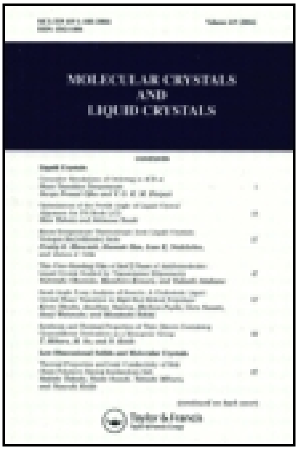

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Orientational Behavior of Stilbene Dyes in Nematic Liquid Crystals

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To cite this article: T. Hanemann & W. Haase (1993): Orientational Behavior of Stilbene Dyes in Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 231:1, 119-127

To link to this article: http://dx.doi.org/10.1080/10587259308032498

Mol. Cryst. Liq. Cryst., 1993, Vol. 231, pp. 119–127
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Printed in the United States of America

Orientational Behavior of Stilbene Dyes in Nematic Liquid Crystals

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(Received November 11, 1991; in final form July 24, 1992)

Four different guest-host systems containing stilbene molecules solved in the liquid crystalline compound CB5 were investigated to study the orientational behavior of these dyes in the nematic phase. The estimation of the optical order parameter S_{op} was done using UV/Vis dichroism measurements. The dye's structure and concentration influence the nematic phase order and the phase range. This will be demonstrated in concentration dependent measurements of the optical order parameter and the change of the clearing point with the amount of solved dye molecules. Besides the common decrease of the optical order parameter with increasing dye concentration the opposite behavior, i.e., a slight increase of S_{op} was observed also.

Keywords: guest-host systems, stilbene dyes, optical order parameter, phase transition temperature

INTRODUCTION

General Considerations

With regard to display applications a large number of guest-host (gh) systems were investigated to optimize, e.g., the contrast ratio between the on- and off-state, the extinction of the solved dye molecules and the longtime stability against air and UV/Vis radiation. Different kinds of dye molecules containing chromophor moieties like azo, azomethine, anthraquinone and related groups were examined to achieve the above mentioned properties.[1-5] Therefore we felt the need to examine the change of the optical order parameter S_{op} and the nematic-isotropic phase transition temperature with an increasing dye concentration solved in a low mass liquid crystal (4-cyano-4′-pentyl-biphenyl, CB5). We decided to use the important class of stilbene dyes, which are very promising in nonlinear optics because of their large hyperpolarizability values.[6]

Orientational Order

The orientational order of an oriented nematic liquid crystal with cylindrical symmetry is in general specified by the Saupe order matrix S_{ij} (i, j, $= x, y, z$) where

x, y, z represent the internal cartesian molecular axes (Figure 1). Diagonalization leads to two elements S and D (Equations 1 and 2).

$$S = S_{ZZ} = \langle 1 - 1.5 \times \sin^2\theta \rangle \tag{1}$$

$$D = S_{XX} - S_{YY} = \langle 1.5 \times \sin^2\theta \times \cos 2\phi \rangle \tag{2}$$

S represents the average deviation of the orientational axis from the director **n** and D reflects the deviation of the ordering matrix from cylindrical symmetry. Based on the mean field theory[7] which describes a dependency of D with S, methods for the determination of S and D from the temperature dependence of the anisotropic absorption of light measured in two different regions of the spectra were presented,[8-10] but this approach is restricted to molecules with a symmetry different from C_1, C_2, C_i, C_s and C_{2h}. For applications only the knowledge about the macroscopic or optical order parameter S_{op}[11] is of main interest. S_{op}, measured by linear dichroism experiments, can be described by Equation (3), where α and β specify the direction of the dipole transition moment vector in the molecular frame (Figure 1).

$$S_{op} = (1 - 1.5 \times \sin^2\alpha) \times S + 0.5 \times \sin^2\alpha \times \cos 2\beta \times D \tag{3}$$

