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

Unusual Orientational Behavior of Anthraquinone Dyes in Nematic Cyanophenylcyclohexane Derivatives

S. Imazeki [a], A. Mukoh [a], N. Tanaka [b] & M. Kinoshita [c]

[a] Hitachi Research Laboratory, Hitachi Ltd., 4026 Kuji-cho, Hitachi, Ibaraki, 319-12, Japan

[b] Advanced Research Laboratory, Hitachi, Ltd., Hatoyama, Saitama, 350-03, Japan

[c] Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo, 106, Japan

Version of record first published: 24 Sep 2006.

To cite this article: S. Imazeki , A. Mukoh , N. Tanaka & M. Kinoshita (1993): Unusual Orientational Behavior of Anthraquinone Dyes in Nematic Cyanophenylcyclohexane Derivatives, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 225:1, 197-210

To link to this article: http://dx.doi.org/10.1080/10587259308036229

Mol. Cryst. Liq. Cryst., 1993, Vol. 225, pp. 197–210
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Unusual Orientational Behavior of Anthraquinone Dyes in Nematic Cyanophenylcyclohexane Derivatives

SHUJI IMAZEKI and AKIO MUKOH

Hitachi Research Laboratory, Hitachi Ltd., 4026 Kuji-cho, Hitachi, Ibaraki 319-12, Japan

and

NAOKI TANAKA

Advanced Research Laboratory, Hitachi, Ltd., Hatoyama, Saitama 350-03, Japan

and

MINORU KINOSHITA

Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

(Received March 26, 1992; in final form June 1, 1992)

The optical order parameters of a number of anthraquinone and azo dyes are determined in three nematic liquid crystalline hosts. The results are discussed in terms of the effects of the hosts on the dye order parameters. It is found that the anthraquinone dyes show significantly higher order parameters in the host composed of cyanophenylcyclohexane derivatives. This enhancement of the orientational ordering is tentatively interpreted as being due to the supplement of the orientational cohesive forces with the charge-transfer interaction between the dyes and the host.

I. INTRODUCTION

The orientational ordering of a dye molecule in a nematic liquid crystalline host has been the subject of many studies. Considerable effort has been devoted to the systematic study of closely related dyes in order to establish empirical relationships between the order parameter and the dye structure.[1–29] However, little information is available in the literature regarding the host dependence of the order parameters.[30–33] Therefore it seems highly desirable to investigate the orientational behavior of dye molecules in various hosts. It may be expected to obtain valuable insights into the guest-host interactions by examining the host dependence of the order parameters.

In previous papers[34–38] of this series, we have reported the optical order parameters for a large variety of dyes. In the present work, we have examined the order parameters for a number of anthraquinone and azo dyes in three nematic liquid crystalline hosts in order to gain a clear understanding of the influence of the hosts on the orientational behavior of the dyes. An attempt is made to correlate the order parameter of the dye molecules with their shape anisotropy. Further, based on the obtained results, the possibility of the charge-transfer interaction between the dyes and the hosts will be discussed.

II. EXPERIMENTAL

The anthraquinone and azo dyes used in this study are listed in Table I. Dyes a–e and g–i were courteously supplied by Mitsubishi Chemical Industries Ltd. Dyes j and k were obtained from BDH Chemicals Ltd., and dyes l–s from Nippon Kankoh Shikiso Kenkyusho Co. Ltd. These dyes were used without further purification. Dye f was synthesized according to the procedure described by Yasui *et al.*[29]. Three different nematic liquid crystals were employed as hosts in this study. These hosts were selected to provide variations in molecular structure, dielectric anisotropy and polarity. Their molecular structures and compositions are given in Table II, together with their relevant physical properties. Host A is a mixture of cyanophenylcyclohexane derivatives and has a positive dielectric anisotropy. Host B is a mixture of phenylcyclohexylcarboxylate derivatives. Host C is a mixture of alkoxyphenylcyclohexane derivatives. Both Hosts B and C have a negative dielectric anisotropy. Hosts A and C were purchased from E. Merck. Host B was supplied by Dainippon Ink Co., Ltd.

