

Dipole moments of aminophthalimides determined by modified electro-optical absorption and emission measurements

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Abstract

Modified electro-optical absorption and emission methods were used to measure the electric dipole moments of five aminophthalimides in their ground and excited states. The equilibrated ground and excited state dipole moments measured by these methods are in reasonable agreement with those derived from other measurement techniques, confirming the general validity of these methods. A difference is observed between the properties of 3-aminophthalimide (3AP) and 4-amino-*N*-methylphthalimide (4ANMP) in different solvents. The equilibrated dipole moment of 3AP in its excited state is practically independent of the solvent polarity in contrast with 4ANMP. The possible mechanism of this effect is discussed.

Keywords: Aminophthalimides; Absorption; Fluorescence; Electro-optical method; Dipole moment

1. Introduction

Aminophthalimides (APs) are widely used as probes in investigations of static and dynamic inhomogeneous spectral broadening in liquids [1], solvent relaxation in pure and binary solvents [2–5], thermochromic shifts of absorption and emission spectra [6], directed non-radiative energy transfer in rigid media [7], fluorescence quenching in polar solvents [8], the dielectric saturation effect in solutions [9] and general intermolecular effects on fluorescence properties in the vapour phase [10].

The high sensitivity of the fluorescence characteristics of APs to the structure and dynamics of the environment is due to an important property, i.e. the considerable change in the electric dipole moment and polarizability with electronic transition. Electro-optical absorption and emission measurements in solution provide valuable information about the electric dipole moments, polarizabilities and transition moment directions [11–13]. Comparing the electro-optical method with standard dielectric measurements [14] for the determination of the ground state dipole moments, the electro-optical method has the highly desirable advantage of requiring very low concentrations. This is very important for investigations in non-polar solutions, because usually the solubility of dipolar dye molecules in non-polar

solvents is very small. Comparing the electro-optical method with the frequently used solvent shift measurements [6,15,16] for the determination of the excited state dipole moments, the strong advantage of the electro-optical method is that the dipole moments are determined in a single solvent and not averaged, with unknown weighting factors, over the values of the dipole moments in different solvents. It is also possible using the electro-optical method to study the influence of the solvent polarity on the values of the electric dipole moment in the ground and electronically excited states.

In this paper, we describe the application of modified electro-optical absorption and emission methods for the measurement of the electric dipole moments of the five most commonly used APs in their ground and excited states.

2. Methods

The determination of the ground and excited state dipole moments from electro-optical measurements has been represented fully previously [12,13]. Therefore only the basic principles of electro-optical absorption (EOAM) and integrated electro-optical emission (IEOEM) measurements in solution are briefly summarized.

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Using Liptay's formalism [11], the effect of an external electric field E_t on the molar absorption coefficient $\kappa(\nu)$ can be described by a quantity L , which is defined by

$$L = L(\bar{\nu}, \chi) = \frac{\kappa^{E_t}(\bar{\nu}, \chi) - \kappa(\bar{\nu})}{\kappa(\bar{\nu})} \frac{1}{E_t^2} \quad (1)$$

where κ^{E_t} is the molar absorption coefficient in the presence of an applied electric field and χ is the angle between the direction of E_t and the electric field vector of the incident light.

For a homogeneously broadened absorption band, L is given by the following equation [12,17]

$$L = Dr + \frac{1}{2}Es + Frt + Gst + Hru + Isu \quad (2)$$

where the parameters r and s are determined by the angle χ , and the quantities t and u depend on the first and second derivative of the absorption spectrum

$$r = (2 - \cos^2\chi)/5 \quad (3)$$

$$s = (3 \cos^2\chi - 1)/5 \quad (4)$$

$$t = (1/hc)(\kappa/\bar{\nu})^{-1} d(\kappa/\bar{\nu})/d\bar{\nu} \quad (5)$$

$$u = (1/2h^2c^2)(\kappa/\bar{\nu})^{-1} d^2(\kappa/\bar{\nu})/d\bar{\nu}^2 \quad (6)$$