If $D \neq 0$ the molecules show molecular biaxiality. A direct estimation of S and D from the dichroic ratios of two bands with different orientations of the related linear transition moments relative to the molecular axes is possible if the angles α and β are known. Different approaches try to describe S, D and the biaxiality respectively considering the molecular geometry, the deviation from cylindrical symmetry can be estimated using a biaxiality parameter λ.[7,12-14] In general λ can be calculated in terms of any molecular property σ_{ij} (Equation 4) like polarizability, moments of inertia or the molecular extensions,[15] the value of λ changes with the molecular property σ_{ij} used to define it. We decided to consider the molecular size.

$$\lambda = 0.25 \times \sqrt{6} \times (\sigma_{YY} - \sigma_{XX})/(\sigma_{ZZ} - 0.5 \times (\sigma_{YY} + \sigma_{XX})) \tag{4}$$

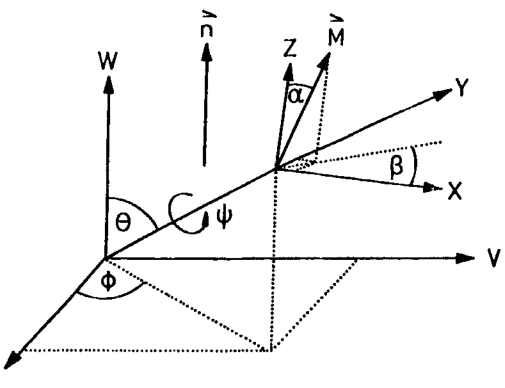


FIGURE 1 Definition of the molecular axes x, y, z, the director **n** and the dipole transition moment **M** relative to the laboratory axes u, v, w, given by the cell geometry.

According to Equation (4) λ is zero for cylindrical molecules if the two short axes are equivalent or $\sqrt{(1.5)}$ if the z-axis is perpendicular to the principal molecular axis. The validity of these descriptions and the use of the molecular extensions for the calculation of λ is restricted on the following items:

- a rigid molecular shape with fixed axes
- a stable geometry with rigid molecular subunits.

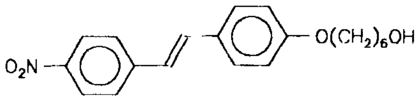
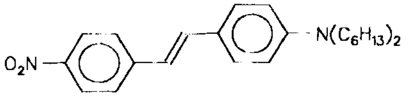
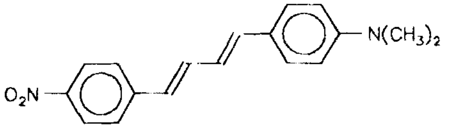
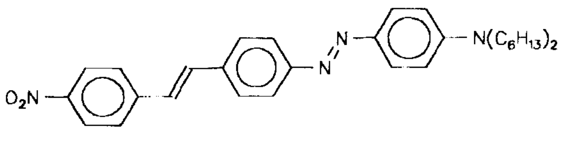
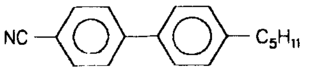
Flexible aliphatic chains attached to an aromatic frame allow for different conformations and make a geometric description of the biaxiality rather complicated and inaccurate.

EXPERIMENTAL

The investigated molecules (Table I) were synthesized either in our group 4-[2-[4-(6-hydroxyhexyloxy)-phenyl]-ethenyl]-nitrobenzene **1** or obtained from E. Merck, Darmstadt: 4-[2-[4-*N*,*N*-dihexylaminophenyl]-ethenyl]-nitrobenzene **2**, 4-[4-[4-*N*,*N*-dimethylaminophenyl]-butadienyl]-nitrobenzene **3**, 4-[2-[4-[2-[4-*N*,*N*-dihexylami-

