Spectral Properties of Some Naphthalene Derivatives of Bicarboxylic Acid; Comparison of Experimental Results with Theoretical Predictions

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Z. Naturforsch. **49a,** 671–679 (1994); received March 24, 1994

The basic electronic quantities of some dichroic dyes, naphthalene derivatives of bicarboxylic acid, have been evaluated theoretically using a semi-empirical INDO (intermediate neglect of differential overlap) CI (configuration interaction) approach. The theoretical data have been compared with the experimental results obtained from the absorption and fluorescence measurements of the dyes dissolved in toluene and oriented in liquid crystal 8CB. Additionally, the order parameters of the dyes in smectic A and nematic phases of 8CB have been determined.

I. Introduction

It had recently been shown [1–4] that the naphthalene derivatives of bicarboxylic acid have many properties which qualify them as possible dichroic dyes in "guest-host" liquid crystal display devices [5–8], working in both passive and active modes. These dyes have a brilliant yellow colour, emit green fluorescence light with very high quantum yield, orientate well in technologically important nematic liquid crystal mixtures, are stable to the sun light and do not considerably influence the mesophase range of the nematic host. Although some naphthalene bicarboxylic acid derivatives had been intensively investigated in the last years [1–4, 9–11], there is still a lack of theoretical and experimental data of the basic parameters of these dyes, such as the dipole moments, the electronic transition energies, the oscillator strengths, and the directions of the transition moments with respect to the molecular frame. Previously, one of us [9] had proposed a method for determining the angles between the absorption and emission transition moments and the symmetry axis of a dichroic dye molecule based on the measurement of the polarized absorption and fluorescence spectra of the dye oriented in an anisotropic medium. This medium had been applied in investigations of several naphthalene bicarboxylic acid derivatives dissolved in the nematic mixture E18 (Merck). Moreover, for the very same dyes the reduced absorption spectra had been obtained and the polarization of the electronic transitions in the UV-visible region had been determined [11].

The aim of the present work is to get further information about the basic electronic properties of the dyes. This is done by comparing the experimentally determined long-wavelength absorption band position, oscillator strength and direction of the transition moment with respect to the long molecular axis with corresponding calculated values.

II. Experimental

As in [9], the fluorescent dichroic dyes with chemical structure given in Table 1 were investigated. Out of the many naphthalene derivatives of bicarboxylic acid these seven dyes were chosen because of their very high fluorescence efficiency and satisfactory orientational ability in liquid crystals [3, 11], which make them very interesting from the technological point of view as the fluorescent guests applicable in active guest-host liquid crystal display devices. The dyes were synthesized and chromatographically purified at the Institute of Dyes, Technical University, Łódź, Poland [12]. They were dissolved in a nonpolar isotropic solvent (toluene) at a concentration of $3 \cdot 10^{-4}$ M/l and the liquid crystal 8CB at a concentration of $1.5 \cdot 10^{-2}$ M/l. 8CB was supplied by BDH Ltd. and used without further purification: the ob-

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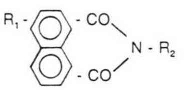
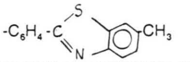
Table 1. Molecular structure of the investigated dyes.



Dye code	R_1	R_2
1	$-N(CH_3)_2$	$CH_2-CH_2-CH_2-CH_3$
2	$-N(CH_3)_2$	$p-C_6H_4-CH_3$
3	$-NHCH_2-CH_2-OCH_3$	$-CH_2-CH_3$
4	$-NHCH_2-CH_3$	$-CH_2-CH_3$
5	$-NHCH_2-CH_2-CH_2-CH_3$	$-CH_2-CH_3$
6	$-N(C_8H_{17})_2$	$-C_6H_4-O-C_6H_4-CH_3$
7	$-N(C_8H_{17})_2$	

served phase transition temperatures were in satisfactory agreement with those reported in [13] and were as follows:

$$\text{crystal} \rightleftarrows \text{smectic A} \rightleftarrows \text{nematic} \rightleftarrows \text{isotropic}$$
$$295.0\ \text{K} \qquad 306.7\ \text{K} \qquad 313.8\ \text{K}.$$

