Permanent Dipole Moment and Polarizability of a Class of Merocyanine Dyes in Their Ground and First Excited Singlet State

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The permanent dipole moment of a class of merocyanine dyes in their ground and first excited singlet state has been determined studying the influence of an external electric field on the absorption of the compounds in various solvents. Evaluation of the experimental results on the basis of the Onsager reaction field model also gives values for the polarizability in the ground and excited state, the latter approaches the value of a respective conducting ellipsoid with the longer chainlength molecules.

1. Introduction

Studying mainly the anomalous fluorescence behaviour of some molecules such as the famous 4-cyano-N,N-dimethylaniline, a strong dependence of the effective dipole moment of molecules in electronically excited states on the polarity of the solvent has been found [1, 2]. A variety of experimental data in that field indicates that at least in some cases a strongly solvent polarity dependent geometry might be the reason for the observed strong solvent dependence of the dipole moment, e.g. [3]. On the other hand assuming a solvent independent geometry, a formal treatment of the experimental values of the dipole moment of these molecules in their fluorescent state by separating the permanent dipole moment from the solvent reaction field induced parts also can explain the experimental data [1, 2]. In that latter view of things polarizabilities of molecules assumed to be rigid stand for the observed effects and thus reflect a solvent dependent electronic structure only.

Up to now the reported large effects have only been observed on excited states dipole moments. The results indicate that in all these cases excited states polarizabilities larger than the ground state polarizability give rise to the observed large effects.

Dähne and Nolte [4] reported large and solvent dependent ground state polarizabilities for some merocyanines what indicates a strongly solvent dependent electronic structure even in the ground state. Radeglia and Dähne [5] also emphasize that part of the observed solvent shift of these molecules is due to the change of the electronic structure with solvent polarity: polyene-like in nonpolar solvents, polymethine-like in polar solvents.

So in this paper a class of merocyanine dyes [6, 7, 8] has been selected to show whether the reported solvent dependent electronic structure shows itself in a large dependence of the ground state and possibly also of the excited state dipole moment on the solvent polarity. The compounds investigated were the following, supplied by Schneider [6] and used without further purification:

$$(\mathrm{CH_3})_2-\mathrm{N}-(\mathrm{CH}=\mathrm{CH})_X-\mathrm{CH}=\mathrm{C}(\mathrm{CN})_2\,.$$

CNX is used as an abbreviation for these molecules with $X = 0, 1, 2, 3$, and 4. No severe solvent dependence of the molecular geometry is to be expected [6, 7].

2. Theoretical and Experimental

2.1. Electro-optical Absorption Measurements

Electro-optical absorption measurements have been developed after the early work of Kuhn [9] mainly by Labhart [10] and Liptay [11]. The most elaborate theory of Liptay [11 – 14] is used here. It is based on a model for the description of the electric field affecting a solute molecule, given by Onsager [15] and further developed by Scholte [16].

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As Liptay's formalism has widely been used in the literature, only the terms are given which can be derived from electro-optical measurements [12–14], without discussing the way of their derivation in detail. For experimental details of this method refer to [15]. The following terms can be derived from experiment:

$$D = 2\beta\,\mathrm{Re}\{\boldsymbol{m}\,\mathbf{f}_\mathrm{e}\,\mathbf{m}'\,\mathbf{f}_\mathrm{e}\,\boldsymbol{\mu}_\mathrm{g}\} + \mathrm{tr}\,(\mathbf{f}_\mathrm{e}\,\mathbf{m}')^2\,, \tag{1}$$

$$\begin{aligned} E = {} & \beta^2[3\,(\boldsymbol{m}\,\mathbf{f}_\mathrm{e}\,\boldsymbol{\mu}_\mathrm{g})^2 - (\mathbf{f}_\mathrm{e}\,\boldsymbol{\mu}_\mathrm{g})^2] \\ & + \beta\,(3\,\boldsymbol{m}\,\mathbf{f}_\mathrm{e}\,\boldsymbol{\alpha}_\mathrm{g}\,\mathbf{f}_\mathrm{e}\,\boldsymbol{m} - \mathrm{tr}\,\mathbf{f}_\mathrm{e}\,\boldsymbol{\alpha}_\mathrm{g}\,\mathbf{f}_\mathrm{e}) \\ & + 6\beta\,\mathrm{Re}\{(\boldsymbol{m}\,\mathbf{f}_\mathrm{e}\,\boldsymbol{\mu}_\mathrm{g})\,\mathrm{tr}\,\mathbf{f}_\mathrm{e}\,\mathbf{m}' + \boldsymbol{\mu}_\mathrm{g}\,\mathbf{f}_\mathrm{e}\,\mathbf{m}'\,\mathbf{f}_\mathrm{e}\,\boldsymbol{m}\} \\ & + 3\,(\mathrm{tr}\,\mathbf{f}_\mathrm{e}\,\mathbf{m}')^2 + 3\,\mathrm{tr}\,(\mathbf{f}_\mathrm{e}\,\mathbf{m}')^2\,, \end{aligned} \tag{2}$$

