3224 © 1991 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 64, 3224—3228 (1991) [Vol. 64, No. 11

Estimation of Angles between the Ground- and Excited-State Dipole Moments from Solvent Spectral Frequency Shifts

Takehiro ABE
College of General Education, Tohoku University, Kawauchi, Aoba-ku, Sendai 980
(Received April 4, 1991)

A method for estimating the angle between the ground- and excited-state dipole moments is presented on the basis of Abe's improved expressions for the solvent frequency shifts of absorption and fluorescence spectra (*Bull. Chem. Soc. Jpn.*, **54**, 327 (1981); **58**, 3415 (1985); **61**, 3797 (1988)). Applications of the method to *N*,*N*-dimethylaniline and aniline give angles of 39.5° and 40.0°, respectively; the excited-state dipole moments are both smaller than the corresponding ground-state dipole moments.

On the basis of theories regarding solvent effects on the frequency shifts of absorption and/or fluorescence, the dipole moments and/or polarizabilities have been estimated for the excited states of organic molecules.[1)] There have, however, been a few attempts to estimate the angles between the ground- and excited-state dipole moments due to solvent spectral shifts, except for solute molecules in which both the dipole moments are obviously collinear. On the basis of the Onsager model,[15)] Suppan[9,16)] has presented a method used to obtain the angles between the ground- and excited-state dipole moments due to the solvent shifts of the absorption and fluorescence spectra for such organic molecules as aniline. His method requires data concerning the solvatochromic shifts in two solvents of nearly the same refractive indices. Recently, Ayachit[11)] has improved Suppan's method. Upon modifying McRae's expression[17)] for solvent absorption-spectral shifts, Prabhumirashi et al.[18,19)] attempted to estimate the angles between the ground- and excited-state dipole moments. Later, Ayachit et al.[6)] improved the method of Prabhumirashi et al. and obtained several angle values for nitroanilines.

Abe's improved expression[3,20)] for the solvent absorption-spectral shift gave excited dipole moments and/or polarizabilities that were comparable to those found by electrooptical measurements.[3)] Moreover, on the basis of the same treatment as in the case of the improved expression, an expression for the solvent fluorescence-spectral shift has been presented.[21)] In this paper, therefore, an attempt has been made to present a method for estimating the angle between the ground- and excited-state dipole moments by combining the improved expression for the solvent absorption-spectral frequency shifts with that for the solvent fluorescence-spectral shifts.

Theory

The wave numbers of a transition from the ground state to the *i*th-excited state of a neutral solute molecule (A) in vapor and in a solvent (S) are denoted by $\sigma^{\circ}_{0i,\mathrm{a}}$ and $\sigma_{0i,\mathrm{a}}$ (cm^{-1}), respectively. The wave numbers of the fluorescence frequencies of the solute molecule in the vapor and in the solvent are denoted by $\sigma^{\circ}_{i0,\mathrm{j}}$ and $\sigma_{i0,\mathrm{j}}$ (cm^{-1}), respectively. The ground and *i*th-excited state dipole moments are denoted by $\boldsymbol{P}_{00}$ and $\boldsymbol{P}_{ii}$, respectively; α_{00} and α_{ii} are the isotropic electric polarizabilities of the ground and *i*th-excited states, respectively. The superscripts/subscripts (A and S) denote the solute and solvent molecules, respectively. Suffix f in $\alpha^{\mathrm{A}}_{00,\mathrm{f}}$ and $\alpha^{\mathrm{A}}_{ii,\mathrm{f}}$ indicates that these polarizabilities are not those which correspond ($\alpha^{\mathrm{A}}_{00,\mathrm{a}}$ and $\alpha^{\mathrm{A}}_{ii,\mathrm{a}}$ respectively) to absorption, but to fluorescence. Here, the dipole moments of the ground and *i*th-excited states concerning the fluorescence are assumed to be equal to the corresponding dipole moments regarding absorption, as has usually been assumed in all previous theories concerning fluorescence. This assumption is approximately fulfilled if the nuclear equilibrium configuration of the *i*-th excited state does not significantly differ from that of the ground state, as described in a previous paper.[21)] The improved expression for $\sigma_{0i,\mathrm{a}}$ is given by[3,20)]