Absorption measurements were performed by means of a double beam spectrophotometer SPECORD M40 (Carl Zeiss Jena). Corrections were made for solvent and cell absorption, reflection and scattering. Fluorescence spectra were obtained using a home-made photon-counting fluorimeter. The 436 nm line of a high pressure mercury lamp was used for the excitation of fluorescence. Further experimental details and the measurement geometry were reported in [10, 14]. Appropriate corrections connected with the apparatus and the sample positions were made [15]. In order to obtain the polarized absorption and fluorescence spectra for the dyes oriented in the liquid crystal matrix, the neutral UV polarizers from Carl Zeiss Jena were used.

The measurements of the absorption and fluorescence spectra for the dye-liquid crystal mixtures were made in "sandwich" glass cells of 20 μm in thickness. In order to obtain planar homogenous molecular orientation of the samples the cell surfaces were coated with a thin polyimide layer and rubbed additionally in one direction. The cells were filled after heating the dye-liquid crystal mixtures above the clearing point. Then the samples were annealed very slowly to produce first the nematic and next the smectic A phases. This procedure gave uniformly oriented samples, as was seen under the polarizing microscope.

III. Method of Calculations

III.1. Quantum Chemical Calculations

In the present work we adopt a model Hamiltonian based on the Intermediate Neglect of Differential Overlap approximation (INDO). This method, which has been originally designed to reproduce one-electron properties like ionization potentials and electronic transition energies for organic compounds containing transition metal atoms, allows to calculate electronic key quantities of molecules consisting of 80 atoms with reliable accuracy. The basic capabilities of the method are described in [16–19]. Previously it was shown [20–22] that the adopted INDO/MO-model is of reliable accuracy to reproduce electronic spectra of π-compounds containing different aromatic substructure elements like simple benzene or biphenyl rings, stilbene or tolane systems as well as naphthyl groups.

For the evaluation of the electronic absorption behaviour of molecules the wavefunctions φ_g and φ_e of the electronic ground and the single excited states have to be described using a MO/LCAO-approximation in an atomic orbital basis. Since electronic excitation processes involve an interaction of the electron with the fluctuating electric field of the electromagnetic radiation, it is expected that the absorption depends on common localization properties of φ_g and φ_e in the direction z, which is the principal direction of the oscillating electric vector. Of course an electronic transition is only possible if the direct product of the ground state wavefunction, the excited state one and the dipole moment operator form a totally symmetric representation. For a given excitation the transition probability is usually characterized by the oscillator strength $f_{ge}(\boldsymbol{r})$ given by the expression [23]

$$f_{ge}(\boldsymbol{r}) = \frac{8\pi^2 c\, m_e \bar{\nu}}{3he^2} |\boldsymbol{\mu}_{ge}|^2 \cong 4.7 \cdot 10^{-7}\, \bar{\nu}_{\max} |\boldsymbol{\mu}_{ge}|^2, \quad (1)$$

where m_e and e are the electron mass and charge, respectively, h is Planck's constant, $\bar{\nu}$ the wavenumber in cm^{-1} and $\boldsymbol{\mu}_{ge}$ the electric dipole transition moment in units of Debye. $\boldsymbol{r}$ represents the electron position vector.

$\boldsymbol{\mu}_{ge}$ of one transition is given by

$$\boldsymbol{\mu}_{ge} = \int \varphi_g \boldsymbol{M} \varphi_e \, d\tau, \quad (2)$$

where $\boldsymbol{M}$ is the dipole moment vector, which can be separated in components along the x, y, and z directions:

$$M^2 = M_x^2 + M_y^2 + M_z^2 . \tag{3}$$

The numerical value of $\boldsymbol{\mu}_{ge}$ is a measure for the transition probability [24].