The cells used in the experiment consisted of two glass plates, with an inner area of 4 × 4 cm, each having a transparent electrode layer of indium oxide. The oxide layers were coated with a polymer layer followed by rubbing to attain homogeneous alignment of the guest-host composition. Depending on the solubility of the dye, the cell gaps were varied between about 10 and 100 μm. The optical order parameter S of the dyes dissolved in the nematic liquid crystals was determined using plane-polarized light by the following equation[1,4]:

$$S = \frac{A_{/\!/} - A_{\perp}}{2A_{\perp} + A_{/\!/}} \tag{1}$$

where $A_{\parallel}$ is the absorbance of the dye at its maximum absorption wavelength (λ_{max}) when the polarization is parallel to the alignment direction and $A_{\perp}$ is the absorbance at λ_{max} when the polarization is perpendicular to the alignment direction. The baseline was determined using cells containing only the nematic host liquid crystal. The dye concentrations were typically 0.3–1% by weight. Optical absorption spectra were measured at 22°C using a Hitachi 340 spectrophotometer.

It must be emphasized here that the optical order parameter S as determined from dichroic spectra using Equation (1) is the order parameter of the optical transition moment of a dye molecule. When the direction of the transition moment

TABLE I

Molecular structure and length-to-width ratio of guest dyes

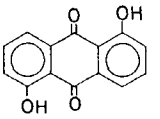
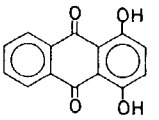
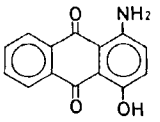
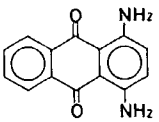
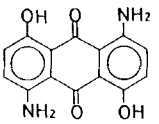
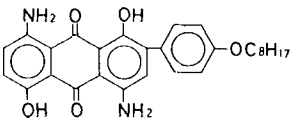
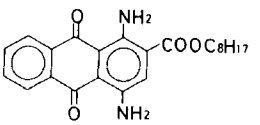
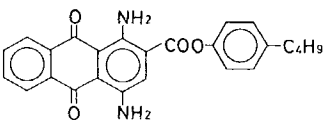
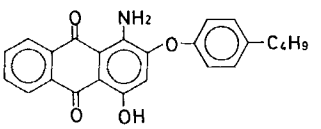
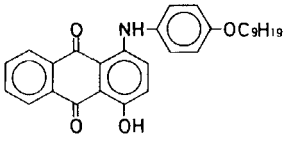
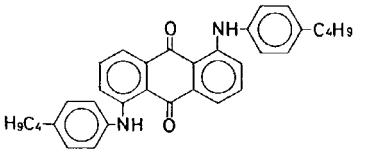
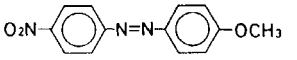
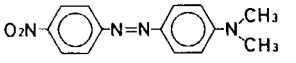
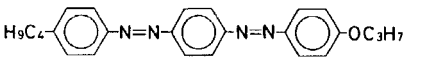
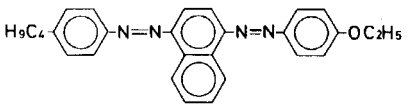
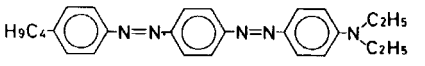
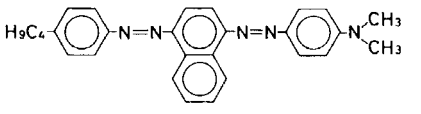
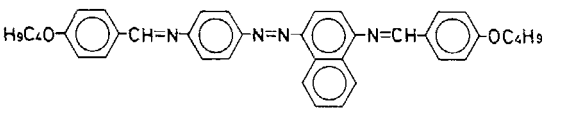
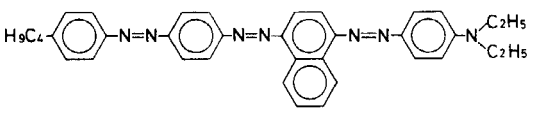
Code	Structure	L/D *
a.		1.35
b.		1.33
c.		1.35
d.		1.33
e.		1.33
f.		1.52
g.		1.70
h.		2.01
i.		1.99