$$\sigma_{0i,\mathrm{a}} = \sigma^{\circ}_{0i,\mathrm{a}} + F \times (p^{\mathrm{S}}_{00})^2 \times A_{\mathrm{a}} + F \times \alpha^{\mathrm{S}}_{00} \times B_{\mathrm{a}}, \tag{1}$$

where

$$F = \frac{\pi}{hc}\left(\frac{4\pi L}{3}\right)^{2/3} \times \frac{(\rho^{\mathrm{S}}/M^{\mathrm{S}}_{\mathrm{r}})^{2/3}}{(r_{\mathrm{A}}+r_{\mathrm{S}})^4}, \tag{2}$$

$$A_{\mathrm{a}} = \frac{2\{(p^{\mathrm{A}}_{00})^2 - \boldsymbol{p}^{\mathrm{A}}_{00}\cdot\boldsymbol{p}^{\mathrm{A}}_{ii}\}}{3(4\pi\varepsilon_0)^2kT} + \frac{\alpha^{\mathrm{A}}_{00,\mathrm{a}} - \alpha^{\mathrm{A}}_{ii,\mathrm{a}}}{4\pi\varepsilon_0}, \tag{3}$$

and

$$B_{\mathrm{a}} = \frac{1}{4\pi\varepsilon_0} \times \{(p^{\mathrm{A}}_{00})^2 - (p^{\mathrm{A}}_{ii})^2 + \frac{3}{2} \times \frac{I^{\mathrm{S}}_0 \cdot I^{\mathrm{A}}_0}{I^{\mathrm{S}}_0 + I^{\mathrm{A}}_0} \times (\alpha^{\mathrm{A}}_{00,\mathrm{a}} - \alpha^{\mathrm{A}}_{ii,\mathrm{a}})\}. \tag{4}$$

Here, *c* is the speed of light in vacuum, *h* Planck's constant, *L* Avogadro's constant, *k* Boltzmann's constant, *T* the thermodynamic temperature, ε_0 the permittivity of a vacuum, M_{r} the relative molecular mass, ρ the density, r the radius of a spherical molecule, and I_0 the ionization potential of the ground state. On the other hand, the expression for $\sigma_{i0,\mathrm{f}}$ is given by[21)]

$$\sigma_{i0,\mathrm{f}} = \sigma^{\circ}_{i0,\mathrm{f}} + F \times (p^{\mathrm{S}}_{00})^2 \times A_\mathrm{f} + F \times \alpha^{\mathrm{S}}_{00} \times B_\mathrm{f}, \tag{5}$$

where

$$A_\mathrm{f} = \frac{2\{\boldsymbol{p}^{\mathrm{A}}_{00} \cdot \boldsymbol{p}^{\mathrm{A}}_{00} - (p^{\mathrm{A}}_{ii})^2\}}{3(4\pi\varepsilon_0)^2 kT} + \frac{\alpha^{\mathrm{A}}_{00,\mathrm{f}} - \alpha^{\mathrm{A}}_{ii,\mathrm{f}}}{4\pi\varepsilon_0}, \tag{6}$$

and

$$B_\mathrm{f} = \frac{1}{4\pi\varepsilon_0} \times \{(p^{\mathrm{A}}_{00})^2 - (p^{\mathrm{A}}_{ii})^2 + \frac{3}{2} \times \frac{I^{\mathrm{S}}_0 \cdot I^{\mathrm{A}}_0}{I^{\mathrm{S}}_0 + I^{\mathrm{A}}_0} \times (\alpha^{\mathrm{A}}_{00,\mathrm{f}} - \alpha^{\mathrm{A}}_{ii,\mathrm{f}})\}. \tag{7}$$

By combining Eq. 1 and Eq. 5, one can easily obtain the following equations:

$$\sigma_{0i,\mathrm{a}} + \sigma_{i0,\mathrm{f}} = a + A \times b + B \times d, \tag{8}$$

and

$$\sigma_{0i,\mathrm{a}} - \sigma_{i0,\mathrm{f}} = a' + C \times b' + B \times d', \tag{9}$$

where

$$A = F \times \left\{ \frac{2(p^{\mathrm{S}}_{00})^2}{3(4\pi\varepsilon_0)^2 kT} + \frac{2\alpha^{\mathrm{S}}_{00}}{(4\pi\varepsilon_0)} \right\}, \tag{10}$$