For the molecules discussed in this paper, explicit polarizability and transition polarizability effects can be neglected compared with the electric dipole moment terms. With this assumption, the coefficients D , E , F , G , H and I are given as follows

$$D \approx 0, \text{ within the approximation used here} \quad (7)$$

$$E = (1/kT)f_e^2[3(m_a\mu_g)^2 - \mu_g^2] \quad (8)$$

$$F = (1/kT)f_e^2\mu_g\Delta^a\mu \quad (9)$$

$$G = (1/kT)f_e^2(m_a\mu_g)(m_a\Delta^a\mu) \quad (10)$$

$$H = f_e^2(\Delta^a\mu)^2 \quad (11)$$

$$I = f_e^2(m_a\Delta^a\mu)^2 \quad (12)$$

where k is Boltzmann's constant, T is the temperature, m_a is the unit vector in the direction of the transition moment for absorption and $\Delta^a\mu$ is the change in the dipole moment vector on excitation to the considered Franck-Condon excited state. From a set of these coefficients, the values of μ_g , $\Delta^a\mu$ and the angles between the transition moment m_a and μ_g and $\Delta^a\mu$ can be determined. The cavity field correction f_e is defined according to Onsager's model [18] as introduced to the electro-optical method by Liptay [11]

$$f_e = 3\epsilon/(2\epsilon + 1) \quad (13)$$

where ϵ is the relative permittivity of the solvent.

The experimental set-up for EOAM has been described in detail previously [12,13]. The quantity $L(\bar{\nu}, \chi)$ in the present work was determined for two values of the angle χ ($\chi=0$ and $\chi=\pi/2$) and for a set

of wavenumbers within the first absorption band. Then the coefficients (Eqs. (7)–(12)) and their standard deviations were obtained by multiple linear regression.

Regrettably, for APs, as sometimes for other derivatives, the coefficients H and I cannot be determined with sufficient accuracy. However, the values of the dipole moment terms μ_g and $\Delta^a\mu$ can be determined if additional information on the symmetry (or the angles between the moments) is available. Recently, a new method for the determination of the angle between the vectors μ_g , $\Delta^a\mu$ and m_a has been suggested. It has been shown [19] that, in the case when $\mu_g \parallel \Delta^a\mu$, the function $L(\bar{\nu}, \chi=0) = f[L(\bar{\nu}, \chi=\pi/2)]$ is given in good approximation by the simple linear relationship

$$L(\bar{\nu}, \chi=0) = AL(\bar{\nu}, \chi=\pi/2) + B \frac{\mu_g^2}{6k^2T^2} \quad (14)$$

where $A = (1 + 2\cos^2\theta)/(2 - \cos^2\theta)$, $B = (3\cos^2\theta - 1)/(2 - \cos^2\theta)$ and θ is the angle between μ_g and m_a . Hence the angle between the vectors μ_g and m_a can be determined from the slope of the function $L(\bar{\nu}, \chi=0) = f[L(\bar{\nu}, \chi=\pi/2)]$ following Eq. (14).

In this work, the equilibrated electric dipole moment μ_e in the excited state has been determined by IEOEM. IEOEM is presented in detail in Refs. [20,21] on the basis of the theory given in Ref. [22]. The experimental set-up for IEOEM is described in Ref. [12].

If explicit polarizability and transition polarizability effects can be neglected, the total fluorescence photon current $q^{E_t}(\Phi)$ observed from solutions in an external electric field E_t is dependent on the square of E_t and on the angle Φ between the direction of E_t and the polarization direction of emission given by an analysing polarizer

$$q^{E_t}(\Phi) = q^{E_t=0}[1 + X(\Phi)E_t^2] \quad (15)$$

In a typical measurement, the quantity X is determined for two polarizations $\Phi=0$ and $\Phi=\pi/2$. Similar to formula (14), the relationship between $X(\Phi=0)$ and $X(\Phi=\pi/2)$ is given by

$$X(\Phi=0) = AX(\Phi=\pi/2) + B \left[\frac{\mu_e^2}{6k^2T^2} - L(\bar{\chi}=\pi/2) \right] \quad (16)$$

where $A = (1 + 2\cos^2\phi)/(2 - \cos^2\phi)$, $B = (3\cos^2\phi - 1)/(2 - \cos^2\phi)$ and ϕ is the angle between the emission transition dipole moment m_e and μ_e .