TABLE I

Stilbene dyes and host lc investigated

Compound	Structure
1	
2	
3	
4	
CB5	

nophenyl]-diazo]-phenyl]-ethenyl]-nitrobenzene **4**, and CB5 as lc host. The substances were taken without further purification. The concentration of the guest compound was increased in steps of 0.1 weight% up to the solubility limit in CB5 and was measured in the cells using Lambert-Beer's law with an uncertainty of 5%. The mixtures were tempered for several days at 60°C, cooled down to room temperature and strained through a micron filter. The dicroism measurements were made in oriented "sandwich" cells of 12 μm thickness. The cell glass plates were coated firstly with ITO, secondly with a commercial polyimide (PI-KIT ZLI 2650, Merck). The plates were rubbed with Joseph's paper to obtain homogeneous alignment of the lc host. The temperature of the mounted cells was changed from 24°C to 40°C with an accuracy of ±0.1 K. All investigations were done using a modified Cary 17 UV/Vis/NIR spectrophotometer (Varian) equipped with adjustable polarizers (Kaesemann) to obtain linear polarized light. All spectra were taken in the region of 350-600 nm. In order to calculate the optical order parameter S_{op} from the experiment the well known relationships (Equations 5–6) were used.

$$R = E^{\parallel}/E^{\perp} \tag{5}$$

$$S_{op} = (R - 1)/(R + 2) \tag{6}$$

R represents the dichroic ratio, $E^{\parallel}$ and $E^{\perp}$ are the extinction parallel and perpendicular to the director's orientation. The influence of the local field according to the polarization field anisotropy in the liquid crystal host which results in a correction factor for R was not considered because of the existence of various approaches described in literature.[3,16,17] The maximum experimental error in S_{op} with the equipment used was ±0.02 and has its origins in the uncertainty of the spacer's thickness and in the spectrometer's accuracy. All experimental data for the estimation of the optical order parameter were taken at a reduced temperature T_{red} of 0.965 to have comparable results, the definition of T_{red} is shown in Equation (7). T_x is the actual temperature in the cell, T_{NI} is the temperature of the clearing point, all values taken in Kelvin.

$$T_{\text{red}} = T_x/T_{NI} \tag{7}$$

The estimation of the clearing points were done using a polarizing microscope (Leitz Orthoplan Pol) provided with a Mettler Hotstation FP-52 and a S-VHS video recording equipment (Sony/Panasonic). The phase transition temperatures could be determined with an accuracy of ±0.1 K. **1**, **3**, and **4** show less solubility in CB5, only **2** allows for higher concentrations close to 2.5 weight/%. Because of the large absorption coefficients the higher concentrations were not investigated in their orientational behavior.

In the present work a Configuration Interaction (CI) method in combination with a semiempirical model Hamiltonian based on the Intermediate Neglect of Differential Overlap approximation (INDO) with a 15 × 15 matrix was used to evaluate the electronic spectra[18] and the molecular size. The molecular extensions were calculated from the known values of bond lengths, angles, dihedral angles and van der Waals radii.[19-20]. The long axis was defined as the straight line between the atoms with the largest distance including the van der Waals radii.

RESULTS AND DISCUSSION

Influence of Dye Concentration on the Clearing Point

As a result of the different dye's structure anisotropy the nematic phase is either stabilized or destabilized. But independent of the individual tendency of each solute a small biphasic range less than 0.1 K at the temperature of the nematic-isotropic transition was observed using polarizing microscopy. Table II shows the clearing temperatures of all investigated guest-host systems. The effect of the solute on the transition temperature can be better demonstrated using the change of T_{NI} with the amount of the mole fraction x_i (Figure 2). The influence of the dye and its amount is more complex than expected. **1**, **2**, and **4** lower the value of the clearing point. In the case of **2** larger dye amounts up to a mole fraction of 6.1×10^{-3} (i.e., 1.0 weight%) lead to a decrease of 1.4 K. The same tendentious behavior shows **4** with a lowering of 0.6 K for a mole fraction of 5.0×10^{-3} (i.e., 1.0 weight%). Rather interesting is the result for **3**. With increasing dye concentration a smooth increase of the clearing point around 0.2 K for a mole fraction of 4.0×10^{-3} (i.e., 0.5 weight%) was observed. This solute influence on the value of the nematic-isotropic phase transition temperature was observed before[2,4,5] also and can be explained probably by the increase of released orientational energy of a pair of particles which exceeds the increase of the deviation from cylindrical symmetry[7] or with a low biaxiality parameter under consideration of the mentioned restrictions. Another possible explanation for the different solute influence might be the different ability of the dye molecules to destroy the CB5-dimers.