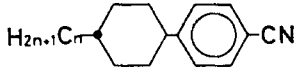
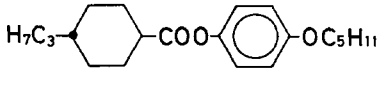
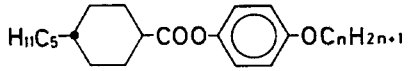
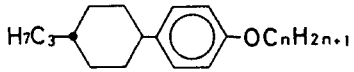
TABLE I (*continued*)

Code	Structure	L/D *
j.		1.69
k.		2.38
l.		2.25
m.		2.41
n.		3.11
o.		2.33
p.		3.28
q.		2.45
r.		2.98
s.		3.15

* length-to-width ratio of the rigid portion of the dyes

TABLE II

Chemical compositions and physical properties of nematic liquid crystalline hosts

Designation	major components	T_{NI}/°C [a]	$\varepsilon_{//}$ [b]	$\varepsilon_{\perp}$ [b]	$n_{//}$ [c]	$n_{\perp}$ [c]
A.	 (n=3, 5, 7)	70	14.8	4.7	1.6353	1.4928
B.	  (n=2, 5)	68	3.76	4.58	1.5900	1.4866
C.	 (n=2, 4, 5)	59	2.77	3.36	1.585	1.485

a) clearing point; b) dielectric constant; c) refractive index

deviates from that of the long axis of the dye molecule, the relation between the optical order parameter S and the order parameter S_0 of the long axis is expressed as[31,39–41]

$$S = \frac{A_{/\!/} - A_{\perp}}{2A_{\perp} + A_{/\!/}} = \frac{1}{2}(3\cos^2\alpha - 1)\cdot S_0 \tag{2}$$

where α denotes the angle between the direction of the transition moment and the long axis. Accordingly, when the direction of the transition moment is not parallel to the long axis, the optical order parameter S is necessarily less than the order parameter S_0 of the long axis. If one wants to determine S_0, α has to be known. However, α is difficult to accurately estimate. Therefore, in the present work, it has been assumed that α equals zero. This assumption seems to be valid in most of the dyes listed in Table I. However, it is quite likely that dyes j and k have α substantially different from zero. Hence, it seems natural to consider that the 'apparent' order parameter S of these anthraquinone dyes is lower than the 'real' order parameter S_0.

III. ESTIMATION OF SHAPE ANISOTROPY OF DYE MOLECULES

In the present work, the length-to-width ratio (L/D) is used as a measure of the shape anisotropy of dye molecules. The length (L) and width (D) of the dye molecule in its fully extended conformation have been calculated assuming standard bond lengths, angles and van der Waals radii. A planar geometry has been exclusively assumed in all cases. Some examples of the van der Waals' repulsion envelopes used in the evaluation of the L/D ratio are shown in Figure 1. On evaluating the L/D ratio, terminal flexible chains such as alkyl and alkoxy groups have been precluded except for the first atom in the chain. This treatment may be rationalized by our earlier reported findings[37,38] which suggest that the terminal flexible chain can be, to a first approximation, ignored compared with the rigid core in influencing the orientational order of the dye molecule. The L/D ratio of each dye is given in Table I.

IV. RESULTS

The optical order parameters for the dyes in the three different hosts are summarized in Table III. The results demonstrate clearly that there is a marked difference in sensitivity of S to hosts between the anthraquinone dyes (a ~ k) and the azo dyes (l ~ s). The anthraquinone dyes have significantly larger order parameters in Host A than in Hosts B and C. This tendency is particularly pronounced in dyes a ~ f, which have a relatively low L/D ratio. However, the S values for the azo dyes appear to be rather insensitive to the nematic host. No simple relation exists between the physical properties of the hosts listed in Table II and the S values of the azo dyes.