$$B = F \times \left\{ (p^{\mathrm{S}}_{00})^2 + \frac{3\alpha^{\mathrm{S}}_{00}}{2} \times \frac{I^{\mathrm{S}}_0 \cdot I^{\mathrm{A}}_0}{I^{\mathrm{S}}_0 + I^{\mathrm{A}}_0} \right\}, \tag{11}$$

$$C = F \times \frac{2(p^{\mathrm{S}}_{00})^2}{3(4\pi\varepsilon_0)^2 kT}, \tag{12}$$

$$a = \sigma^{\circ}_{0i,\mathrm{a}} + \sigma^{\circ}_{i0,\mathrm{f}}, \tag{13}$$

$$a' = \sigma^{\circ}_{0i,\mathrm{a}} - \sigma^{\circ}_{i0,\mathrm{f}}, \tag{14}$$

$$b = (p^{\mathrm{A}}_{00})^2 - (p^{\mathrm{A}}_{ii})^2, \tag{15}$$

$$b' = (p^{\mathrm{A}}_{00})^2 - 2(\boldsymbol{P}^{\mathrm{A}}_{00} \cdot \boldsymbol{P}^{\mathrm{A}}_{ii}) + (p^{\mathrm{A}}_{ii})^2, \tag{16}$$

$$d = \frac{1}{4\pi\varepsilon_o} \times \{(\alpha^{\mathrm{A}}_{00,\mathrm{a}} - \alpha^{\mathrm{A}}_{ii,\mathrm{a}}) + (\alpha^{\mathrm{A}}_{00,\mathrm{f}} - \alpha^{\mathrm{A}}_{ii,\mathrm{f}})\}, \tag{17}$$

and

$$d' = \frac{1}{4\pi\varepsilon_o} \times \{(\alpha^{\mathrm{A}}_{00,\mathrm{a}} - \alpha^{\mathrm{A}}_{ii,\mathrm{a}}) - (\alpha^{\mathrm{A}}_{00,\mathrm{f}} - \alpha^{\mathrm{A}}_{ii,\mathrm{f}})\}, \tag{18}$$

From Eqs. 13 and 14, one obtains

$$\sigma^{\circ}_{0i,\mathrm{a}} = \frac{1}{2} \times (a + a'), \tag{19}$$

and

$$\sigma^{\circ}_{i0,\mathrm{f}} = \frac{1}{2} \times (a - a'). \tag{20}$$

From Eqs. 15, one obtains

$$p^{\mathrm{A}}_{ii} = \{(p^{\mathrm{A}}_{00})^2 - b\}^{1/2}. \tag{21}$$

When one writes $\boldsymbol{p}^{\mathrm{A}}_{00} \cdot \boldsymbol{p}^{\mathrm{A}}_{ii} = p^{\mathrm{A}}_{00} p^{\mathrm{A}}_{ii} \cos\theta$, the value of $\cos\theta$ is obtained from Eq. 16 as

$$\cos\theta = \frac{1}{2} \times \left(\frac{p^{\mathrm{A}}_{00}}{p^{\mathrm{A}}_{ii}} + \frac{p^{\mathrm{A}}_{ii}}{p^{\mathrm{A}}_{00}} - \frac{b'}{p^{\mathrm{A}}_{00} p^{\mathrm{A}}_{ii}} \right). \tag{22}$$

The values for F, A, B, and C can be calculated. In calculating these values, the values observed for p_{00} and I_0 in the vapor phase are used, the values for α_{00} are calculated from the sums of the bond refractions and the values for r_{AorS} may be calculated according to $r_{\mathrm{AorS}} = (3M_\mathrm{r}^{\mathrm{AorS}}/4\pi L\rho^{\mathrm{AorS}})^{1/3}$, as discussed in a previous paper.[3)] Accordingly, the values for a, b, and d and those for a', b', and d' can be obtained by means of a least-squares analysis of data for the solvent absorption- and fluorescence-spectral frequency shifts, according to Eqs. 8 and 9, respectively. One can, therefore, obtain values for $\sigma^{\circ}_{0i,\mathrm{a}}$, $\sigma^{\circ}_{i0,\mathrm{f}}$, p^{A}_{ii}, and $\cos\theta$ according to Eqs. 19, 20, 21, and 22, respectively. Thus, one can estimate the angle of θ between the ground- and excited-state dipole moments.