In Eq. (16), the small term $L(\bar{\chi}=\pi/2)$ describes the field effect on the excitation process at the excitation wavelength and can usually be neglected.

Eq. (16) is the basis of a very simple method of dipole moment determination in the equilibrated excited state, if the angle ϕ between m_e and μ_e is known with sufficient approximation from symmetry or if it is measured experimentally.

3. Materials

Fig. 1 presents the five AP molecules studied in this work. Four derivatives (except 3,6TMDANMP) were purified by double sublimation. 3,6TMDANMP was purified by repeated liquid chromatography, as it was found that this dye decomposes at the melting point (188–190 °C). The purity of all the APs was checked by thin layer chromatography. All solvents were purified by the methods described in Ref. [23]. In general, the purified solvents were dried prior to use in electro-optical measurements by distillation under reflux over sodium/potassium alloy employing an argon atmosphere. The purity of all the solvents was checked by UV absorption measurements (1 cm cell; reference air).

4. Experimental results and discussion

4.1. Electro-optical absorption measurements (EOAM)

The electro-optical absorption spectra of all five APs are accurately reproducible, and there is no indication of inhomogeneity within the considered wavenumber range. As examples, experimental data points of the electro-optical absorption spectra of 3AP and 4ANMP in dioxan are shown in Figs. 2 and 3. The optical absorption spectra of 3AP and 4ANMP in dioxan are displayed in Fig. 4, where the bar indicates the wavenumber range of the electro-optical measurements. The optical absorption spectra of both substances are broad and structureless. A regression analysis according to Eqs. (2)–(6) using the experimental data for 3AP and 4ANMP yields the electro-optical coefficients D , E , F and G (Table 1). The coefficients H and I proved to be zero for both molecules within experimental error and were omitted in the subsequent regressions.

Regrettably, as follows from the measurements for the other APs, the coefficients H and I cannot be determined with sufficient accuracy. In order to cal-

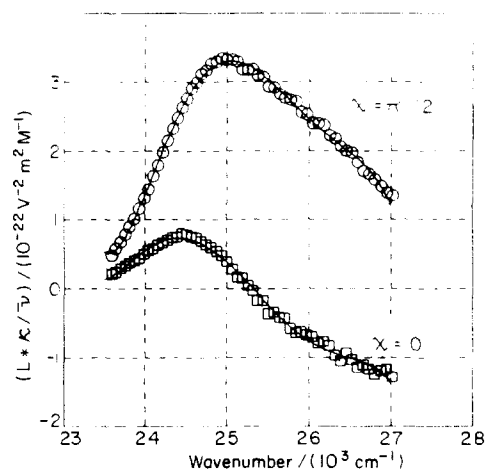


Fig. 2. Electro-optical absorption spectrum of 3AP in dioxan at $T=298$ K. The spectrum shows the mean experimental data points and a best fit curve estimated by multiple linear regression.

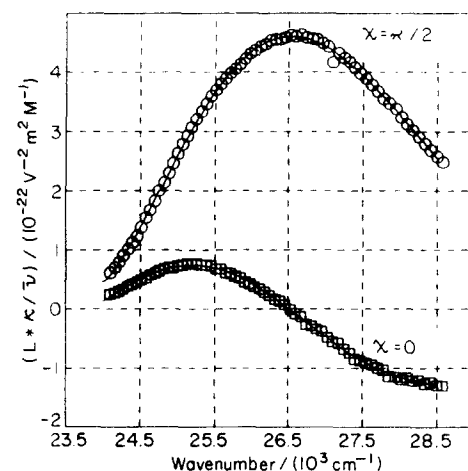


Fig. 3. Electro-optical absorption spectrum of 4ANMP in dioxan at $T=298$ K. The spectrum shows the mean experimental data points and a best fit curve estimated by multiple linear regression.