The description of molecular quantities by quantum chemical methods underlies some principle restrictions, i.e. there exists a compromise between the complexity of the studied systems and the accessible theoretical accuracy. For example semi-empirical MO-models were formulated on the basis of selfconsistent-field (SCF) methods, and for the calculation of electronic spectra the configuration interaction (CI) method is a widely employed approach [24, 25]. Using a CI-procedure in combination with a semi-empirical model Hamiltonian an evaluation of electronic absorption spectra of large organic molecules becomes possible. The examined dyes consist of more than 30 atoms, and on the base of a substituted naphthalene system the principal absorption bands are due to $\pi-\pi^*$ transitions [27].

III.2. Computational Conditions

All calculations were done using an IBM 3090-E200VF mainframe computer. Figure 1 gives a description of the basic structure geometry, the labelling scheme and the definition of the Cartesian coordination system. Common structural parameters of the considered systems like bond lengths and angles were taken from [28, 29]. The CI-calculations refer to isolated molecules in the gas phase at zero temperature. In the subsequent CI-calculations a 15 × 15 array has been used, i.e. 15 occupied and 15 unoccupied states were considered. Model calculations have shown that this is a reliable compromise between the necessary computational time and the observed accuracy and stability of the numerical results. Unfortunately, due to this small matrix only transitions with lowest energy can be reproduced in good agreement with experiment.

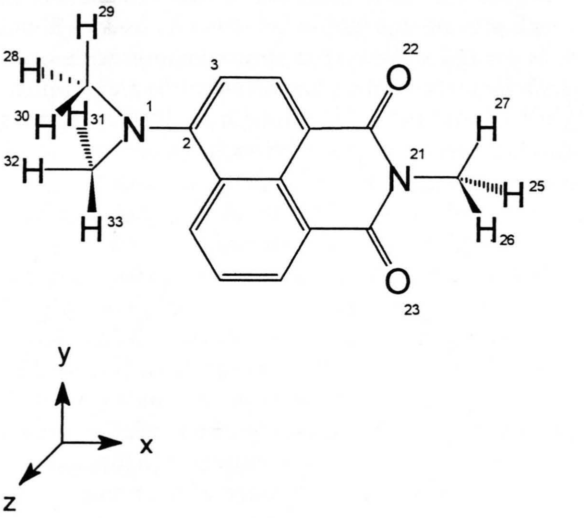


Fig. 1. Basic structural scheme of the naphthalene derivatives of bicarboxylic acid: definition of the Cartesian system and the internal numbering.

IV. Results and Discussion

IV.1. Basic Electronic Quantities

Table 2 shows the basic electronic quantities obtained from quantum chemical calculations and from experiment. In this table the values of the ground state electric dipole moment, μ_g, the position of the absorption maximum, λ_{max}, and the oscillator strength, f_{ge}, for the long-wavelength absorption band are gathered. The experimental values of λ_{max} and f_{ge} were obtained from the absorption measurement of the dyes dissolved in toluene. The oscillator strength is related to the integrated intensity of the absorption band through the expression [23]

$$f_{ge} = \frac{2303\, m_e c^2}{\pi n_0 N_A e^2} \int_{\text{band}} \varepsilon(\bar{\nu})\, d\bar{\nu} \cong \frac{4.32 \cdot 10^{-9}}{n_0} \int_{\text{band}} \varepsilon(\bar{\nu})\, d\bar{\nu}, \tag{4}$$

where ε is the extinction coefficient in units of $l\,M^{-1}\,cm^{-1}$, n_0 the mean index of refraction of the solution in the region of the band, N_A Avogadro's number and c the light velocity.

The naphthalene derivatives of bicarboxylic acid show a very broad absorption band in the visible region (halfband-width up to 4500 cm^{-1}), what sug-

Table 2. Basic electronic quantities of the dyes under investigation.