$$\begin{aligned} F = {} & \beta\,\mathbf{f}_\mathrm{e}\,\boldsymbol{\mu}_\mathrm{g}\,\mathbf{f}_\mathrm{e}\,\Delta\boldsymbol{\mu} + \tfrac{1}{2}\,\mathrm{tr}\,\mathbf{f}_\mathrm{e}\Delta\boldsymbol{\alpha}\,\mathbf{f}_\mathrm{e} \\ & + 2\,\mathrm{Re}\{\boldsymbol{m}\,\mathbf{f}_\mathrm{e}\,\mathbf{m}'\,\mathbf{f}_\mathrm{e}\Delta\boldsymbol{\mu}\}\,, \end{aligned} \tag{3}$$

$$\begin{aligned} G = {} & \beta\,(\boldsymbol{m}\,\mathbf{f}_\mathrm{e}\,\boldsymbol{\mu}_\mathrm{g})\,(\boldsymbol{m}\,\mathbf{f}_\mathrm{e}\Delta\boldsymbol{\mu}) + \tfrac{1}{2}\,\boldsymbol{m}\,\mathbf{f}_\mathrm{e}\Delta\boldsymbol{\alpha}\,\mathbf{f}_\mathrm{e}\,\boldsymbol{m} \\ & + \mathrm{Re}\{(\boldsymbol{m}\,\mathbf{f}_\mathrm{e}\Delta\boldsymbol{\mu})\,\mathrm{tr}\,\mathbf{f}_\mathrm{e}\,\mathbf{m}' + \Delta\boldsymbol{\mu}\,\mathbf{f}_\mathrm{e}\,\mathbf{m}'\,\mathbf{f}_\mathrm{e}\,\boldsymbol{m}\} \end{aligned} \tag{4}$$

$$H = (\mathbf{f}_\mathrm{e}\Delta\boldsymbol{\mu})^2\,, \tag{5}$$

$$I = (\boldsymbol{m}\,\mathbf{f}_\mathrm{e}\Delta\boldsymbol{\mu})^2\,. \tag{6}$$

Here $\beta = (kT)^{-1}$ with the Boltzmann constant k and the temperature T. $\boldsymbol{m}$ is a unit vector in the direction of the transition moment involved in the absorption process, $\mathbf{m}'$ is a tensor that describes the field dependence of the transition moment, as defined in [16].

$$\boldsymbol{\mu}_\mathrm{g} = (\mathbf{1} - \mathbf{f}\,\boldsymbol{\alpha}_\mathrm{g}^\circ)^{-1}\,\boldsymbol{\mu}_\mathrm{g}^\circ\,, \tag{7}$$

$$\boldsymbol{\alpha}_\mathrm{g} = (\mathbf{1} - \mathbf{f}\,\boldsymbol{\alpha}_\mathrm{g}^\circ)^{-1}\,\boldsymbol{\alpha}_\mathrm{g}^\circ\,, \tag{8}$$

$$\begin{aligned} \Delta\boldsymbol{\mu} = {} & (\mathbf{1} - \mathbf{f}'\,\boldsymbol{\alpha}_\mathrm{a}^{\circ\,\mathrm{FC}})^{-1}(\mathbf{1} - \mathbf{f}\,\boldsymbol{\alpha}_\mathrm{a}^{\circ\,\mathrm{FC}})\,(\mathbf{1} - \mathbf{f}\,\boldsymbol{\alpha}_\mathrm{g}^\circ)^{-1} \\ & \cdot (\mathbf{1} - \mathbf{f}'\,\boldsymbol{\alpha}_\mathrm{g}^\circ)\,[\boldsymbol{\mu}_\mathrm{a}^\mathrm{FC} - \boldsymbol{\mu}_\mathrm{g}]\,, \end{aligned} \tag{9}$$

$$\boldsymbol{\mu}_\mathrm{a}^\mathrm{FC} = (\mathbf{1} - \mathbf{f}\,\boldsymbol{\alpha}_\mathrm{a}^{\circ\,\mathrm{FC}})^{-1}\,\boldsymbol{\mu}_\mathrm{a}^{\circ\,\mathrm{FC}}\,, \tag{10}$$

$$\begin{aligned} \Delta\boldsymbol{\alpha} = {} & (\mathbf{1} - \mathbf{f}'\,\boldsymbol{\alpha}_\mathrm{a}^{\circ\,\mathrm{FC}})^{-1}(\mathbf{1} - \mathbf{f}\,\boldsymbol{\alpha}_\mathrm{g}^\circ)^{-2}(\mathbf{1} - \mathbf{f}'\boldsymbol{\alpha}_\mathrm{g}^\circ) \\ & \cdot (\boldsymbol{\alpha}_\mathrm{a}^{\circ\,\mathrm{FC}} - \boldsymbol{\alpha}_\mathrm{g}^\circ)\,. \end{aligned} \tag{11}$$