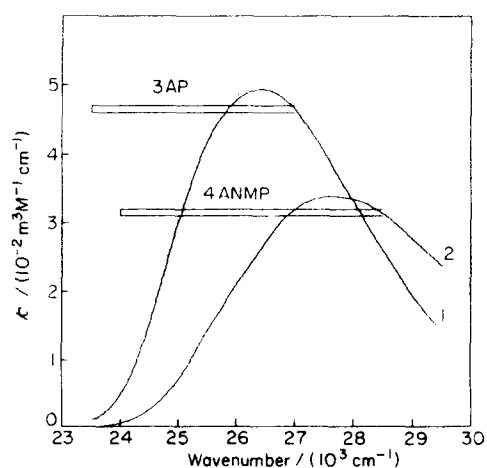


Fig. 4. Molar absorption coefficient spectra of 3AP (curve 1) and 4ANMP (curve 2) in dioxan solution at $T=298$ K. The bars indicate the spectral range of the electro-optical measurements.

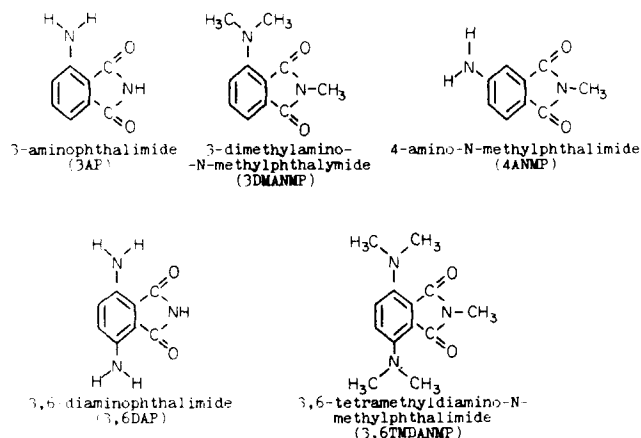


Fig. 1. Aminophthalimides studied in this work.

Table 1
Results from the electro-optical absorption measurements on 3AP and 4ANMP in dioxan solutions at $T=298$ K

Coefficient	Molecule	
	3AP	4ANMP
D ($V^{-2} m^2$)/ 10^{-20}	6 ± 5	176 ± 4
E ($V^{-2} m^2$)/ 10^{-20}	1402 ± 10	4270 ± 25
F ($C V^{-1} m^2$)/ 10^{-40}	557 ± 4	1503 ± 17
G ($C V^{-1} m^2$)/ 10^{-40}	395 ± 3	1024 ± 17

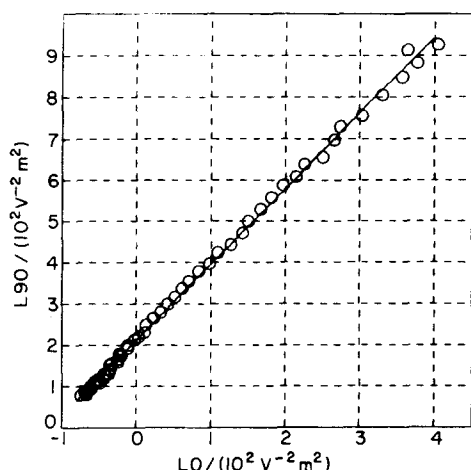


Fig. 5. Quantity $L(\bar{\nu}, \chi = \pi/2)$ vs. $L(\bar{\nu}, \chi = 0)$ for 3AP in dioxan at $T=298$ K. The points show the experimental data and the line their approximation by a linear function.

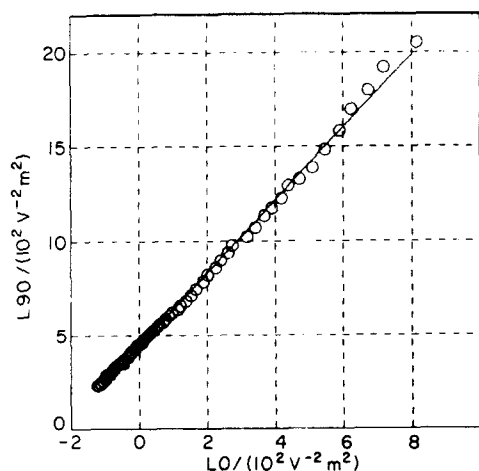


Fig. 6. Quantity $L(\bar{\nu}, \chi = \pi/2)$ vs. $L(\bar{\nu}, \chi = 0)$ for 4ANMP in dioxan at $T=298$ K. The points show the experimental data and the line their approximation by a linear function.