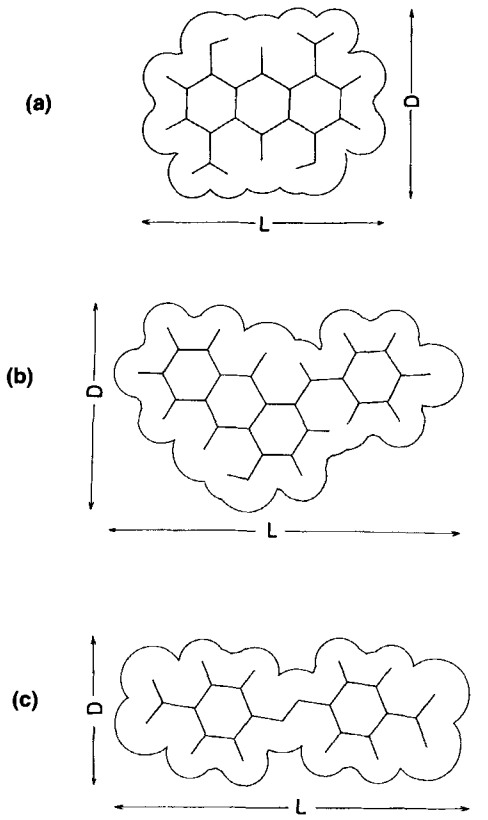


FIGURE 1 Examples of van der Waals' repulsion envelopes used for evaluation of shape anisotropy: (a) dye e; (b) dye j; (c) dye m.

The maximum absorption wavelengths (λ_{max}) of the dyes in the nematic hosts are given in Table III. Among the dyes in Table III, dyes m, p, q and s, which involve a dialkylamino group, exhibit noticeable solvent-shift effects; these azo dyes show significantly bathochromic shifts with increasing polarity of the hosts. On the contrary, in the remaining azo dyes and the anthraquinone dyes, the magnitude of wavelength displacement is relatively small and the correlation between the λ_{max} and the host polarity is somewhat irregular.

V. DISCUSSION

The order parameter of a guest molecule in a nematic liquid crystalline host is commonly thought to be closely related to the shape anisotropy of the guest molecule. However, only a few publications[2,24,42,43] relate to the quantitative study of this relation. Therefore, it is of interest to see whether or not there is a regular relation between the order parameter of the dyes investigated in this study and their L/D ratio, which is used as a measure of the shape anisotropy. Figures 2–4

TABLE III

Order parameters and absorption wavelengths of dyes in different nematic hosts

Host / Dye	Host A		Host B		Host C	
	S	λ_{max}/nm	S	λ_{max}/nm	S	λ_{max}/nm
a.	0.50	436	0.35	436	0.32	440
b.	0.52	486	0.33	486	—	—
c.	0.64	531	0.37	533	0.33	534
d.	0.68	554	0.44	554	0.40	553
e.	0.65	632	0.31	628	0.39	628
f.	0.79	639	0.56	640	0.58	637
g.	0.68	638	0.64	638	0.58	636
h.	0.77	643	0.68	643	0.64	641
i.	0.68	520	0.55	518	0.53	516
j.	0.66	590	0.52	590	0.51	588
k.	0.66	548	0.60	543	0.60	542
l.	0.59	380	0.63	379	0.62	375
m.	0.63	494	0.70	484	0.66	478
n.	0.72	392	0.72	392	—	—
o.	0.72	436	0.74	438	0.72	438
p.	0.73	498	0.72	486	0.74	482
q.	0.75	525	0.75	520	0.74	514
r.	0.78	446	0.77	443	0.79	445
s.	0.76	567	0.77	557	0.77	555

show the plots of the order parameter S of each dye in the three different hosts against L/D of the dye. A clear correlation is found for the dyes dissolved in Hosts B and C: the order parameter of the dyes increases with increasing the L/D ratio. It appears that the quality of the correlation in Host C is somewhat better than that in Host B. Considering uncertainty involved in the evaluation of the L/D ratio as well as the approximation made in the determination of the S values, it may be said that the regularity in Figures 3 and 4 is rather unexpectedly definite. These figures suggest that the shape anisotropy is a predominant factor in determining