Dye code	Calculations			Experiment	
	μ_g [D]	λ_{max} [nm]	f_{ge}	λ_{max} [nm]	f_{ge}
1	6.7	421	0.07	406	0.14
2	7.8	417	0.10	400	0.16
3	5.0	421	0.10	419	0.15
4	6.9	427	0.13	421	0.16
5	6.4	424	0.13	422	0.16
6	9.0	418	0.12	423	0.20
7	8.6	434	0.20	424	0.25

gests that the energy gap between the ground and excited states is very sensitive to intermolecular interactions. As the calculations refer to isolated molecules the lack of perfect coincidence between the experimental and calculated values is not surprising. The general trend of the numerical results, however, coincides quite well with the experimental data. Both the calculations and experiments indicate the strong influence of the substituents in the aromatic skeleton on the position of the absorption maximum and on the value of the oscillator strength. The latter effect is most distinctly shown in the case of dye 7 possessing a considerably complex substituent R_2. It is seen that the introduction of such a substituent to the basic aromatic skeleton of the dye can lead to an intensity enhancement of the electronic transition. The calculations show also the influence of the terminal substituent on the value of the dipole moment in the ground state. The deviations between the calculated energies for the lowest absorption and the experimental ones are smaller than 4%.

IV.2. Directions of the Transition Moments

The aromatic skeleton of the naphthalene derivatives of bicarboxylic acid, which is the basic part of the molecular structure, has C_{2V} symmetry. In such a case symmetry dictates that in the absence of perturbations the observed electronic transitions can be polarized along either the C_2 axis or the in-plane axis perpendicular to C_2. The presence of the terminal groups reduces the molecular symmetry. The structure of the substituents in the vicinity of the planar π system would suggest C_S symmetry. In molecules of such a symmetry the electronic transition moments can lie in any direction in the molecular plane. As mentioned above, a broad long-wavelength absorption band of the dyes investigated could indicate the existence of more than one transition in the visible region. However, on the basis of the polarized absorption of the dyes in an oriented liquid crystal matrix it had been found previously [11] that only one transition is responsible for the absorption in this spectral region. It had been also ascertained that the angle between the long axis of the dyes molecules and the direction of the lowest energy transition should not be very large, but different from zero. The long-wavelength absorption transition, which is responsible for the absorption of the visible light results from the charge transfer (CT) between the nitrogen atom in the substituent R_1 (donor) and that at the substituent R_2 (acceptor), what suggests that the direction of this transition must deviate from that of the long axis of the dye molecule (the long axis has been defined as the straight line between the atoms along the x-axis direction).

Table 3. Calculated data of the direction of the long-wavelength absorption transition moment for the investigated dyes.

Dye code	x	y	z	α
1	0.98	−0.23	0.02	13.2°
2	0.98	−0.19	0.00	11.0°
3	0.98	−0.21	0.01	12.0°
4	0.98	−0.21	0.01	12.0°
5	0.98	−0.21	0.02	12.0°
6	0.98	−0.17	0.08	9.8°
7	1.00	−0.08	0.00	4.6°

Table 3 shows the calculated data giving the direction of the long-wavelength absorption transition moment for the dyes studied. As expected on the basis of previous investigations only one electronic transition is responsible for the absorption in the visible region. This transition is strongly polarized in the direction of the x-axis with a small contribution in the y-direction. Because of the small z-values the transition can be assumed to be polarized in the plane of the aromatic core. In the table the angles between the long axis of the dye molecule and the direction of the transition moments, defined as $\alpha = \mathrm{tg}(y/x)$ are also listed. The transition moment direction is marked in Fig. 2, which presents the molecular structure of dyes **5** and **6**, as examples. As a valid approximation with small deviations, the straight line between the amino-nitrogen no. 1 and the imino-nitrogen no. 21 (Fig. 1) gives the direction of the absorption transition due to its origin as an intramolecular charge transfer.