TABLE II

Clearing points of all investigated guest-host mixtures and biaxiality parameter λ of the pure compounds

Compound	conc. [weight%]	mole fraction	T_{NI} [°C]	λ
CB5	100	1.0	35.3	0.01
1	0.1	7.6 * 10^{-4}	35.3	0.07
	0.5	3.8 • 10^{-3}	35.1	
2	0.1	6.1 • 10^{-4}	35.0	0.34
	0.5	3.1 * 10^{-3}	34.6	
	1.0	6.1 • 10^{-3}	33.9	
3	0.1	8.0 * 10^{-4}	35.4	0.13
	0.5	4.0 • 10^{-3}	35.5	
4	0.1	4.9 * 10^{-4}	35.1	0.21
	0.5	2.4 • 10^{-3}	34.8	
	1.0	5.0 * 10^{-3}	34.7	

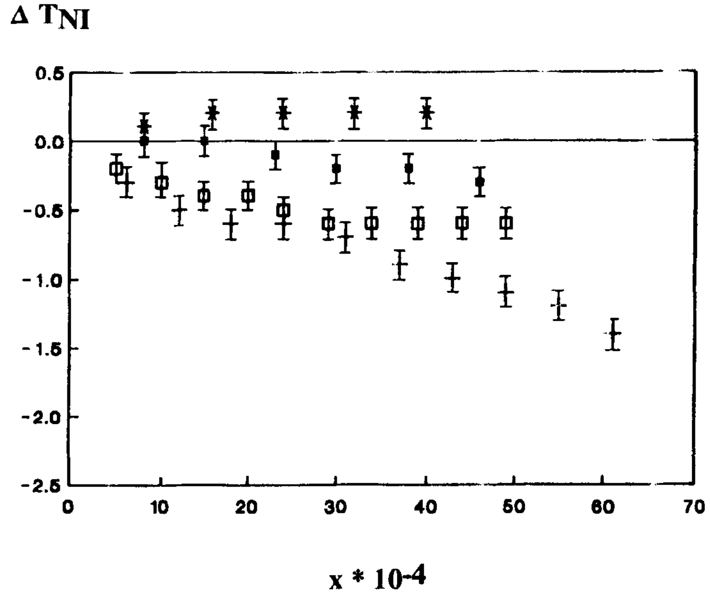


FIGURE 2 Deviation of the mixtures clearing point with the dye's mole fraction *x*, (dots: **1**, crosses: **2**, stars: **3**, rectangles: **4**).

Table II shows the calculated biaxiality parameter λ for all investigated molecules using the approach according to Jede *et al.*[15] But as mentioned only the calculation of rigid molecules leads to an accurate value for λ. From an energetic point of view an all-trans-conformation of an aliphatic chain is the most stable one because of the hindered rotation around the carbon-carbon bond. In the examined temperature range molecular statistics allow for a large number of different gauche conformations. Therefore reasonable values of λ are difficult to obtain because of the flexibility of the aliphatic chains. In our case **1**, **2**, and **4** contain one respectively two hexyl groups and therefore the estimated biaxility parameter should be interpreted very carefully, only the value for **3** is more accurate because of the small methyl groups at the extended aromatic system. The obtained values are always higher than for pure CB5 (0.01) and vary from 0.07 for **1** up to 0.34 for **2**. Except for the value **1** the molecules with extended aliphatic chains show larger values than the more rigid dye **3** (0.13).

Optical Order Parameter S_{op}

The optical order parameter S_{op} of the dyes **1**, **2**, **3**, and **4** were determined as a function of their concentrations in the nematic host CB5 using dichroism measurements of the most intensive absorption band in the visible region. In agreement with earlier investigations[2,4,5,21] on guest-host systems a strong dye concentration dependence of the optical order parameter is observed (Table III). The order parameter S_{ZZ} of pure CB5 is between 0.58 and 0.67,[2,17,22] depending on the experimental method used. The addition of small amounts (e.g., up to a mole fraction of 7.6×10^{-3} for **1**) of **1**, **2**, and **4** leads to a small decrease of the measured