Using an ellipsoidal cavity the main axes of which are a_i ($i = x, y, z$), the main axis components of the tensors $\mathbf{f}_\mathrm{e}$, $\mathbf{f}$ and $\mathbf{f}'$ are given as

$$f_{\mathrm{e}i} = \frac{\varepsilon}{\varepsilon - (\varepsilon - 1)\,\varkappa_i}\,, \tag{12}$$

$$f_i = \frac{1}{4\pi\,\varepsilon_0}\,\frac{1}{a_x\,a_y\,a_z}\,g_i \tag{13}$$

with

$$g_i = \frac{3\,(\varepsilon - 1)\,(1 - \varkappa_i)\,\varkappa_i}{\varepsilon - (\varepsilon - 1)\,\varkappa_i}\,, \tag{14}$$

$$f_i' = \frac{1}{4\pi\,\varepsilon_0}\,\frac{1}{a_x\,a_y\,a_z}\,g_i' \tag{15}$$

with

$$g_i' = \frac{3\,(n^2 - 1)\,(1 - \varkappa_i)\,\varkappa_i}{n^2 - (n^2 - 1)\,\varkappa_i}\,. \tag{16}$$

$$\varkappa_i = \frac{a_x\,a_y\,a_z}{2} \cdot \int_0^\infty \frac{\mathrm{d}s}{(s + a_i^2)\,[(s + a_x)^2\,(s + a_y^2)\,(s + a_z^2)]^{1/2}}\,. \tag{17}$$

ε is the dielectric constant and n the refractive number of the solvent used. ε_0 is the permittivity of the vacuum. Right upper index ° indicates moments of the free molecule, right upper index FC marks a Franck-Condon state. $\boldsymbol{\mu}_\mathrm{g}^\circ$ and $\boldsymbol{\alpha}_\mathrm{g}^\circ$ are the permanent dipole moment and the polarizability of the molecule in its ground state, $\boldsymbol{\mu}_\mathrm{a}^{\circ\,\mathrm{FC}}$ and $\boldsymbol{\alpha}_\mathrm{a}^{\circ\,\mathrm{FC}}$ are the respective quantities in the excited FC state, as reached by the absorption process. The quantities $\boldsymbol{\mu}_\mathrm{g}$, $\boldsymbol{\mu}_\mathrm{a}^\mathrm{FC}$ and $\boldsymbol{\alpha}_\mathrm{g}$, as defined by (7), (8) and (10), may be considered as something like effective dipole moments and polarizabilities observed in solutions. But as they are related to the well defined dipole moments and polarizabilities of a free molecule by some model only, in this paper for $\boldsymbol{\mu}_\mathrm{g}$, $\boldsymbol{\mu}_\mathrm{a}^\mathrm{FC}$ and $\boldsymbol{\alpha}_\mathrm{g}$ the expressions dipole moment and polarizability shall not be used.

2.2. Dielectric Investigations

The classical method for the determination of the ground state dipole moment $\boldsymbol{\mu}_\mathrm{g}^\circ$ of a solute molecule uses the concentration dependence of the dielectric constant, the refractive number and the density of dilute solutions in nonpolar solvents. This method is widely used and various neglects and simplifications are made in the literature. In order to get results from dielectric investigations which are comparable with those from electro-optical absorption measurement, Liptay [17] has used the same Onsager-Scholte model to describe this effect in a most rigorous way.

For the molecules investigated in this paper, $\mathrm{tr}\,\mathbf{f}_\mathrm{e}\,\boldsymbol{\alpha}_\mathrm{g} \ll \beta\,\boldsymbol{\mu}_\mathrm{g}\,\mathbf{f}_\mathrm{e}\,\boldsymbol{\mu}_\mathrm{g}$ holds. Thus for nonpolar solutions where $\varepsilon_\mathrm{LM} \approx n_\mathrm{LM}^2$, from Liptay's Eq. (49) in

[17] the following Eq. (18) results in a very good approximation:

$$\boldsymbol{\mu}_g \mathbf{f}_e \boldsymbol{\mu}_g = \frac{3\,\varepsilon_0 M}{N\,\beta\,\varrho_{LM}}\,\frac{3}{2\,\varepsilon_{LM}+1} \cdot \left[\frac{2\,\varepsilon_{LM}+1}{3\,\varepsilon_{LM}} - \frac{\varepsilon_{LM}-1}{2\,\varepsilon_{LM}+1}\,\frac{1}{2\,\pi\,\varepsilon_0\,a_{LM}^3}\,\frac{\mathrm{tr}\,(\boldsymbol{\alpha}_{LM}^2)}{\mathrm{tr}\,\boldsymbol{\alpha}_{LM}}\right] \cdot \left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}w} - \frac{\mathrm{d}n^2}{\mathrm{d}w}\right)_{w\to 0}. \qquad (18)$$

M is the molar mass, N is Avogadro's constant, ϱ_{LM} is the density, w is the mass fraction and right lower index LM denotes solvent quantities. $\left.\frac{\mathrm{d}\varepsilon}{\mathrm{d}w}\right/_{w\to 0}$ has been determined experimentally, using a Dekameter (WTW, Weilheim), which had been modified to assure measurement under dry nitrogen. $\left.\frac{\mathrm{d}n^2}{\mathrm{d}w}\right/_{w\to 0}$ could not be determined because of poor solubility of the molecules discussed here in nonpolar solvents.

3. Experimental Results

3.1. On the Field Parameters $\mathbf{f}_e$, $\mathbf{g}$ and $\mathbf{g}'$

For the evaluation of dipole moments from EOAM as well as from dielectric investigations, the size and shape of the Onsager cavity must be fixed. There is some arbitrariness in this point, but the choice of cavity parameters does not influence $\mathbf{f}_e$, $\mathbf{g}$ and $\mathbf{g}'$ so much, as these are dependent only on the shape of the cavity whereas $\mathbf{f}$ and $\mathbf{f}'$ depend on the size. Table 1 shows the size parameters used for further evaluation of molecular data. It is assumed that these parameters are solvent independent. With these size parameters $\varkappa_x = \varkappa_y$ and $\varkappa_z$ according to (17) are calculated and with these f_{ez}, g_z and g_z'. In the case of dioxane, the macroscopic dielectric constant has been used for the calculation of f_{ez} but as a microscopic dielectric constant a value of six has ben adopted which generally describes the reaction field influence on spectra sufficiently, in the case of dioxane.