To obtain information about the transition-moment-directions from the experiment, those using polarized light are particularly powerful [30]. They require an at least partially oriented assembly of molecules such as solute molecules dissolved in liquid crystalline materials in the nematic phase [11, 30–36]. These methods had, however, some limitations such as providing information only about relative transition moment directions. Therefore in [9] a method was proposed which takes advantage of the results of the polarized absorption and fluorescence measurements simultaneously. From the polarized fluorescence spectra two emission anisotropies can be determined,

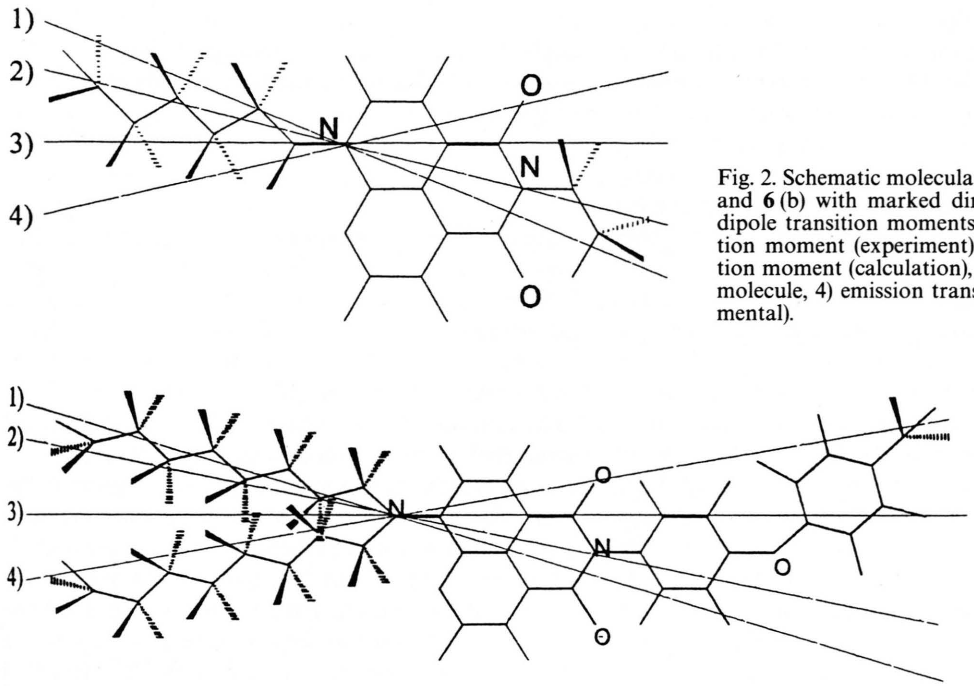


Fig. 2. Schematic molecular structure of dyes **5** (a) and **6** (b) with marked directions of the electric dipole transition moments: 1) absorption transition moment (experiment), 2) absorption transition moment (calculation), 3) long axis of the dye molecule, 4) emission transition moment (experimental).

which are defined as [37]:

$$r = \frac{J_{zz} - J_{zy}}{J_{zz} + 2J_{zy}}, \tag{5}$$

$$h = \frac{J_{yz} - J_{yy}}{J_{yz} + 2J_{yy}}, \tag{6}$$

where the J_{ij}'s denote intensities of the fluorescence light. The subscripts *i* and *j* determine the directions of the excited and emitted light polarization, respectively.

Assuming, that the fluorescence lifetime τ_F is very short in comparison with the rotational relaxation time τ_R ($\tau_F \ll \tau_R$), the anisotropies of emission can be related with the angles between the long axis of the fluorescent solute molecule and the absorption and emission oscillators, respectively, α and ε, in the following way:

$$r = \frac{\frac{1}{3}\langle P_2\rangle P_2(\cos\varepsilon) + A + B\langle P_2\rangle + 6C\langle P_4\rangle}{\frac{1}{3} + \frac{2}{3}\langle P_2\rangle P_2(\cos\alpha)}, \tag{7}$$

$$h = \frac{\frac{1}{3}\langle P_2\rangle P_2(\cos\varepsilon) - \frac{1}{2}(2A + 7C\langle P_4\rangle)}{\frac{1}{3} - \frac{1}{3}\langle P_2\rangle P_2(\cos\alpha) + A - B\langle P_2\rangle + C\langle P_2\rangle}, \tag{8}$$

where $\langle P_2\rangle$ and $\langle P_4\rangle$ are the averages of the Legendre polynomials and describe the orientational order in an oriented anisotropic sample, and *A*, *B*, and *C* are functions of the angles α and ε [9]. It had been assumed that both angles lie in one plane.