culate, using Eqs. (7)–(12), the values of μ_g and $\Delta^* \mu$, additional information about the angles between the moments μ_g , $\Delta^* \mu$ and m_a will be useful. Fortunately, for all studied APs, the function $L(\bar{\nu}, \chi = 0) = f[L(\bar{\nu}, \chi = \pi/2)]$ has a linear character (see, for example, Figs. 5 and 6). As mentioned in Section 2, this means that the vectors μ_g and $\Delta^* \mu$ are parallel and the angle

between the moments μ_g and m_a can be determined from the slope of the quantity L (Figs. 5 and 6).

In Table 2, the values μ_g , $\Delta^* \mu$, μ_e^{FC} and the angle θ between the transition moment m_a and μ_g (and $\Delta^* \mu$), calculated from EOAM, are presented. The electrical properties of asymmetric molecules were derived as follows. First, the angle θ was found from the slope of the $L(\bar{\nu}, \chi = 0) = f[L(\bar{\nu}, \chi = \pi/2)]$ function and from the relation G/F . Then the values of the vectors μ_g and $\Delta^* \mu$ were calculated from the coefficients E and F respectively. In the case of symmetric molecules, it was found, within experimental error, that $F \cong G$. As follows from Eqs. (9) and (10), this means that the transition dipole moment m_a is parallel to the vectors μ_g and $\Delta^* \mu$. Hence the values of μ_g and $\Delta^* \mu$ can be calculated directly from the coefficients E and G .

The permanent dipole moments of all APs in the ground and excited Franck–Condon states have values within the range $(10\text{--}40) \times 10^{-30}$ C m (Table 2). On optical excitation, the electric dipole moment increases by 12×10^{-30} – 20×10^{-30} C m. Of the APs, 4ANMP shows the largest values of μ_g , $\Delta^* \mu$ and μ_e^{FC} . The angle θ between the transition moment m_a and the vectors μ_g and $\Delta^* \mu$ has values in the range 0–35°.

4.2. Integrated electro-optical emission measurements (IEOEM)

Following Eq. (15), the quantity $X(\Phi)$ was determined experimentally by measuring the relative field-induced change in the total fluorescence intensity at the two values of the angle, $\Phi=0$ and $\Phi=\pi/2$. In order to check some possible negative effects caused by superimposed fluorescence bands (impurities, etc.), the measurements were repeated with the removal of part of the fluorescence band by cut-off filters, and the mean value of the equilibrated dipole moment μ_e was calculated using Eq. (16). For this purpose, the value of the angle ϕ between the emission transition moment m_e and the vector μ_e was chosen to be the same as the angle θ between the absorption transition dipole moment m_a and the vectors μ_g and $\Delta^* \mu$ (Table 2). This can be done since it is well known from fluorescence polarization measurements [24] that, for APs, the transition moments m_a and m_e are parallel. On the other hand, APs are fairly rigid molecules, and we may assume with sufficient approximation that there is no essential difference between the directions of the Franck–Condon (μ_e^{FC}) and the equilibrated (μ_e) dipole moments.

The last column of Table 2 shows the values of μ_e determined in this way using Eq. (16). The relative standard error of the mean of 4–6 independent measurements was 1%–8%. As can be seen from Table 2, the values of the Franck–Condon (μ_e^{FC}) and equilibrated excited state (μ_e) dipole moments are equal within experimental error for all APs.

Table 2
Ground and excited state electric dipole moments of APs in dioxan at $T=298$ K

Molecule	$\nu_{\text{abs}}^{\text{max}}$ (cm^{-1})	$\nu_{\text{fl}}^{\text{max}}$ (cm^{-1})	μ_{g} (10^{-30} C m)	$\Delta^* \mu$ (10^{-30} C m)	$\mu_{\text{e}}^{\text{FC}}$ (10^{-30} C m)	θ ($^\circ$)	μ_{e} (10^{-30} C m)
3AP	26378	22630	11.8 ± 0.1	12.7 ± 0.2	24.6 ± 0.3	32	26.3 ± 1.5
3DMANMP	24630	20620	14.9 ± 0.4	19.3 ± 0.5	34.2 ± 0.9	26	31.7 ± 1.4
3,6DAP	22400	19420	12.0 ± 0.4	11.5 ± 0.8	23.4 ± 1.2	0	20.4 ± 1.6
3,6TMDANMP	21473	18232	13.8 ± 0.5	15.2 ± 0.9	29 ± 1.4	0	24.5 ± 1.9
4ANMP	27700	22570	21.5 ± 0.7	19.2 ± 0.8	40.7 ± 1.5	35	39.2 ± 0.4