Table 1. Size parameters of the molecules CN0 to CN4.

	CN0	CN1	CN2	CN3	CN4
$a_x/10^{-10}$ m ($= a_y$)	3	3	3	3	3
$a_z/10^{-10}$ m	3	4.2	5.4	6.6	7.8

3.2. Results from Dielectric Investigations

Unfortunately, dielectric investigations in cyclohexane could not be done because of poor solubility. So Table 2 gives the experimental results and the quantity μ_g determined in dioxane solutions. Values given for $\left.\frac{\mathrm{d}\varepsilon}{\mathrm{d}w}\right/_{w\to 0}$ are mean values with standard deviations determined from four to five measurements with each compound. Because of solubility problems, $\left.\frac{\mathrm{d}n^2}{\mathrm{d}w}\right/_{w\to 0}$ could not be determined, not even in dioxane. So $\left.\frac{\mathrm{d}n^2}{\mathrm{d}w}\right/_{w\to 0}$ has been estimated very roughly from the values given in [14] for some tetraphenylpolyenes. These $\left.\frac{\mathrm{d}n^2}{\mathrm{d}w}\right/_{w\to 0}$ amount to about 1% or less of $\left.\frac{\mathrm{d}\varepsilon}{\mathrm{d}w}\right/_{w\to 0}$. Thus the error introduced by this rough estimation does not influence the result in μ_g to a considerable amount. μ_g has been calculated according to (18) and is given in Table 2, too.

Table 2 shows that the quantity μ_g does not parallel the chain-length. Further calculations in order to get the permanent dipole moment μ_g° from μ_g will be carried out in Section 3.4.

3.3. Results from Electro-optical Absorption Measurements

3.3.1. General Remarks

Electro-optical absorption measurements have been performed in dilute solution at 25 °C. Solvents

Table 2. Results from dielectric investigations in dioxane at 298 K

	CN0	CN1	CN2	CN3	CN4
M/kg	0.121	0.147	0.173	0.199	0.225
$\mathrm{d}\varepsilon/\mathrm{d}w\ (w\to 0)$	66.7 ± 0.7	91.8 ± 0.7	105.5 ± 2.8	98.9 ± 2	91.2 ± 1.9
$\mathrm{d}n^2/\mathrm{d}w\ (w\to 0)$	0.1	0.4	0.7	0.95	1.2
$\mu_g/10^{-30}$ Cm	30.8 ± 0.5	40.8 ± 0.6	48.2 ± 0.8	50.6 ± 0.9	51.9 ± 1

used have been cyclohexane, decaline (cis-trans mixture), dioxane and diisopropylether.

The evaluation of the terms D to I from a regression analysis according to (1)–(6) is not possible over the entire first electronic absorption band. Careful analysis of the experimental material shows, that with each molecule separate spectral ranges exist in which a homogeneous transition is found. These ranges reflect the vibrational transitions in the spectrum although a vibrational structure of the absorption band cannot be seen in some solvents, like in dioxane. The results of regression analyses in these spectral ranges are given in Table 3. As most usual with broad absorption bands, the regression analyses give H and I only within relatively large errors, although the values of H and I fit pretty well to the other results. Thus they are insignificant for further evaluations and therefore are not given here.

Looking at the results Table 3, it appears that E with a given molecule shows different values in different vibrational subbands, mostly out of the error. The polarizability terms (2) cannot explain these differences. This can be seen as a rough estimate by comparison with the term E for the tretraphenylpolyenes given in [14]. Even slightly larger polarizabilities as indicated in [4] for polymethine-like structures will not alter this discussion. So three possible explanations may be discussed:

(i) there is a cis-trans equilibrium mixture,
(ii) there are changes of the direction of the transition moment within a vibronic progression,
(iii) transition polarizability terms cannot be neglected when calculating μ_g from (2).

In [8] it is shown that im most solvents at room temperature these compounds may be considered as pure trans-configurated. This rules out statement (i) as an explanation for different values of E in different subbands. Statement (ii) in principle can explain the results on E. But since terms D are found to show a similar but much larger dependence, it is most probable that according to statement (iii) transition polarizabilities must be taken into account.

Obviously the molecules considered do not show a C_2 axis. Nevertheless, with the assumption that the transition polarizability tensor has only one significant element $(\mathbf{m}')_{\mu\mu}$, the following approximation might be used:

$$(\boldsymbol{m}\,\boldsymbol{\mu}_g)\,\mathrm{tr}\,\mathbf{m}' = \boldsymbol{\mu}_g\,\mathbf{m}'\,\boldsymbol{m}\,. \qquad (19)$$

Then with reference to (1) and (2) it might be seen, that $E-6D$ should no more be dependent on $\mathbf{m}'$ and looking to the respective results Table 4, it turns out that indeed $E-6D$ is independent of the spectral range or the vibrational subband. So in turn this must be seen as a strong hint that $(\mathbf{m}')_{\mu\mu}$ is really the only significant element of $\mathbf{m}'$ and that transition polarizabilities must be taken into account.