Equations (7) and (8) contain four unknowns: α, ε, $\langle P_2\rangle$ and $\langle P_4\rangle$. Independent measurements of the emission anisotropy of the solute in an isotropic medium enable to determine the value of the intramolecular angle $\delta = \alpha - \varepsilon$. In order to obtain α and ε an additional equation is needed. One can use the absorption anisotropy *S*, defined as [38, 39]

$$S = \frac{R-1}{R+2} = \langle P_2\rangle P_2(\cos\alpha), \tag{9}$$

where *R* is the dichroic ratio and $A_\parallel$ and $A_\perp$ are the absorbances of the light polarized parallel and perpendicular to the orientation direction, respectively.

The above described method had been applied to determine the angles α and ε as well as $\langle P_2\rangle$ and $\langle P_4\rangle$ for our seven dyes in nematic E18 [9]. Our experience [10, 41] indicates however, that in the nematic phase the condition $\tau_F \ll \tau_R$ is only approximately valid, thus enabeling only a rough estimation of the transition moment directions. Therefore in this study we have used as orienting matrix the liquid crystal 8CB possessing besides the nematic phase, the more highly oriented smectic A phase. The viscosity of 8CB in this phase is considerably greater than in the nematic one, and therefore the assumption $\tau_F \ll \tau_R$ can be fulfilled in much better approximation. The smectic A phase is characterized both by orientational order of the long molecular axes and by a reduced positional order. The orientational order parameters in the smectic A phase can be evaluated by any of the methods used for the nematic phase, because both these phases are optically uniaxial, as had been confirmed by X-ray diffraction [41]. Thus from polarized absorption and fluorescence measurements of the fluorescent dye dissolved in a smectic A phase the angles α and ε can be obtained.

In Table 4 the dichroic ratios R of the long-wavelength absorption band for our dyes in 8CB at $T = 302$ K are listed. For all the dyes R remained constant over the whole absorption band, confirming once more that in the visible region only one electronic transition is responsible for the absorption. The values of R indicate that the main contribution to the polarization of this transition originates from polarization along the x-axis. In Table 4 the angles α and ε, determined from the experiment and (7)–(9) are also gathered. In Fig. 2 the directions of the absorption and emmission transition moments are marked. The values of the angle δ were taken from [9]. They were estimated from the measurements of the emission anisotropy of the dyes dissolved in solid epoxy resin.

Taking into account the uncertainty in the determination of the angles α and δ, it is seen from Table 4 that the absorption and emission transition moments deviate almost symmetrically with respect to the long axis of the dye molecules. Only dye **7** makes an exception: in this case the emission oscillator is almost parallel to the long molecular axis, whereas the absorption transition moment direction deviates considerably from it.

Comparing the calculated and experimentally obtained values of the angle α it is seen that the latter are in all the cases greater than the former ones, but the general trend is retained. The large deviation for dye **7** is probably due to the complex molecular structure of the R_2 substituent.

Table 4. Dichroic ratio R in the smectic phase, intramolecular angle δ, and experimentally obtained angles between the long molecular axis and the absorption and emission oscillators, α and ε, respectively, for the dyes studied in 8CB.