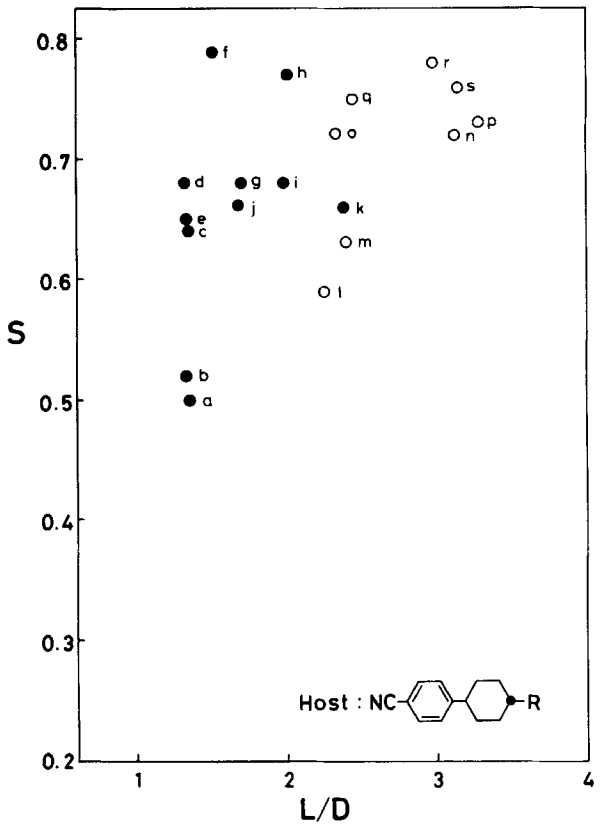


FIGURE 2 Relationship between order parameter S measured in Host A and length-to-width ratio L/D: • anthraquinone dyes; ○ azo dyes.

the order parameter of dyes. This finding is in accord with the widely accepted view.[2,16,24,31,43]

In contrast, the S values measured in Host A show no overall rise with increasing the L/D ratio. Comparing Figure 2 with Figures 3 and 4, it is apparent that the irregularity observed in Figure 2 is due to an unusual orientational behavior of the anthraquinone dyes. Most of the anthraquinone dyes exhibit a strikingly high S value in Host A compared with those in Hosts B and C. Further, the S values of the anthraquinone dyes in Host A show no simple correlation with the L/D ratios. These anomalies cannot be accounted for by only the shape anisotropy. It would be reasonable to consider that in the guest-host systems consisting of the anthraquinone dyes and Host A the orientational cohesive forces are supplemented by some specific interaction between the dye molecules and the cyanophenylcyclohexane molecules constituting Host A. The origin of this specific interaction has to be sought other than the shape anisotropy.

One possibility is that of a charge-transfer (CT) interaction[44–47] between the anthraquinone dyes acting as electron donors and the cyanophenylcyclohexane derivatives acting as electron acceptors. In order to explore this possibility, we

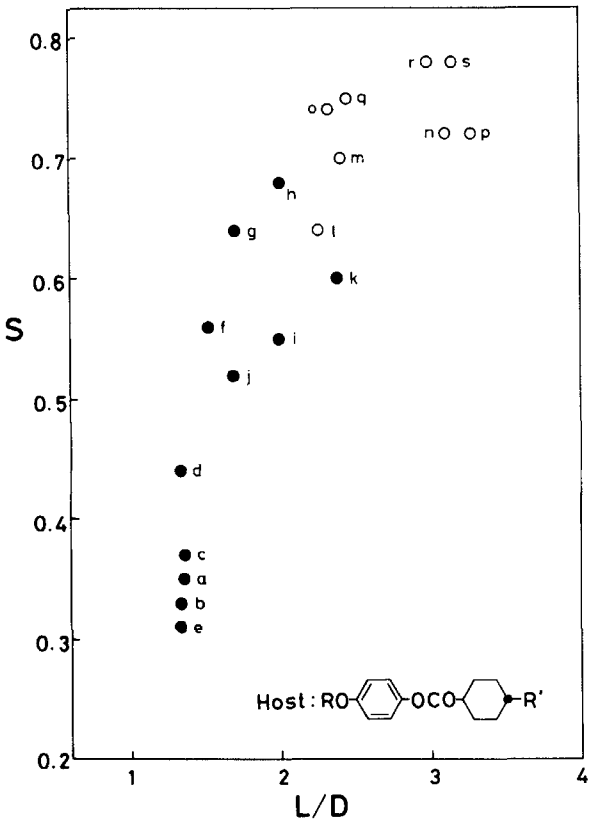


FIGURE 3 Relationship between order parameter S measured in Host B and length-to-width ratio L/D: ● anthraquinone dyes; ○ azo dyes.