$\nu_{\text{abs}}^{\text{max}}$ is the position of the maximum of the absorption spectrum; $\nu_{\text{fl}}^{\text{max}}$ is the position of the maximum fluorescence intensity; μ_{g} is the value of the electric dipole moment in the equilibrated ground state; $\Delta^* \mu$ is the change in the electric dipole moment on optical excitation; $\mu_{\text{e}}^{\text{FC}}$ is the value of the electric dipole moment in the excited Franck–Condon state; θ is the angle between the electric dipole moment μ_{g} and the absorption transition moment m_{a} (see explanation in text); μ_{e} is the value of the electric dipole moment in the equilibrated excited state.

Table 3
Positions of the fluorescence maxima ($\nu_{\text{fl}}^{\text{max}}$) and values of the electric dipole moment in the equilibrated excited state (μ_{e}) of 3AP and 4ANMP in various solvents at $T=298$ K

Solvent	ϵ	3AP		4ANMP	
		$\nu_{\text{fl}}^{\text{max}}$ (cm^{-1})	μ_{e} (10^{-30} C m)	$\nu_{\text{fl}}^{\text{max}}$ (cm^{-1})	μ_{e} (10^{-30} C m)
Cyclohexane	2.015	24040	24.1 ± 2.0	24970	24.8 ± 0.2
Dioxan	2.209 ^a	22625	26.3 ± 1.5	22570	39.2 ± 0.4
Toluene	2.379	22860	26.7 ± 1.0	23450	34.1 ± 0.6
Fluorobenzene	5.420	22880	26.9 ± 2.2	23095	34.4 ± 0.2

^a Microscopic value, 6–7.

Table 3 shows the values of the dipole moments μ_{e} for 3AP and 4ANMP measured by IEOEM in various solvents. The equilibrated dipole moment of 3AP in its excited state is independent of the solvent polarity, in contrast with that of 4ANMP which depends strongly on the solvent polarity. In electro-optical emission measurements, the most polar solvent was fluorobenzene ($\epsilon=5.42$). However, it is well known from solvent shift measurements [12] that the microscopically effective dielectric constant of dioxan is about 6–7. Consequently, for 3AP and 4ANMP, as follows from Table 3, the position of the fluorescence spectrum in dioxan is red shifted compared with that in fluorobenzene (Table 3). Fig. 7 shows that there is a real correlation between the values of μ_{e} and the position of the fluorescence maxima $\nu_{\text{fl}}^{\text{max}}$ in the case of 4ANMP. This means that, for 4ANMP, there is a solvent-induced contribution to the total equilibrated excited state dipole moment, which may be due to the polarizability, solvent-dependent conformational distributions or intramolecular charge transfer.

It seems probable that the substitution of an electron-donating group in the 4-position leads to a stronger charge transfer in polar solvents in both the ground and excited states than substitution in the 3-position. In addition, it is suggested that the difference between the properties of 3AP and 4ANMP is due to the presence

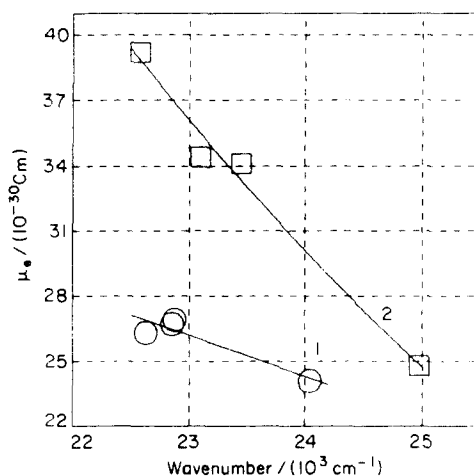


Fig. 7. Electric dipole moment in the equilibrated excited state for 3AP (curve 1) and 4ANMP (curve 2) in different solvents vs. the position of the fluorescence intensity maximum.