TABLE III

Optical order parameter of all investigated guest-host mixtures

	Sop			
Conc. [weight%]	**1**	**2**	**3**	**4**
0.1	0.65	0.57	0.66	0.64
0.3	0.57	0.53	0.69	0.59
0.5	0.54	0.50	0.68	0.57
0.7	-	0.45	-	-

order parameter. The opposite behavior was observed for the dye **3**, i.e., a small increase of the estimated value for S_{op} appears. The latter result is in agreement with earlier investigations where for similar molecules with short aliphatic chains an increase in S_{op} was observed also.[2] We suppose that in all guest-host systems containing a dye with a larger value of λ (under assumption of a rigid molecular skeleton) a consideration of a pronounced contribution of D to the measured value of S_{op} according to Equation (3) is realistic. As mentioned before the values of the biaxiality parameter are rather sensitive to molecules with flexible aliphatic chains. Therefore a correlation of our measured optical order parameter with λ should be done very carefully. A more qualitative description considers the predominant effect of extended and, more important, flexible aliphatic moieties which destabilize the nematic orientation and the phase range.[23] Short aliphatic groups at the same aromatic core stabilize the nematic phase range, e.g., a similar molecule to **2** with methyl groups instead hexyl units increases the clearing point and show a large value around 0.60 for S_{op} at a reduced temperature of 0.967.[2] Therefore in **3** the rigid aromatic frame predominates the small methyl groups and a pronounced cylindrical shape is given. This leads to an increase in the nematic-isotropic phase transition temperature like an added nematogene[24] and to a large value for S_{op}. All measured values of S_{op} for the mixtures with low dye concentrations are in the same region like the pure host. Even larger guest concentrations up to 0.5 weight% do not cause dramatically changes in the S_{op}. From theory in very diluted systems the order parameter should be independent from the concentration under the assumption that cylindrical symmetry for both components is given.[25] Only in the case of **3** this assumption is fulfilled. The values for S_{op} are rather constant and differ only in the range of the experimental error. In the case of the other dyes the ratio of the long molecular axis relative to the two short axes is smaller and the resulting cylinder more distorted and compressed. This might cause the observed small dependency of S_{op} with the dye's concentration and the different rank of S_{op} (**3** $\approx$ **1** $\approx$ **4** $>$ **2**), respectively, the slope dT_{NI}/dx (**3** $>$ **1** $>$ **4** $\approx$ **2**).

The results concerning the gross order of the different guest-host systems measured via UV/Vis dichroism agree with the conclusions made from the change of the clearing point. Unfortunately D couldn't be estimated with the given experimental setup and therefore we were restricted to the visible spectral region with only one observable absorption band. It is planned to choose a commercial CCH mixture (Licristal ZLI 1695, Merck) which is transparent in the UV-region and allows for the estimation of the dichroism of additional bands.

TABLE IV

Comparison of the main absorption wavelength of all investigated dyes either experimentally obtained or calculated using a SCF-CI approach

	Absorption wavelength [nm]	
Compound	exp.	calc.
1	390	414
2	455	431
3	455	440
4	486	470

Besides the experimentally obtained data calculated values for the absorption maxima are presented here and show a resonable agreement with the spectroscopic ones. Table IV shows experimentally obtained (in CB5) and calculated main absorption wavelength of the investigated dyes. The calculated value for HHNS were taken from literature[26] and shows the lowest value (390 nm) for the absorption maxima in comparison to the other dye molecules because of the ether group instead of a amino function. Double substitution of the amino nitrogen with aliphatic chains leads to a red-shift (**2** and **3**: 455 nm). **4** possesses a larger conjugated π-systems which results in a stronger shift to higher wavelengths (486 nm). The used model calculates the polarization of the related absorptions to be parallel to the principal molecular axis. The knowledge about the band polarization is essential for further investigations on the estimation of D via UV/Vis dichroism.

Acknowledgments

T. Hanemann thanks the Technische Hochschule Darmstadt for a Ph.D. fellowship and the Deutsche Forschungsgemeinschaft (DFG) for financial support. We are grateful to E. Merck Company, Darmstadt, for providing us with CB5 and the dyes **2**–**4**.