compare the energy levels of the frontier π-orbitals[48,49] for the simple anthraquinone dyes a ~ e with those for Hosts A ~ C. For dyes a ~ e, the energy values of the frontier orbitals calculated with the Pariser-Parr-Pople (PPP) method are found in the literature.[50] The energy levels of the frontier π-orbitals for Hosts A ~ C have been calculated using the program for the PPP MO calculation disclosed in Reference 50. For computational simplicity, the fragments illustrated in Figure 5 have been used for each host. All the molecules have been assumed to be planar, with a bond angle of 120°. Ionization potentials, one-centre repulsion and core-resonance integrals are those described in Reference 50. Figure 6 shows the relative energy levels of dyes a ~ e and Hosts A ~ C. It is noteworthy that the energy level of the lowest unoccupied molecular orbital (LUMO) for Host A is considerably lower than those for Hosts B and C, thus leading to enhanced CT interaction between the dyes and Host A. This finding seems to support our interpretation that the unusual orientational behavior of the anthraquinone dyes dissolved in Host A results from the supplement of the orientational cohesive forces with the CT interaction between the dyes and Host A.

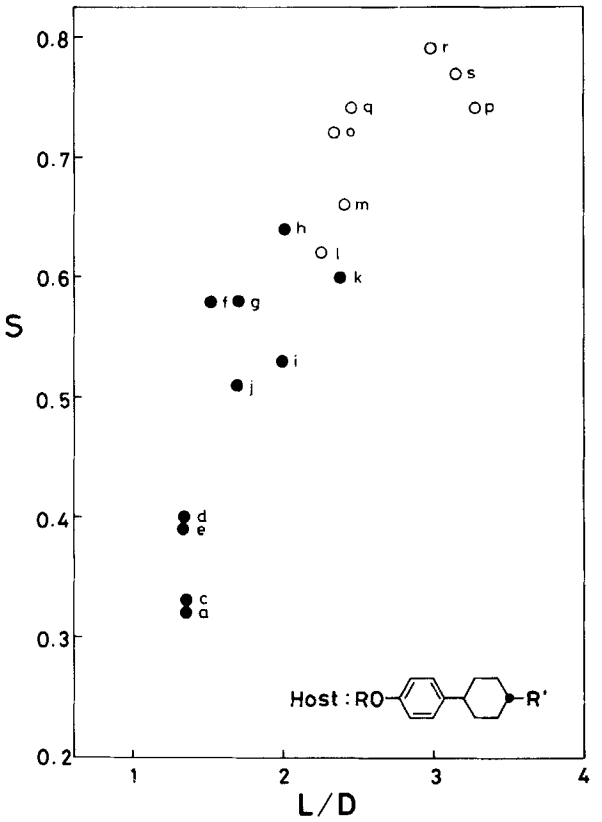


FIGURE 4 Relationship between order parameter S measured in Host C and length-to-width ratio L/D: ● anthraquinone dyes; ○ azo dyes.

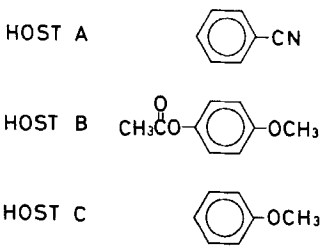


FIGURE 5 Fragments used in molecular orbital calculations.

Further, the energy level diagram depicted in Figure 6 gives a clue for understanding the orientational behavior of dyes a ~ e in Host A. Although these dyes have almost the same L/D ratio and the sections of their van der Waals' repulsion envelopes are essentially similar, they show a wide variation of the order parameters in Host A, depending on the number, positions and electron-donating power of the substituents. For example, dye d exhibits an order parameter of 0.68 in Host A, whereas dye a gives a value of 0.50 in the same host. Such widely differing