of intramolecular hydrogen bonding in the case of 3AP. Hence 3AP, with its stable intramolecular hydrogen bond ($-\text{C}=\text{O} \cdots \text{H}-\text{N}-$), is not very sensitive to the solvent-induced polarizability or conformational distribution effects. 3AP is a more suitable fluorescence probe for studying solvation dynamics in liquids, for example by time-dependent fluorescence Stokes shift measurements, because its dipole moment in the excited state is not very sensitive to the polarity of the environment and is constant during intermolecular relaxation in solution. On the other hand, 4ANMP is a better probe than 3AP for studying solvation effects integrated in time, because its fluorescence characteristics will be more sensitive to the solvent properties.

4.3. Comparison of dipole moments obtained from electro-optical measurements and other methods

The values of the ground and excited state dipole moments and $\Delta^* \mu$ can be compared with those obtained by other methods, in particular by techniques such as spectral shifts [25], solvatochromic shifts [8], universal

Table 4

Comparison of the dipole moments obtained by electro-optical measurements and other methods

Molecule	μ_g (10^{-30} C m)	$\Delta^a\mu$ (10^{-30} C m)	μ_e (10^{-30} C m)	Method	Reference
3AP	11.8	12.7	26.3	Electro-optical	This work
	8.7	11.0	19.7	Modified spectral shifts	[27]
	8.7	8.7	17.3	Spectral shifts	[25]
	8.7	7.7	16.3	Solvatochromic shifts	[8]
3DMANMP	14.9	19.3	31.7	Electro-optical	This work
	9.0 ^a	9.7 ^a	18.7 ^a	Spectral shifts	[25]
3,6DAP	12.0	11.5	20.4	Electro-optical	This work
	7.7	8.0	15.7	Spectral shifts	[25]
	6.9	7.7	14.7	Modified spectral shifts	[27]
3,6TMDANMP	13.8	15.2	24.5	Electro-optical	This work
	7.3 ^b	11.7 ^b	18.8 ^b	Spectral shifts	[25]
4ANMP	21.5	19.2	39.2	Electro-optical	This work
	12.0	21.3	33.3	Modified spectral shifts	[27]
	11.7	16.7	28.3	Universal relation between absorption and fluorescence spectra	[26]

^a The data were obtained for 3-dimethylaminophthalamide (3DMAP).

^b These data were obtained for 3,6-tetramethyldiaminophthalamide (3,6TMDAP).

relation between absorption and fluorescence spectra [26] and modified spectral shifts [27]. Table 4 shows that, in general, the dipole moments obtained from electro-optical measurements are in reasonable agreement with those derived from independent solvent shift methods. It is interesting to note that all values of μ_g , $\Delta^a\mu$ and μ_e measured by electro-optical methods and listed in Table 4 are greater than those derived from the different spectral shift methods. This effect is not surprising because all the above-mentioned methods [8,25–27] are based on the measurement of the absorption and fluorescence spectra only. They do not take into account the intermolecular hydrogen bond, the dependence of the dipole moments on the solvent polarity, etc., and so have a disadvantage compared with electro-optical methods. In addition, all solvent shift methods require an estimate of the molecular interaction radius of the solute.

5. Conclusions

The investigated APs have a permanent dipole moment in their ground state of $(10\text{--}20)\times 10^{-30}$ C m. After optical excitation, the dipole moment increases by approximately $12\times 10^{-30}\text{--}20\times 10^{-30}$ C m. The Franck–Condon excited state and the equilibrated excited state dipole moments are found to be equal (except for 3,6TMDANMP) within experimental error. The equilibrated dipole moment of 3AP in its fluorescent excited state is independent of the solvent polarity in contrast with that of 4ANMP. A comparison of the dipole moment values determined in this work with

the results obtained by other (spectral) methods shows reasonable agreement. However, all the values of μ_g , $\Delta^a\mu$ and μ_e measured by electro-optical methods are greater than those derived from other methods. This is not surprising given the disadvantages of the spectral shift methods in comparison with electro-optical methods.

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