3.3.2. The Angle between $\boldsymbol{m}$ and $\boldsymbol{\mu}_g$ and the Value of $\boldsymbol{\mu}_g$ in Various Solvents

From the mean value of $E-6D$ over the whole first absorption band $3(\boldsymbol{m}\,\boldsymbol{\mu}_g)^2-\mu_g^2$ can be calculated from (2) if polarizability terms are neglected. Combination of these results with μ_g (Table 2) from dielectric investigations shows, that with all molecules the angle $\sphericalangle\,(\boldsymbol{m},\boldsymbol{\mu}_g)$ is less than 20° with CN0 falling down to zero with CN4.

Since $\cos \sphericalangle\,(\boldsymbol{m},\boldsymbol{\mu}_g)$ is larger than 0.94 for angles less than 20°, μ_g can be calculated in all solvents using in good approximation to (20):

$$3(\boldsymbol{m}\,\boldsymbol{\mu}_g)^2-\mu_g^2=2\,\mu_g^2\,. \qquad (20)$$

Table 5 gives the results in μ_g determined with (20) from the values Table 4. Table 5 also shows that the quantity μ_g increases with chainlength and solvent polarity. The latter effect is in agreement with Dähne's [4] statement of a strongly solvent dependent electronic structure. In Sect. 3.4 the attempt shall be made to describe this solvent dependence as due to polarizability parts induced by the reaction field of the solute.

3.3.3. The Value of $\Delta\mu$ in Various Solvents

From the discussion in Sect. 3.3.2 follows that in good approximation $\boldsymbol{m}\,\boldsymbol{\mu}_g=\mu_g$. Table 3 shows that in a given range and a given solvent the values of F and G are almost the same in their range of errors. This means

$$\boldsymbol{\mu}_g\,\Delta\boldsymbol{\mu}=(\boldsymbol{m}\,\boldsymbol{\mu}_g)(\boldsymbol{m}\,\Delta\boldsymbol{\mu})=\mu_g(\boldsymbol{m}\,\Delta\boldsymbol{\mu})\,,$$

from which follows $\boldsymbol{m}\parallel\Delta\boldsymbol{\mu}$, in the range of errors, and from this $F=G$. So neglecting polarizability and transition polarizability terms in (3) and (4), $\Delta\mu$ can be calculated in good approximation from the values for $\frac{1}{2}/(F+G)$ from Table 3.

Table 3. Results from EOAM on some merocyanine dyes in some solvents at 25 °C.

	CN 0		CN 1		CN 2			CN 3			CN 4		
Range no	I	II	I	II	I	II	III	I	II	III	I	II	III
Cyclohexane													
Range/$10^5\,\mathrm{m}^{-1}$	32.6–33.7	34.1–36.0	25.9–26.9	27.5–28.1	21.1–21.6	22.6–23.5	23.9–24.5	18.3–19.2	19.6–20.3	20.9–21.7	16.4–17.2	17.4–18.2	18.6–19.6
$D/10^{-19}\,\mathrm{V}^{-2}\,\mathrm{m}^2$	0 ± 10	10 ± 2	35 ± 4	15 ± 4	210 ± 5	36 ± 3	12 ± 3	145 ± 2	65 ± 2	13 ± 3	190 ± 30	100 ± 10	20 ± 10
$E/10^{-18}\,\mathrm{V}^{-2}\,\mathrm{m}^2$	129 ± 7	138 ± 3	225 ± 3	210 ± 1	409 ± 10	299 ± 8	287 ± 7	415 ± 6	395 ± 12	376 ± 10	449 ± 20	388 ± 15	326 ± 15
$F/10^{-39}\,\mathrm{CV}^{-1}\,\mathrm{m}^2$	35 ± 9	18 ± 6	106 ± 5	150 ± 5	162 ± 15	354 ± 8	386 ± 8	574 ± 20	657 ± 20	726 ± 70	830 ± 100	814 ± 100	807 ± 90
$G/10^{-39}\,\mathrm{CV}^{-1}\,\mathrm{m}^2$	44 ± 13	30 ± 15	114 ± 7	145 ± 7	77 ± 17	331 ± 10	387 ± 10	555 ± 20	598 ± 20	717 ± 70	812 ± 100	773 ± 120	789 ± 10
Decaline													
Range/$10^5\,\mathrm{m}^{-1}$			25.7–26.6	27.0–27.9	20.9–21.9	22.4–23.4		18.0–18.9	19.4–20.2		16.1–16.6	17.3–17.9	18.5–19.1
$D/10^{-19}\,\mathrm{V}^{-2}\,\mathrm{m}^2$			34 ± 3	21 ± 6	55 ± 4	44 ± 3		147 ± 3	59 ± 6		196 ± 20	115 ± 7	35 ± 4
$E/10^{-18}\,\mathrm{V}^{-2}\,\mathrm{m}^2$			235 ± 4	227 ± 4	345 ± 5	332 ± 6		452 ± 6	397 ± 6		487 ± 10	437 ± 10	391 ± 10
$F/10^{-39}\,\mathrm{CV}^{-1}\,\mathrm{m}^2$			111 ± 6	158 ± 6	347 ± 10	422 ± 10		622 ± 10	610 ± 20		924 ± 40	919 ± 40	947 ± 60
$G/10^{-39}\,\mathrm{CV}^{-1}\,\mathrm{m}^2$			115 ± 6	143 ± 6	215 ± 3	354 ± 17		610 ± 25	576 ± 20		921 ± 40	868 ± 50	895 ± 60
Diisopropylether													
Range/$10^5\,\mathrm{m}^{-1}$											15.2–15.8	16.5–17.3	17.8–19.1
$D/10^{-19}\,\mathrm{V}^{-2}\,\mathrm{m}^2$											329 ± 35	133 ± 15	43 ± 5
$E/10^{-18}\,\mathrm{V}^{-2}\,\mathrm{m}^2$											683 ± 16	599 ± 16	536 ± 15
$F/10^{-39}\,\mathrm{CV}^{-1}\,\mathrm{m}^2$											1350 ± 70	1500 ± 65	1440 ± 65
$G/10^{-39}\,\mathrm{CV}^{-1}\,\mathrm{m}^2$											1430 ± 70	1490 ± 75	1440 ± 75
Dioxane													
Range/$10^5\,\mathrm{m}^{-1}$		34.0–36.0	25.3–26.3	26.4–27.2	20.8–21.5	21.9–22.9		17.7–18.2	19.0–19.7		15.0–15.6	15.6–17.2	
$D/10^{-19}\,\mathrm{V}^{-2}\,\mathrm{m}^2$		– 4.6 ± 1	37 ± 6	26 ± 3	100 ± 6	60 ± 10		183 ± 8	100 ± 5		178 ± 15	– 9 ± 18	
$E/10^{-18}\,\mathrm{V}^{-2}\,\mathrm{m}^2$		169 ± 2	298 ± 2	292 ± 4	441 ± 10	417 ± 10		594 ± 10	542 ± 10		604 ± 40	523 ± 15	
$F/10^{-39}\,\mathrm{CV}^{-1}\,\mathrm{m}^2$		9 ± 6	71 ± 7	203 ± 40	325 ± 15	526 ± 20		935 ± 30	1140 ± 40		1690 ± 40	2010 ± 42	
$G/10^{-39}\,\mathrm{CV}^{-1}\,\mathrm{m}^2$		23 ± 25	81 ± 10	260 ± 40	348 ± 20	547 ± 30		914 ± 35	1140 ± 35		1760 ± 60	1950 ± 60	