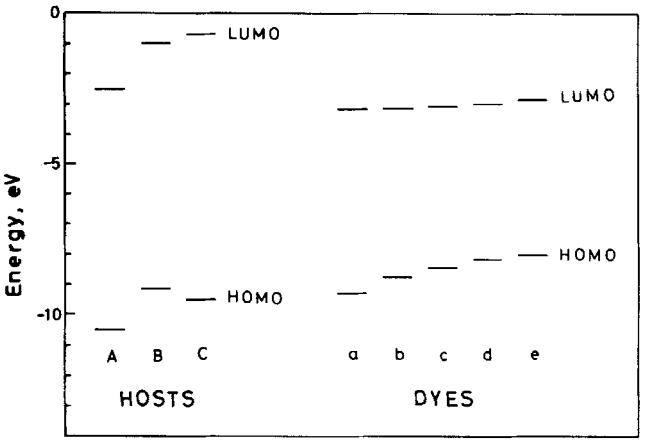


FIGURE 6 Relative energy levels of frontier orbitals of dyes and hosts.

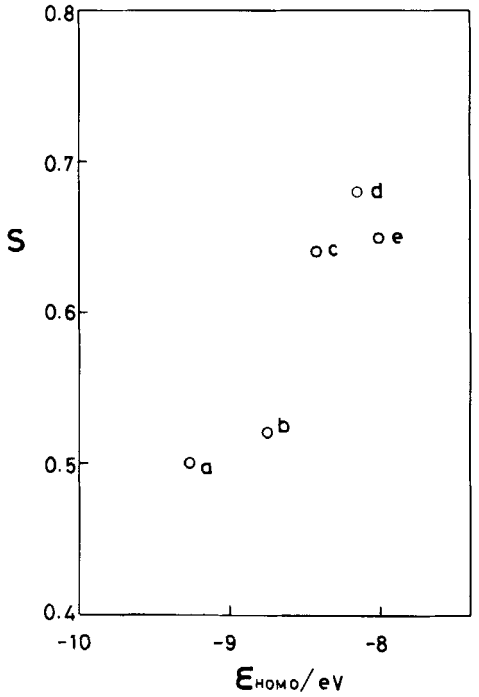


FIGURE 7 A plot of S values measured in Host A against HOMO levels of dyes a ~ e.

order parameters for dyes a ~ e may be accounted for by using the energy diagram shown in Figure 6. That is, it is seen from this diagram that the energy of the highest occupied molecular orbitals (HOMO) for these dyes changes appreciably with the electron-donating power of the substituents, whereas the energy of the LUMO remains virtually unchanged. Figure 7 shows a plot of the S values measured in Host A vs. the HOMO levels for dyes a ~ e. As can be seen from this figure,

dyes a ~ e show the trend of increasing S as the dye HOMO level rises, i.e., moves closer to the LUMO level of Host A. This finding suggests that in the systems consisting of these dyes and Host A the CT interaction can contribute to the enhancement of the orientational order of the dyes but to different extents, depending on the difference between the dye HOMO level and the host LUMO level.

Preliminary MO calculations reveal that the HOMO levels of the remaining anthraquinone dyes lie close to those of dyes a ~ e. Accordingly, it seems plausible to consider that the above-mentioned mechanism may also operate in the cases of dyes f ~ k. However, in this series of dyes, the variety and complexity of the molecular structure does not permit a simple treatment directly relating the S values to the HOMO levels.

Unfortunately, CT absorption bands have not been ascertained yet in the guest-host systems examined in this study. Further experiments are under way to confirm the CT bands. Therefore, at the present stage, the above interpretation is still tentative. Nevertheless, we believe that the present discussion does much to clarify a difficulty which has been felt by researchers for a long time.

An interesting alternative interpretation of the orientational behavior of simple anthraquinone dyes such as dyes a ~ e has been proposed by Myrvold *et al.*[22]

VI. CONCLUSION

In order to gain a clear understanding of the influence of the hosts on the orientational behavior of the dyes, the order parameters of a number of anthraquinone and azo dyes have been examined in three different nematic liquid crystals; namely, cyanophenylcyclohexane, phenylcyclohexylcarboxylate and alkoxyphenylcyclohexane liquid crystals. The main conclusions are as follows:

1. The anthraquinone dyes have high sensitivity of the order parameter to the hosts, whereas the azo dyes are rather insensitive.
2. The anthraquinone dyes show significantly larger order parameters in the cyanophenylcyclohexane host.
3. In the liquid crystals other than the cyanophenylcyclohexane, a distinct correlation is found between the order parameter and the shape anisotropy of the dye molecules.
4. However, in the systems consisting of the anthraquinone dyes and the cyanophenylcyclohexane host, the dye order parameter shows no simple correlation with the shape anisotropy.
5. This unusual orientational behavior of the anthraquinone dyes dissolved in the cyanophenylcyclohexane host is tentatively interpreted as being due to the supplement of the orientational cohesive forces with the charge-transfer interaction between the dyes and the host.