Results and Discussion

The present expressions used for the solvent absorption- and fluorescence-spectral frequency shifts have been derived on the assumption that the solvent molecules form no hydrogen bonds or complexes with the solute.[20,21)] In applying Eqs. 8 and 9, therefore, data for solvents which are capable of forming hydrogen bonds and complexes with solutes should be excluded. When this restriction is taken into consideration, there is no available data reported for interesting molecules, except for data regarding only *N*,*N*-dimethylaniline. The *N*,*N*-dimethylaniline molecule may be assumed not to be coplanar, since it is well-known that in the similar aniline molecule the plane containing an amino group does not lie in the plane of the benzene ring. Accordingly, the dipole moments of the ground states of *N*,*N*-dimethylaniline and aniline do not lie in the planes of the benzene rings. In view of this point *N*,*N*-dimethylaniline is appropriate for the present purpose.

Therefore, Eqs. 8 and 9 were applied to data reported by Köhler[22)] regarding the solvent maximum absorption- and fluorescence-spectral shifts of *N*,*N*-dimethylaniline (22°). The data points for 8 solvents were chosen, out of his reported total of 12 solvents, by excluding protic solvents. Unfortunately, he did not give all of the numerical values for $\sigma_{0i,\mathrm{a}}$ except for three values for hexane, tetrahydrofuran and dioxane.. Therefore, the $\sigma_{0i,\mathrm{a}}$ values for the 5 remaining solvents were obtained by using the Stokes shifts ($\sigma_{0i,\mathrm{a}}-\sigma_{i0,f}$), from which values could be read off a magnified version of Fig. 1 in Ref. 22. The following values were used for *N*,*N*-dimethylaniline: $r_{\mathrm{A}}=0.369$ nm, $p_{00}^{\mathrm{A}}=1.61$ D (gas)[23] (1 D$=3.333\times10^{-30}$ C m), $\alpha_{00}^{\mathrm{A}}=155.69\times10^{-25}$ cm^3 (see Ref. 3) and $I_0^{\mathrm{A}}=7.6$ eV[24] (1 eV$=1.602\times10^{-19}$ J). For convenience, the temperature was assumed to be 20 °C. Thus, the present analysis by using Eqs. 8 and 9 gives $p_{ii}^{\mathrm{A}}=1.02$ D, $\theta=39.5°$ ($\cos\theta=0.772$), $\sigma^{0}_{0i,\mathrm{a}}=34100$ cm^{-1} and $\sigma^{0}_{i0,\mathrm{f}}=31820$ cm^{-1}. By applying the values of $\sigma^{0}_{0i,\mathrm{a}}=34100$ cm^{-1} and $\cos\theta=0.772$ to Eq. 1, the same p_{ii}^{A} value of 1.02 D and the $\alpha_{ii,\mathrm{a}}^{\mathrm{A}}$ value of 290.6×10^{-25} cm^3 were estimated by means of Calculation 1 in Ref. 3. A similar calculation, by applying the values of $p_{ii}^{\mathrm{A}}=1.02$ D and $\cos\theta=0.772$ to Eq. 5, gave the same $\sigma^{0}_{i0,\mathrm{f}}$ value of 31820 cm^{-1} and $\alpha_{00,\mathrm{f}}^{\mathrm{A}}-\alpha_{ii,\mathrm{f}}^{\mathrm{A}}=-435.4\times10^{-25}$ cm^3 by means of a least-squares analysis. According to Eqs. 1 and 5, the values for $\sigma_{0i,\mathrm{a}}$ and $\sigma_{i0,\mathrm{f}}$, respectively, can be calculated by using the values so estimated for $\sigma^{0}_{0i,\mathrm{a}}$, $\sigma^{0}_{i0,\mathrm{f}}$, p_{ii}^{A}, $\alpha_{ii,\mathrm{a}}^{\mathrm{A}}$, ($\alpha_{00,\mathrm{f}}^{\mathrm{A}}-\alpha_{ii,\mathrm{f}}^{\mathrm{A}}$) and $\cos\theta$. The values ($\sigma_{0i,\mathrm{calcd}}$) so calculated for $\sigma_{0i,\mathrm{a}}$ and $\sigma_{i0,\mathrm{f}}$ were compared with those ($\sigma_{0i,\mathrm{obsd}}$) observed, as shown in Fig. 1. The correlations between the experimental and calculated frequencies are good. The estimated $\sigma^{0}_{0i,\mathrm{a}}$ value of 34100 cm^{-1} agrees roughly with the observed value[25] of 34700 cm^{-1}. These facts may support the validity of Eqs. 8 and 9.