Table 4. $(E - 6D)/10^{-18}\,\mathrm{V}^{-2}\,\mathrm{m}^2$ as derived from the experimental results.

	CN 0		CN 1		CN 2			CN 3			CN 4		
Range no	I	II	I	II	I	II	III	I	II	III	I	II	III
in cyclohexane	129 ± 7	132 ± 4	204 ± 5	204 ± 3	283 ± 13	277 ± 10	280 ± 9	328 ± 7	356 ± 13	368 ± 12	335 ± 38	328 ± 21	314 ± 21
in decaline			215 ± 6	314 ± 8	312 ± 7	306 ± 8		364 ± 8	362 ± 10		369 ± 22	368 ± 14	370 ± 12
in diisopropylether											486 ± 37	519 ± 25	510 ± 18
in dioxane		172 ± 3	276 ± 10	277 ± 6	381 ± 14	381 ± 14	484 ± 15	482 ± 13		497 ± 21	528 ± 26		

Table 5. $\mu_g/10^{-30}$ Cm in various solvents, determined by EOAM.

Solvent	CN0	CN1	CN2	CN3	CN4
cyclohexane	27.7 ± 0.5	36.3 ± 0.4	43.8 ± 0.8	50.1 ± 0.8	49.1 ± 1.2
decaline		36.8 ± 0.6	45.6 ± 0.6	50.6 ± 0.6	52.0 ± 0.9
diisopropylether					59.2 ± 1.1
dioxane	31.1 ± 0.4	41.7 ± 0.4	50.7 ± 1	58.4 ± 0.7	61.2 ± 1.3

The influence of transition polarizabilities on F and G can be neglected: assume $\Delta\mu \approx \mu_g$, for estimation. The $\beta^{-1} \cdot D$ gives the transition polarizability term affecting F. It is in almost all cases at least in the ranges II and III in the range of the error of F.

Polarizability changes $\Delta\boldsymbol{\alpha}$ are unknown. Even adopting $\Delta\boldsymbol{\alpha}$ as high as found for the related tetraphenylpolyenes [14], the results on $\Delta\mu$ are not very much influenced for the longer chainlength molecules, whereby $\Delta\mu$ of CN0 and CN1 might be erroneous from this point of view. Also the large angles between $\boldsymbol{\mu}_g^\circ$ and $\boldsymbol{\mu}_a^\circ - \boldsymbol{\mu}_g^\circ$ of CN0, which have been reported from quantum chemical calculations [6, 7], together with the very small values of F and G of CN0 impose some uncertainty on $\Delta\mu$ of CN0, too.

If the values of F and G of one molecule are compared in different ranges, there is a tendency of increasing $\Delta\mu$ with increasing transition energy. Because of measuring errors and neglect of polarizability and transition polarizability terms, arguing on this tendency would be overinterpretation of data.