References

1. H. W. Schmidt, *Angew. Chem. Adv. Mater.*, **101**, 964 (1989).
2. D. Bauman, *Mol. Cryst. Liq. Cryst.*, **159**, 197 (1988).
3. W. Haase and H. Wedel, *Mol. Cryst. Liq. Cryst.*, **38**, 61 (1977).
4. P. Diot, J. K. Foitzik and W. Haase, *Revue Phys. Appl.*, **20**, 121 (1985).
5. W. Haase, O. Trinquet, U. Quotschalla and J. K. Foitzik, *Mol. Cryst. Liq. Cryst.*, **148**, 15 (1987).
6. J. B. Stamatoff, A. Buckley, G. Calundann, E. W. Choe, R. DeMartino, G. Khanarian, T. Leslie, G. Nelson, D. Stuetz, C. C. Teng and H. N. Yoon, *Molecular and Polymeric Optoelectronic Materials: Fundamentals and Applications*, G. Khanarian, Ed., *Proc. SPIE*, **682**, 85 (1987).
7. G. R. Luckhurst, C. Zannoni, P. L. Nordio and U. Segre, *Mol. Phys.*, **30**, 1345 (1975).
8. A. Strauss and H.-G. Kuball, *Poster Presentation ASI Meeting "New Development in Polarized Optical Spectroscopy on Ordered Systems"*, Rimini, Italy 1987.
9. H.-G. Kuball, R. Memmer, A. Strauss, M. Junge, G. Scherowsky and A. Schönhofer, *Liq. Cryst.*, **5**, 1405 (1989).
10. H.-G. Kuball, M. Junge, B. Schultheis and A. Schönhofer, *Ber. Bunsenges. Phys. Chem.*, **95**, 1219 (1991).
11. M. G. Clark and F. C. Saunders, *Mol. Cryst. Liq. Cryst. (Lett.)*, **82**, 267 (1982).

12. J. W. Emsley, R. Hashim, G. R. Luckhurst and G. N. Shilstone, *Liq. Cryst.*, **1**(5), 437 (1986).
13. W. S. Park and T. Uchida, *Liq. Cryst.*, **5**, 1405 (1989).
14. R. Hashim, C. R. Luckhurst, and S. Romano, *Molec. Phys.*, **56**, 1217 (1985).
15. F. Jede, A. W. Stratmann and B. Schrader, *Mol. Cryst. Liq. Cryst.*, **140**, 297 (1986).
16. L. M. Blinov, V. A. Kizel, V. G. Rumyantsev and V. V. Titov, *J. Physique Colloq. Suppl. C1*, **36**, 6 (1975).
17. S. Sen, P. Brahma, S. K. Roy, D. K. Mukherjee and S. B. Roy, *Mol. Cryst. Liq. Cryst.*, **100**, 327 (1983).
18. M. C. Böhm and R. Gleiter, *Theoret. Chim. Acta (Berl.)*, **59**, 127 (1981).
19. L. Pauling, *The Nature of the Chemical Bond*, (Cornell University Press, Ithaca, New York, 1960).
20. L. E. Sutton and D. G. Jenkin, *Tables of Interatomic Distances and Configuration in Molecules and Ions*, (Special Publication No. 11, The Chemical Society, London, 1958).
21. U. Quotschalla, T. Hanemann, M. C. Böhm and W. Haase, *Mol. Cryst. Liq. Cryst.*, **207**, 103 (1991).
22. S. T. Wu, *Applied Optics*, **26**, 3434 (1987).
23. P. L. K. Hung and A. Bloom, *Mol. Cryst. Liq. Cryst.*, **59**, 1 (1980).
24. R. Hashim, G. R. Luckhurst and S. Romano, *Liq. Cryst.*, **1**, 133 (1986).
25. R. L. Humphries, P. G. James and G. R. Luckhurst, *Symp. Faraday Soc.*, **5**, 107 (1971).
26. T. Hanemann, M. C. Böhm, W. Haase and S. T. Wu, *Liq. Cryst.*, **11**, 917 (1992).