Dye code	R	δ $\Delta\delta = \pm 3.0°$	α $\Delta\alpha = \pm 4.0°$	ε
1	3.26	33°	20°	−13°
2	3.48	28°	16°	−14°
3	2.92	41°	16°	−25°
4	2.92	31°	13°	−18°
5	2.55	33°	17°	−16°
6	6.82	29°	14°	−15°
7	5.50	28°	20°	−8°

IV.3. Order Parameters

As it has been mentioned above, the method proposed in [9] allows to determine not only the angles between the long molecular axis of the dye and the absorption and emission oscillators, but also the order parameters describing the orientational order of the dye oriented in an anisotropic matrix. One of the asssumptions of this method is however cylindrical symmetry of the dye molecules. Our dyes have only approximately such a symmetry, and in general the molecular biaxiality should be taken into account. This would involve five independent order parameters up to rank 4 for the full description of the long orientational order [42]. The parameter D, which describes the biaxiality of the molecule, had been calculated for the naphthalene derivatives of bicarboxylic acid [11] and had been found to be 0.05–0.1. As it is small compared to $\langle P_2 \rangle$, we have neglected it in our consideration and determined only the order parameter $\langle P_2 \rangle$ and the fourth-rank parameter $\langle P_4 \rangle$. With respect to $\langle P_2 \rangle$ the order parameter $\langle P_4 \rangle$ provides further information about the orientation of the molecules as it is in fact more sensitive to molecular fluctuations. The knowledge of $\langle P_4 \rangle$ in addition to $\langle P_2 \rangle$ allows to obtain the orientational molecular distribution function [10, 14].

In the following it has been assumed that the angles α and ε do not change with rising temperature and at the transition from the smectic A to the nematic phase. Moreover, we have supposed that the order parameter $\langle P_2 \rangle$ determined from the fluorescence measurement and (7)–(8) is equal to that obtained from the absorption spectra and (9) only in the smectic phase at room temperature. The values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for our dyes in the smectic A and nematic phases of 8CB are listed in Table 5, which shows that the long orientational order in the dye-liquid crystal mixtures changes with the temperature, but in the smectic A phase less than in the nematic one. Moreover, it is seen that the $\langle P_2 \rangle$ order parameters estimated from the absorption ($\langle P_2 \rangle_A$) and fluorescence ($\langle P_2 \rangle_F$) data are only equal up to a certain temperature in the smectic phase. In the vicinity of the smectic A-nematic phase transition both values begin to differ, and this

Table 5. Order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ as functions of temperature for the dyes **1**–**7** in 8CB. $\Delta\langle P_2\rangle_A = \pm 0.02$, $\Delta\langle P_2\rangle_F = \pm 0.04$, $\Delta\langle P_4\rangle_F = \pm 0.08$.

Dye code	T [K]	$\langle P_2\rangle_A$	$\langle P_2\rangle_F$	$\langle P_4\rangle_F$
1	299	0.52	0.52	+0.05
	302	0.51	0.52	+0.07
	304	0.49	0.50	+0.05
	307	0.41	0.32	−0.25
	309	0.38	0.31	−0.27
	312	0.34	0.25	−0.30
2	299	0.51	0.51	+0.05
	302	0.51	0.51	+0.05
	304	0.50	0.49	−0.00
	307	0.42	0.36	−0.15
	309	0.38	0.31	−0.20
	312	0.35	0.28	−0.24
3	299	0.44	0.44	+0.10
	302	0.43	0.41	−0.02
	304	0.41	0.35	−0.05
	307	0.37	0.26	−0.15
	309	0.35	0.23	−0.19
	312	0.31	0.20	−0.25
4	299	0.42	0.42	−0.09
	302	0.42	0.41	−0.13
	304	0.42	0.40	−0.14
	307	0.40	0.32	−0.26
	309	0.37	0.28	−0.32
	312	0.29	0.25	−0.35
5	299	0.39	0.39	−0.09
	302	0.37	0.43	−0.05
	304	0.38	0.40	−0.10
	307	0.32	0.31	−0.26
	309	0.29	0.29	−0.27
	312	0.25	0.22	−0.33
6	299	0.73	0.75	+0.45
	302	0.72	0.73	+0.45
	304	0.69	0.68	+0.34
	307	0.62	0.60	+0.15
	309	0.58	0.49	−0.02
	312	0.56	0.39	−0.21
7	200	0.72	0.72	+0.42
	302	0.71	0.70	+0.40
	304	0.71	0.71	+0.42
	307	0.65	0.69	+0.38
	309	0.63	0.54	+0.04
	312	0.59	0.50	−0.04