So Table 6 gives results on $\Delta\mu$ for range II which is assumed to be the most accurate one from the experimental point of view, because the corresponding vibrational band is in most cases the most intense one and so should not be disturbed by superposition, also not by cis-absorption. The value of $\Delta\mu$ most drastically increases with chainlength and solvent polarity. Together with the solvent dependence of μ_g the latter effect shall be discussed in Section 3.4.

3.3.4. The Value of $m'_{\mu\mu}$ in Various Solvents and Vibronic Transitions

In Sect. 3.3.2 and 3 it has been shown that $\boldsymbol{m} \parallel \boldsymbol{\mu}_g \parallel \Delta\boldsymbol{\mu}$ is valid within an error of less than 20°. So with the values of D in Table 3, $m'_{\mu\mu}$ according to (1) can be calculated. The results are given in Table 7.

Looking at the values Table 7 two effects may be observed, more or less distinctly: $m'_{\mu\mu}$ increases with

(i) increasing solvent polarity,
(ii) decreasing transition energy.

Because of large scatter, effect (i) can only be qualitatively understood as an effect of the reaction field on the transition polarizability. Effect (ii) is in good agreement with the solvent dependent intensity profile of the first electronic absorption.

To get more insight into the solvent dependence of $m'_{\mu\mu}$, the solvent dependence of the absorption intensity profile must be studied. It will be done quantitatively in a forthcoming paper.

3.4. Interpretation of the solvent dependence of μ_g and $\Delta\mu$

In this paragraph the geometrical structure of these molecules is assumed to be independent of the solvent. Thus the solvent dependence of μ_g and $\Delta\mu$ reflects the solvent dependence of the electronic structure. In the framework of Onsager's reaction field theory this solvent dependence then is to be described as mainly electronic polarizabilities of

Table 6. $\Delta\mu/10^{-30}$ Cm in various solvents, determined from EOAM.

Solvent	CN0	CN1	CN2	CN3	CN4
cyclohexane	2.5 ± 1.0	12.8 ± 1.0	25.6 ± 1.6	43.5 ± 4.0	58.2 ± 9.3
decaline		12.5 ± 1.2	27.8 ± 3.8	40.3 ± 2.8	61.3 ± 6.0
diisopropylether					85.2 ± 5.3
dioxane	1.4 ± 1.4	17.0 ± 5.0	34.7 ± 2.0	67.0 ± 3.0	115.0 ± 7.0

Table 7. $m'_{\mu\mu}/10^{-10}\,\mathrm{CV^{-1}\,m^{1}}$ in some solvents and vibrational transitions.

	CN 0		CN 1		CN 2			CN 3			CN 4		
Range	I	II	I	II	I	II	III	I	II	III	I	II	III
cyclohexane	0	0.5	1.5	0.7	7.8	1.4	0.5	5.0	2.3	0.5	6.8	3.6	0.7
decaline			1.4	0.9	2.0	1.6		4.9	2.0		6.6	3.9	1.2
diisopropylether											9.1	3.8	1.2
dioxane		− 0.2	1.4	1.0	3.2	1.9		5.3	2.9		5.1	− 0.3	

Table 8. Permanent dipole moments and polarizabilities of CN 0 to CN 4.

	CN 0	CN 1	CN 2	CN 3	CN 4
$\mu_g^\circ/10^{-30}$ Cm	24.5	31.3 ± 0.2	38.0 ± 1.1	41.8 ± 0.7	39.2 ± 1.4
$(\alpha_{gzz}^\circ/(a_x\,a_y\,a_z))/10^{-10}\,\mathrm{CV^{-1}\,m^{-1}}$	0.31	0.47 ± 0.02	0.60 ± 0.13	0.82 ± 0.09	1.33 ± 0.25
$\mu_a^\circ/10^{-30}$ Cm		39.6 ± 1.3	55.0 ± 2.6	56.8 ± 8.2	50.2 ± 2.8
$(\alpha_{azz}^{\circ\mathrm{FC}}/(a_x\,a_y\,a_z))/10^{-10}\,\mathrm{CV^{-1}\,m^{-1}}$		0.63 ± 0.07	0.91 ± 0.12	1.87 ± 0.34	3.22 ± 0.22
$\alpha_{zz}^{\mathrm{El}}/(a_x\,a_y\,a_z)/10^{-10}\,\mathrm{CV^{-1}\,m^{-1}}$	1.12	1.48	1.89	2.35	2.92
$\alpha_{azz}^{\circ\mathrm{FC}}/\alpha_{gzz}^\circ$		1.35	1.53	2.27	2.43
$\alpha_{gzz}^\circ/10^{-40}\,\mathrm{CV^{-1}\,m^{2}}$	8.5	17.7	29.0	48.9	93.1
$\alpha_{azz}^{\circ\mathrm{FC}}/10^{-40}\,\mathrm{CV^{-1}\,m^{2}}$		23.9	44.3	111.1	226.3

rigid molecules. Then (7) and (9) may be rewritten to give

$$\frac{1}{\mu_g}=\frac{1}{\mu_g^\circ}-\frac{1}{4\pi\varepsilon_0}\,\frac{1}{\mu_g^\circ}\,\frac{\alpha_{gzz}^\circ}{a_x\,a_y\,y_z}\,g_z \tag{21}$$

and

$$X=\mu_a^{\circ\mathrm{FC}}+\frac{1}{4\pi\varepsilon_0}\,\frac{\alpha_{azz}^{\circ\mathrm{FC}}}{a_x\,a_y\,a_z}\,Y \tag{22}$$

with

$$X=\Delta\mu\,\frac{1-f\,\alpha_{gzz}^\circ}{1-f'\,\alpha_{gzz}^\circ}+\mu_g \tag{23}$$

and

$$Y=\Delta\mu\,\frac{1-f\,\alpha_{gzz}^\circ}{1-f'\,\alpha_{gzz}^\circ}\,g'_z+\mu_g\,g_z\,. \tag{24}$$

