however, distinctly higher than that determined by us.

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