Ground- and Excited-State Dipole Moments of 6-Propionyl-2-(dimethylamino)naphthalene Determined from Solvatochromic Shifts*

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The dipole moments in the ground- and excited-state of the fluorescence probe 6-propionyl-2-(dimethylamino)naphthalene (PRODAN) are determined from solvatochromic shifts to be $\mu_g = 2.1$ D and $\mu_e = 6.4$ D. These values concern the free molecule. In the first excited singlet state the dipole moment is only 3 times greater than in the ground state.

1. Introduction

The hydrophobic fluorescent probe 6-propionyl-2-(dimethylamino)naphthalene (PRODAN), is highly sensitive to the solvent polarity and can potentially reveal the polarity of its immediate environment. The spectral properties of PRODAN (Figure 1) are of interest in biochemistry and are described by Weber and Farris [1] and by Lakowicz [2].
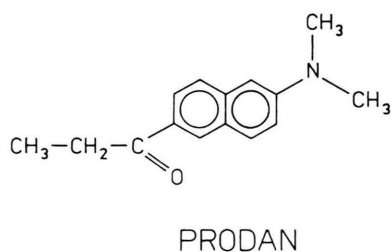

Fig. 1. Structural formula of 6-propionyl-2-(dimethylamino)naphthalene (PRODAN).

The change of the electric dipole moment, $\Delta\mu = \mu_e - \mu_g$ (where μ_e and μ_g are the dipole moments in the excited- and ground-state, respectively) of PRODAN has been experimentally studied by several authors [1, 3, 4], using the Lippert-Mataga equation [5, 6]. It was shown that the increments in the dipole moments, $\Delta\mu$, determined for different fluorescent molecules, based on the Lippert-Mataga solvent polarity parameter are much overrated in comparison to the values μ_e obtained by electrooptical methods [7–10].

In the present paper we determine the dipole moments μ_g and μ_e of PRODAN by the "solvent perturbation method" [8, 11], utilizing the absorption and fluorescence shifts in different solvents measured by Catalan et al. [4].

2. Basic Equations of the Analysis of Dipole Moments

The following equations are based on the quantum-mechanical perturbation theory [8, 11] of the absorption ($\tilde{\nu}_A$) and fluorescence ($\tilde{\nu}_F$) band shifts (in wavenumbers) in different solvents, when the dipole moments μ_g and μ_e are parallel and when $\alpha/a^3 = 1/2$ (α is the polarizability and a the Onsager interaction radius of the solute) [10]:

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

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

where

$$f(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \qquad (3)$$
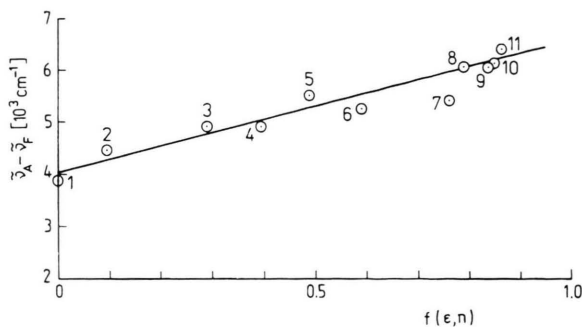
Fig. 2. Plots of $\bar{v}_A - \bar{v}_F$ versus $f(\varepsilon, n)$ (3) for PRODAN in different solvents: 1 – cyclohexane, 2 – triethylamine, 3 – anisole, 4 – chloroform, 5 – ethyl acetate, 6 – dichloromethane, 7 – benzonitrile, 8 – acetone, 9 – N,N-dimethylformamide, 10 – dimethyl sulfoxide, 11 – acetonitrile.
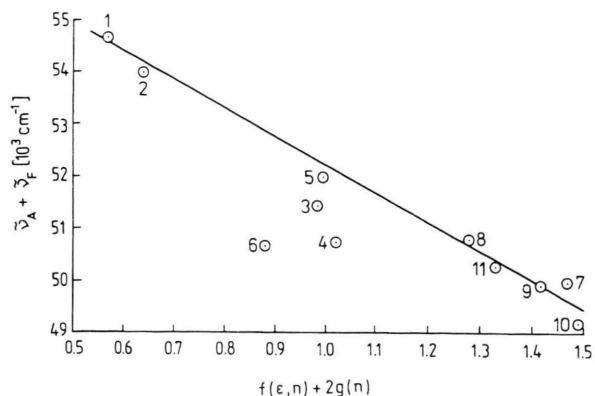

Fig. 3. Plots of $\bar{v}_A + \bar{v}_F$ versus $f(\varepsilon, n) + 2g(n)$ for PRODAN in the same solvents as in Figure 2.

is the solvent polarity parameter [12] and

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

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

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

ε and n are the permittivity and the refractive index of the solvent, respectively, h is the Planck constant, and c the velocity of light in vacuo.

The parameters m_1 and m_2 can be determined from the absorption and fluorescence band shifts (1) and (2), and the values of μ_g and μ_e from (5) and (6) [10, 13]:

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

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

or

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

Thus, for a given Onsager radius, the ground- and excited-state dipole moments can simultaneously be determined by the spectroscopic method. The solvent polarity function, $f(\varepsilon, n)$, (3), different from Lippert-Mataga function, depends most strongly on ε over the interval $2 < \varepsilon < 10$, and to a lesser degree on n.