The p_{ii}^{A} value of 1.02 D, estimated in the present work, is smaller than the ground-state dipole moment of 1.61 D by 0.59 D, while the p_{ii}^{A} values of 3.58 D ($\theta=66°$)[19] and 5.1 D[2] and the ($p_{ii}^{\mathrm{A}}-p_{00}^{\mathrm{A}}$) value of 2.0 D[22] have been estimated from solvent spectral-shift theories. Whether $p_{ii}^{\mathrm{A}}>p_{00}^{\mathrm{A}}$ or $p_{ii}^{\mathrm{A}}<p_{00}^{\mathrm{A}}$ is a serious problem for considering the electronic structure of the excited state of *N*,*N*-dimethylaniline.

In the case of a similar molecule, aniline, Lombardi[26] determined that the magnitude of the dipole moment change is $|p_{ii}^{\mathrm{A}}-p_{00}^{\mathrm{A}}|=(0.85\pm0.15)$ D by a technique involving the optical Stark effect in the gas phase. As mentioned above, aniline is not appropriate for the present purpose, because the amino group of aniline is capable of forming hydrogen bonds with aprotic solvents which are high on the β scale regarding the hydrogen-bond acceptor strength.[27] For example, dioxane ($\beta=0.37$), dibutyl ether ($\beta=0.46$), diethyl ether ($\beta=0.47$), tetrahydrofuran ($\beta=0.55$) and acetonitrile ($\beta=0.31$) are involved in the solvents used by Köhler.[22] Nevertheless, an attempt has been made to apply Eqs. 8 and 9 to the 8 spectral data points[22] of Köhler for aniline in similar way in order to compare the estimated value of $|p_{ii}^{\mathrm{A}}-p_{00}^{\mathrm{A}}|$ with the reliable one of Lombardi. The values used for aniline are the same as those given in a previous paper:[3] $r_{\mathrm{A}}=0.331$ nm, $p_{00}^{\mathrm{A}}=1.48$ D(gas), $\alpha_{00}^{\mathrm{A}}=117.3\times10^{-25}$ cm^3, and $I_0^{\mathrm{A}}=7.68$ eV. According to Eqs. 8 and 9, the results of $p_{ii}^{\mathrm{A}}=0.75$ D, $\theta=40.0°$ ($\cos\theta=0.766$), $\sigma^{0}_{0i,\mathrm{a}}=34630$ cm^{-1} and $\sigma^{0}_{i0,\mathrm{f}}=31810$ cm^{-1} were estimated. By applying the values of $\sigma^{0}_{0i,\mathrm{a}}=34630$ cm^{-1} and $\cos\theta=0.766$ to Eq. 1, the same p_{ii}^{A} value of 0.75 D and the $\alpha_{ii,\mathrm{a}}^{\mathrm{A}}$ value of 132.0×10^{-25} cm^3 were estimated. A similar calculation, by applying the values of $p_{ii}^{\mathrm{A}}=0.75$ D and $\cos\theta=0.766$ to Eq. 5, gave a $\sigma^{0}_{i0,\mathrm{f}}$ value of 34600 cm^{-1} and $\alpha_{00,\mathrm{f}}^{\mathrm{A}}-\alpha_{ii,\mathrm{f}}^{\mathrm{A}}=-620.9\times10^{-25}$ cm^3. The correlations between the observed and calculated values for $\sigma_{0i,\mathrm{a}}$ and $\sigma_{i0,\mathrm{f}}$ are shown in Fig. 2. On the whole, the correlations

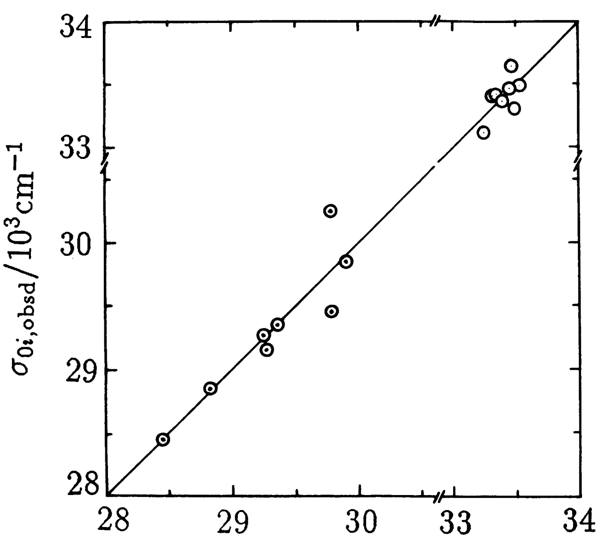

Fig. 1. Plot of the observed frequencies vs. calculated frequencies for *N*,*N*-dimethylaniline. ○, absorption frequencies; ⊙, fluorescence frequencies.