First, a linear regression of experimental values of $1/\mu_g$ in various solvents against g_z yields μ_g° and $\alpha_{gzz}^\circ/(a_x\,a_y\,a_z)$. The results are given in Table 8, together with errors derived from the errors of the regression coefficients. Then with these values X and Y can be calculated for the solvents used and a linear regression of X against Y according to (22) yields $\mu_a^{\circ\mathrm{FC}}$ and $\alpha_{azz}^{\circ\mathrm{FC}}/(a_x\,a_y\,a_z)$. The results are given in Table 8, too, also the ratio $\alpha_{azz}^\circ/\alpha_{gzz}^\circ$. These latter results cannot be given for CN 0 because of the reasons already discussed in Section 3.3.3.

The results from this evaluation procedure shows that the solvent dependence of μ_g and $\Delta\mu$ can be described as due to reaction field induced moments. The resulting permanent dipole moments of the groud state as well as of the first excited singlet state are nearly independent of the chain length for the longer chain length molecules CN 2, CN 3 and CN 4. With all compounds the excited state dipole moment is about 30 to 40% larger than the ground state dipole moment, the results being different from those preliminary results used in [6, 7], where induced effects have not been separated.

Values of $\alpha_{gzz}^\circ/a_x\,a_y\,a_z$ range from 0.5 to 1.3 and those of $\alpha_{azz}^\circ/a_x\,a_y\,a_z$ from 0.6 to 3.2. The large values found for the latter with the longer chain lengths may be compared to the polarizability $\alpha_{zz}^{\mathrm{El}}$ of an electrically conducting ellipsoid with the same half-axes. This is given in [18] as:

$$\alpha_{zz}^{\mathrm{El}}=\frac{4\pi\,a_x\,a_y\,a_z}{3}\,\frac{\varepsilon_0}{\varkappa_z}\,. \tag{25}$$

From this follows

$$\alpha_{zz}^{\mathrm{El}}/a_x\,a_y\,a_z=4\pi\,\varepsilon_0/(3\,\varkappa_z)\,. \tag{26}$$

The value of $\alpha_{zz}^{\mathrm{El}}$ of a conducting ellipsoid of the same half-axes as the respective compound is given for comparison in Table 8, too, where the used value of $\varkappa_z$ has been calculated according to (17), using the data given in Table 1.

The value of $\alpha^{\circ}_{azz}/a_x a_y a_z$ approaches the value of a conducting ellipsoid with increasing chain length, which means that the longer chain length molecules are almost as polarizable as a conducting ellipsoid.

In order to determine the values of α°_{gzz} and $\alpha^{\circ\,FC}_{azz}$ now the absolute size of the Onsager cavity is necessary, whilst up to this point the shape only has influenced the results. With the estimates for a_x, a_y, and a_z from Table 1, α°_{gzz} and α°_{azz} are calculated and given in Table 8, too. Errors are not given because of the ambiguity in the choice of a_x, a_y and a_z. In turn, estimating α°_{gzz} from group polarizabilities, $a_x a_y a_z$ could be determined. On the other hand this estimation is not very good with polyene or polymethine-like molecules. So no numbers shall be given here.

A more general remark should be attached here at the end: if one is interested in the permanent dipole moment of an isolated molecule, every influence of a solvent (reaction field) or an external electric field on the dipole moment may per definition be described as due to a polarizability, in first order. Thus a formal treatment of the solvent dependence of μ_g and $\Delta\mu$ according to this section most probably must be able to describe the solvent dependence but regrettably without giving any insight into the field (≡ solvent) dependent structural changes that manifest themselves as polarizabilities. Especially it is impossible in these experiments to decide between pure electronic and geometrical structural changes. This one must bear in mind, too, discussing dipole moments of molecules with more or less freely rotatable groups [1, 2, 3, 19].

In this paper the assumed purely dielectric interaction between solute and solvent has turned out to be fully sufficient to describe the experimentally observed effects. As mentioned above, in a forthcoming paper this conception shall be proved by studying the solvent dependence of the absorption spectrum in more detail.

4. Concluding Remarks

The startling result of these measurements is the large solvent effect on the quantities μ_g and $\Delta\mu$. It has been shown in 3.4 that taking into account a solvent independent polarizability, the solvent dependence of the quantity μ_g can be understood satisfactorily, using the Onsager reaction field model. The in solution effective quantity α_g according to (8) is solvent dependent, too, but this must not be mixed up with Dähne's [4] finding for a similar class of merocyanines who reports solvent polarity dependent polarizabilities determined at light frequency. An exact comparison is not possible since Dähne does not give the detailed evaluation procedure; but there seems to be some discrepancy of unknown reason.

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