difference increases strongly with rising temperature in the nematic phase. As this phase is less viscous than the smectic A one, the thermal motions cannot be neglected and the assumption $\tau_F \ll \tau_R$ is not valid in the whole temperature range. This can lead to a misinterpretation of the fluorescence emission data and cause the difference between $\langle P_2\rangle_A$ and $\langle P_2\rangle_F$.

As regards $\langle P_4\rangle$, Table 5 shows that this order parameter, except for dyes **6** and **7** in smectic A phase, is very low and in the nematic phase is mostly negative. These results are in disagreement with theoretical calculations: neither Maier and Saupe [43] nor Humphries, James and Luckhurst [44] predict a negative $\langle P_4\rangle$ parameter. However, the non-typical behaviour of $\langle P_4\rangle$ for some nematic liquid crystals had been observed by many authors studying the orientational order using Raman scattering [45–48] and fluorescence depolarization [10, 14, 49] methods. Many attempts were undertaken to explain the non-typical behaviour of $\langle P_4\rangle$ [14, 46, 47, 50, 51], but up till now the reason of the deviation of the experimentally obtained $\langle P_4\rangle$ values from the theories has not been found.

$\langle P_2\rangle_A$ for the mixtures of 8CB with dyes **6** and **7** are in substantial agreement with $\langle P_2\rangle$ values obtained for pure 8CB on the basis of the refractive index measurements [10, 52]. This means, that not only dyes with a molecular structure similar in size and shape to that of an anisotropic host can be used as the fluorescent probes to study the orientational behaviour of the oriented matrix. If the angles α and ε can be determined, dye molecules with non-zero biaxiality parameter D but elongated in shape, like dyes **6** and **7**, may also be successfully used as fluorescent probes. In comparison with fluorescent dyes, utilized often to this purpose e.g. dimethyl-amino-nitrostilbene (DANS) [14, 40, 49, 53, 54] the naphthalene derivatives of bicarboxylic acid have very high quantum fluorescence yields, which is doubtless an advantage.

V. Conclusions

We have calculated the electric dipole moment as well as the electronic transition energy, the oscillator strength and the direction of the transition moment with respect to the molecular frame for the long-wavelength absorption band of seven dichroic dyes by means of a semi-empirical INDO/MO method. The calculated electronic transition energy and oscillator strength have been compared with the experimental results obtained from measurements of the absorption of the dyes dissolved in toluene. The angles between the long molecular axis of the dye and the absorption and emission oscillators have been determined experimentally from the polarized absorption and fluorescence spectra for the dyes oriented in liquid crystal 8CB in the smectic A phase. Although perfect agreement between the calculated and experimental values is not obtained, the general trend of the numerical results is consistent with the experimental data. The mean reason of the differences seems to be the intermolecular interactions between the dye and neighbouring solvent molecules. Especially in the case of the liquid crystalline matrix, in which the solute molecules acquire alignment, the influence of the solvent on the electronic quantities of the dyes must be considerable, because such "mechanical" alignment is already a clear manifestation of solute-solvent interactions.

Additionally determined order parameters of the dyes in smectic A and nematic phases of 8CB enable to ascertain that some naphthalene derivatives of bicarboxylic acid (e.g. dye **6** or **7**) can be utilized as fluorescent probes to study the long range orientational order of liquid crystal matrices.

Acknowledgements

The work was supported by the Polish Research Project No. 2 P302 001 04, coordinated by KBN. One of us (T.H.) thanks also the Technische Hochschule Darmstadt for a Ph.D. fellowship. The authors are gratefully acknowledged to Prof. Dr. M. C. Böhm for his help and stimulating discussions.

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