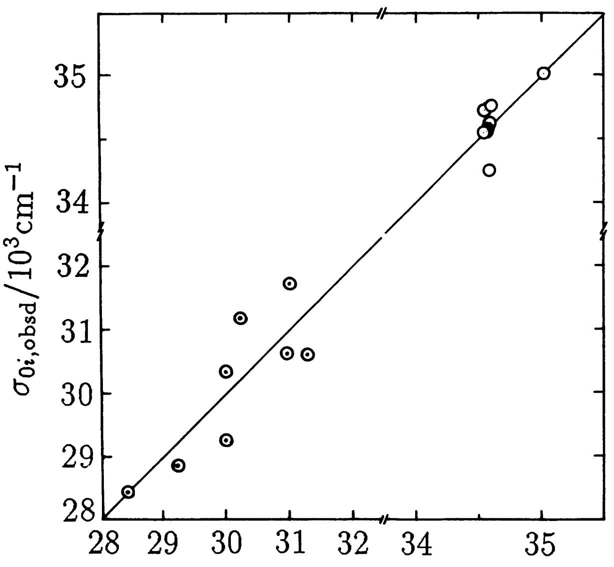

Fig. 2. Plot of the observed frequencies vs. calculated frequencies for aniline. ○, absorption frequencies; ⊙, fluorescence frequencies.

given in Fig. 2 are good, but worse than are those given in Fig. 1. The estimated $\sigma^{\circ}_{0i,a}$ value of 34630 cm^{-1} considerably deviates from the observed values of 35490[28,29] and 35500[25] cm^{-1}. Especially, the $\sigma^{\circ}_{i0,f}$ value of 31810 cm^{-1}, estimated according to Eqs. 8 and 9, does not agree with that (34600 cm^{-1}) estimated from Eq. 5, although there is agreement between the corresponding values for *N*,*N*-dimethylaniline, as shown above. These worse results for aniline in comparison with the results for *N*,*N*-dimethylaniline are probably due to the use of data points for the aprotic solvents with which aniline is capable of forming hydrogen bonds. However, the p^{A}_{ii} and θ values estimated by applying Eqs. 8 and 9 for aniline may be roughly correct, since these values are close to the corresponding ones for *N*,*N*-dimethylaniline.

Here, the reliability of the θ value obtained by the present method will be investigated. Baba et al.[30] reported on the solvent effects on the absorption and fluorescence spectra of diazines, although data points for only 3 solvents could be used for the present purpose. Ony data for pyridazine are used, since the solvent spectral shifts of pyrimidine are small and pyrazine has no dipole moments in both the ground and excited states due to molecular symmetry. According to Baba et al.,[30] the cos θ value for pyridazine should be unity, since the directions of p^{A}_{00} and p^{A}_{ii} for the molecule are the same. By using r_A=0.306 nm, p^{A}_{00}=4.221 D,[24] α^{A}_{00}=91.75×10^{-25} cm^3 and I^{A}_{0}=8.706 eV,[24] Eqs. 8 and 9 were applied to the data for pyridazine in 2,2,4-trimethylpentane, in diethyl ether and in acetonitrile (25 °C). The result that cos θ=1.098 was obtained. This cos θ value is approximately unity, thus leading to the suggestion that the present estimation of θ may be fairly reliable.