Using standard methods of statistical analysis, Koutek [14] verified sixteen equations, based on the existing theories of long range solute-solvent interactions that describe the dependence of the absorption and fluorescence band maxima shifts, $\bar{v}_A$ and $\bar{v}_F$, respectively. Nine selected luminescent compounds have been studied in view of characteristic functions of the electric permittivity ε and the refractive index n. The values of μ_e thus obtained were compared to those determined independently by electrooptical measurements. The optimum results (mean relative error $\pm 11.7 \div 14.6\%$) were obtained for the solvent polarity parameter $f(\varepsilon, n)$ expressed by (3), [14].

3. Results and Discussion

In Figs. 2 and 3 the spectra shifts $\bar{v}_A - \bar{v}_F$ and $\bar{v}_A + \bar{v}_F$ of PRODAN, observed by Catalan et al. [4], are plotted for eleven selected solvents versus the solvent polarity functions $f(\varepsilon, n)$ and $f(\varepsilon, n) + 2g(n)$, respectively. A linear regression was carried out and a fit to these data was obtained. The measured points satisfied well (1) and (2) except for chloroform (point 4) and dichloromethane (point 6) (see Figure 3). Points 4 and 6 indicate less polar solvents, as one could expect based on the high permittivity. These polar molecules are very small and have a notable dipole moment. The pairing of dipoles can form non-dipolar dimers (self-associating liquid) and reduce the microscopic polarity of the solvent [15].

The slopes of the fitted lines presented in Figs. 2 and 3 were found to be $m_1 = 2500 \text{ cm}^{-1}$ and $m_2 = 5000 \text{ cm}^{-1}$,

respectively. Assuming the Onsager interaction radius of the solute, $a = 4.2$ Å, adopted from crystallographic data by Weber and Farris [1], we obtain from (7) and (8) $\mu_g = 2.14$ D ($7.14 \cdot 10^{-30}$ Cm) and $\mu_e = 6.43$ D ($21.45 \cdot 10^{-30}$ Cm). The dipole moment difference $\Delta\mu = \mu_e - \mu_g$ between the excited and ground states is about 4.3 D. From (9) one can determine μ_e if μ_g is known from dielectric measurements. Thus the absolute μ_e value can be derived independently of any assumption on a. Based on (9), for $\mu_g = 2.14$ D we have $\mu_e = 6.42$ D.

The solvent polarity function $f(\varepsilon, n)$, which is related to the non-specific interactions, can be correlated with the empirical parameter π^* [16]. As was shown by Koutek [14], the equation

$$\pi^* = 1.04 f(\varepsilon, n) + 0.014 \tag{10}$$

between π^* and $f(\varepsilon, n)$ is fullfilled.

The shifts of $\tilde{\nu}_A - \tilde{\nu}_F$ and $\tilde{\nu}_A + \tilde{\nu}_F$ of the studied compound in the same solvents plotted versus the π^* values are linear (except for points 4 and 6), and from the slopes we obtain $m_1 = 2450$ cm^{-1} and $m_2 = 4900$ cm^{-1}. In this case the dipole moments μ_g and μ_e (from (7) and (8)) are 2.15 D and 6.45 D, respectively. The difference between the dipole moments determined by the use of the empirical parameter π^* (10) and the polarity function $f(\varepsilon, n)$ (3) is very small. Meanwhile, the dipole moments of PRODAN determined by Balter et al. [3] and Catalan et al. [4] are greater, as one should expect from the solvent polarity parameter in the form $\Delta f = \dfrac{\varepsilon - 1}{2\,\varepsilon + 1} - \dfrac{n^2 - 1}{2\,n^2 + 1}$. The presently received volume $\mu_g = 2.14$ D is close to

2 D, the value approximated by Macgregor and Weber [17]. However, $\mu_e \approx 20$ D in the fluorescent state is incorrect, as was shown by Balter et al. [3].

Assuming $a = 4.6$ Å, the calculated Onsager cavity radius of a sphere with the volume being the sum of the volumes of all atoms [18], we obtain now for $m_1 = 2500$ cm^{-1} and $m_2 = 5000$ cm^{-1} from (7) and (8) $\mu_g = 2.46$ D and $\mu_e = 7.37$ D. These values are only somewhat greater than the μ_g and μ_e values for $a = 4.2$ Å.

It is necessary to mention that one determines the dipole moment of a free molecule on the ground state by our theory [8]. In order to eliminate the specific solute-solvent association as a result of the formation of hydrogen bonds, and the formation of solvation shells around the solute molecule in two component solvents (non-polar/polar) it is useful to apply the thermochromic shifts method [10, 19–23].

4. Conclusions

a) The dipole moments in the ground and excited states determined by the "solvent perturbation method" are $\mu_g = 2.1$ D and $\mu_e = 6.4$ D for $a = 4.2$ Å, and $\mu_g = 2.5$ D and $\mu_e = 7.4$ D for $a = 4.6$ Å.

b) These dipole moments concern the free PRODAN molecule.

c) The dipole moment in the first excited state is only 3 times greater than in the ground state.

A detailed study of the thermochromic shifts of PRODAN in one selected solvent is in progress.

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