The p^{A}_{ii} value (0.75 D) estimated for aniline is smaller than the p^{A}_{00} value (1.48 D), as in the case of *N*,*N*-dimethylaniline. All of the p^{A}_{ii} values which have hitherto been estimated for aniline from the solvent shifts of the absorption and/or fluorescence spectra are larger than p^{A}_{00}: The p^{A}_{ii} value has been estimated by Mataga (2—2.5 D),[31] Murrell (5 D),[32] Iweibo et al. (a value nearly equal to p^{A}_{00}),[33] Suppan (5 D),[2,9,16] and Prabhumirashi et al. (2.13 and 3.30 D, θ=14°).[10,18,19] Recently, Ayachit[11] estimated the values of p^{A}_{ii}=5.3 D and θ=25° for aniline, improving on the method of Suppan.[16] In a previous paper,[3] the p^{A}_{ii} value of 2.33 D was alternatively estimated for aniline by applying Eq. 1 to only three data points for solvents. Even though only three data points are the minimum for applying the expression, it is desirable to use at least several data points. The present estimation of $p^{A}_{00}-p^{A}_{ii}$=0.75 D for aniline agrees well with the reliable value ($|p^{A}_{ii}-p^{A}_{00}|$=(0.85±0.15)D) of Lombardi. The discrepancy between the solvatochromic shift measurements and reliable gas phase Stark effect measurements is fundamentally due to insufficient theoretical expressions for the solvatochromic shifts, as pointed out by Lombardi.[34] As mentioned in a previous paper,[3] comparisons between the excited-state dipole moments and/or polarizabilities estimated from the solvent spectral shifts with those determined from the electrooptical measurements are necessary in order to justify the theoretical expressions used for the solvent spectral frequency shifts. Among the many theoretical expressions, those giving excited-state dipole moments and polarizability values that are comparable to those of the electrooptical measurements will survive. As described above, Abe's improved expression (Eq. 1) gave excited-state dipole moments and/or polarizabilities that were comparable to those of electrooptical measurements.[3] The present estimation that $p^{A}_{00}>p^{A}_{ii}$ for aniline can be reasonably accounted for according to MO calculations as follows: All of the MO calculations of Baba,[35] Mataga,[31] and Nagakura et al.[25,36] show a decrease in the π-electron density at the nitrogen atom in the excited state of aniline. As described in a previous paper,[3] this decrease only increases the magnitude of the excited-state dipole moment component parallel to the plane containing both the benzene ring and nitrogen atom in the same direction as that of the corresponding ground-state dipole moment component, the positive and negative terminals of which do not change sign upon excitation. Accordingly, the excited-state dipole moment component should be larger than the corresponding ground-state dipole moment component. The inclination of the calculated ground-state dipole moment (1.44 D) was obtained by Hehre et al.[37] to be 67° to the plane containing the benzene ring by means of ab initio MO theory. The corresponding inclination of p^{A}_{ii} may be smaller than that (67°) of p^{A}_{00} by 40°, since both the p^{A}_{00} and p^{A}_{ii} components parallel to the benzene ring are in the same direction. By using an inclination of 67°, the p^{A}_{00} and p^{A}_{ii} components containing the benzene ring were calculated to be 1.48 D cos 67°=0.58 D and 0.75 D cos (67°−40°)=0.67 D, respectively. These estimations satisfy the result of the above-mentioned MO calculations. Therefore, the result that the excited-state dipole moment (0.75 D) is smaller than the ground-state dipole moment (1.48 D) does not conflict with the result concerning the above-mentioned MO calculations. Accordingly, the p^{A}_{ii} value of 0.75 D estimated for aniline is reasonable.

The MO calculation of Kimura, Tsubomura, and Nagakura[25] for *N*,*N*-dimethylaniline similarly shows a decrease of the π-electron density at the nitrogen atom in the excited state of *N*,*N*-dimethylaniline. Therefore, the circumstances of *N*,*N*-dimethylaniline are the same as those of aniline. Based on the assumption of the same inclination of 67° for *N*,*N*-dimethylaniline as in the case of aniline, the p^{A}_{00} and p^{A}_{ii} components parallel to the plane containing the benzene ring were estimated as 1.61 D cos 67°=0.63 D and 1.02 D cos (67°−39.5°)=0.90 D, respectively. Also, these estimations do not conflict with the MO calculation. Thus, the present estimation of $p^{A}_{00}>p^{A}_{ii}$ for *N*,*N*-dimethylaniline may be reasonable.

As shown above, the θ values have been estimated for

N,*N*-dimethylaniline and aniline. Prabhumirashi et al.[19] estimated θ values of 66° and 14° for *N*,*N*-dimethylaniline and aniline, respectively. These θ values seem to differ too greatly. Ayachit[11] estimated a θ value of 25° for aniline. However, his estimation of p^{A}_{ii}=5.3 D is too large in comparison with the magnitude of the dipole moment change of Lombardi.[26] The present estimations using Eqs. 8 and 9 give similar θ values for similar molecules of *N*,*N*-dimethylaniline and aniline, as does the $|p^{A}_{ii}-p^{A}_{00}|$ value, agreeing with the reliable value of Lombardi for aniline, as described above. In conclusion, the angle between the ground- and excited-state dipole moments may be estimated by applying Eqs. 8 and 9 to data for the solvent absorption- and fluorescence-frequency shifts of a solute molecule.

References

1) For example, see the following recent papers, Refs. 2—14.

2) P. Suppan and E. Guerry-Butty, *J. Lumin.*, **33**, 335 (1985).

3) T. Abe and I. Iweibo, *Bull. Chem. Soc. Jpn.*, **58**, 3415 (1985).

4) H. Lami and N. Glasser, *J. Chem Phys.*, **84**, 597 (1986).

5) L. S. Prabhumirashi and S. S. Kunte, *Spectrochim. Acta, Part A*, **42**, 435 (1986).

6) N. H. Ayachit, D. K. Deshpande, M. A. Shashidhar, and K. S. Rao, *Spectrochim. Acta, Part A*, **42**, 585 (1986).

7) K. C. Medhi, *Spectrochim. Acta, Part A*, **42**, 1393 (1986).

8) J.-J. Aaron and M. D. Gaye, *J. Mol. Struct.*, **156**, 119 (1987).

9) D. Noukakis and P. Suppan, *Spectrochim. Acta, Part A*, **43**, 1317 (1987).

10) L. S. Prabhumirashi and S. S. Kunte, *Spectrochim. Acta, Part A*, **44**, 213 (1988); **45**, 1147 (1989).

11) N. H. Ayachit, *Chem. Phys. Lett.*, **164**, 253 (1989).

12) G. M. Anstead and J. A. Katzenellenbogen, *J. Phys. Chem.*, **92**, 6249 (1988).

13) M. Van Damme, J. Hofkens, and F. C. De Schryver, *Tetrahedron*, **45**, 4693 (1989).

14) N. Ghoneim and P. Suppan, *J. Chem. Soc., Faraday Trans.*, **86**, 2079 (1990).

15) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

16) P. Suppan, *Chem. Phys. Lett.*, **94**, 272 (1983).

17) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

18) L. S. Prabhumirashi, *Spectrochim. Acta, Part A*, **39**, 91 (1983).

19) L. S. Parabhumirashi, D. K. N. Kutty, and A. S. Bhide, *Spectrochim. Acta, Part A*, **39**, 663 (1983).

20) T. Abe, *Bull. Chem. Soc. Jpn.*, **54**, 327 (1981).

21) T. Abe, *Bull. Chem. Soc. Jpn.*, **61**, 3797 (1988).

22) G. Köhler, *J. Photochem.*, **38**, 217 (1987).

23) L. G. Groves and S. Sugden, *J. Chem. Soc.*, **1937**, 1782.

24) "Kagaku Binran," 3rd ed, ed by The Chemical Society of Japan, Maruzen Publishing Co., Tokyo (1984), Kisohen (Fundamental Part), II, p. II-581, 721.

25) K. Kimura, H. Tsubomura, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **37**, 1336 (1964).

26) J. R. Lombardi, *J. Chem. Phys.*, **50**, 3780 (1969).

27) M. J. Kamlet, J.-L. M. Abboud, and R. W. Taft, *Prog. Phys. Org. Chem.*, **13**, 485 (1981).

28) W. W. Robertson and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5252 (1950).

29) K. Kimura and S. Nagakura, *Mol. Phys.*, **9**, 117 (1965).

30) H. Baba, L. Goodman, and P. C. Valenti, *J. Am. Chem. Soc.*, **88**, 5410 (1966).

31) N. Mataga, *Bull. Chem. Soc. Jpn.*, **36**, 1607 (1963).

32) J. N. Murrell, *Tetrahedron*, **19**, Suppl. 2, 277 (1963).

33) I. Iweibo, R. A. Oderinde, and J. A. Faniran, *Spectrochim. Acta, Part A*, **38**, 1 (1982).

34) J. R. Lombardi, *Spectrochim. Acta, Part A*, **43**, 1323 (1987).

35) H. Baba, *Bull. Chem. Soc. Jpn.*, **34**, 76 (1961).

36) F. Hirota and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **43**, 1010 (1970).

37) W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 1496 (1972).