Acknowledgment

The authors are indebted to Mitsubishi Chemical Industries for supplying them the dyes. The authors are sincerely grateful to Mr. T. Nakada and Mrs. M. T. Inanobe for their assistance during the various phases of this work.

References

1. D. L. White and G. N. Taylor, *J. Appl. Phys.*, **45**, 4718 (1974).
2. G. Meier, E. Sackmann and J. G. Grabmaier, "*Applications of Liquid Crystals*," Springer Verlag, Berlin, 1975.
3. T. Uchida, C. Shishido, H. Seki and M. Wada, *Mol. Cryst. Liq. Cryst.*, **34**, 153 (1977).
4. A. Bloom and P. L. K. Hung, *Mol. Cryst. Liq. Cryst.*, **40**, 213 (1977).
5. A. Bloom and P. L. K. Hung, *Mol. Cryst. Liq. Cryst.*, **44**, 323 (1978).
6. R. J. Cox, *Mol. Cryst. Liq. Cryst.*, **55**, 1 (1979).
7. P. L. K. Hung and A. Bloom, *Mol. Cryst. Liq. Cryst.*, **59**, 1 (1980).
8. J. Costant, E. P. Raynes, I. A. Shanks, D. Coates, G. W. Gray and D. G. McDonnell, *J. Phys.*, **D11**, 479 (1978).
9. M. G. Pellatt, I. H. C. Roe and J. Constant, *Mol. Cryst. Liq. Cryst.*, **59**, 299 (1980).
10. F. Jones and T. J. Reeve, *Mol. Cryst. Liq. Cryst.*, **60**, 99 (1980).
11. G. W. Gray, *Chimia*, **34**, 47 (1980).
12. J. Cognard, T. H. Phan and N. Basturk, *Mol. Cryst. Liq. Cryst.*, **68**, 207 (1981).
13. S. Aftergut and H. S. Cole, Jr., *Mol. Cryst. Liq. Cryst.*, **78**, 271 (1981).
14. J. Cognard and T. H. Phan, *Mol. Cryst. Liq. Cryst.*, **70**, 1 (1981).
15. H. Seki, C. Shishido, S. Yasui and T. Uchida, *Jpn. J. Appl. Phys.*, **21**, 191 (1982).
16. G. W. Gray, *Dyes and Pigments*, **3**, 203 (1982).
17. C. Blackburn and J. Griffiths, *Mol. Cryst. Liq. Cryst.*, **101**, 341 (1983).
18. G. Heppke, B. Knippenberg, A. Moeler and G. Scherowsky, *Mol. Cryst. Liq. Cryst.*, **94**, 191 (1983).
19. F. C. Saunders, K. J. Harrison, E. P. Raynes and D. J. Thompson, *IEEE Trans.*, **ED30**, 499 (1983).
20. F. Jones and F. A. Kirby, *Mol. Cryst. Liq. Cryst.*, **108**, 165 (1984).
21. U. Clausen, A. Brockes, E. F. Kops, F. W. Kroeck and R. Neeff, *Proc. SID*, **26**, 17 (1985).
22. B. O. Myrvold and P. Klaeboe, *Acta Chem. Scand.*, **A39**, 733 (1985).
23. S. Matsumoto, K. Mizunoya, H. Hatou and H. Tomii, *Mol. Cryst. Liq. Cryst.*, **122**, 285 (1985).
24. H. Seki, T. Uchida and Y. Shibata, *Mol. Cryst. Liq. Cryst.*, **138**, 349 (1986).
25. A. V. Ivashchenko and V. G. Rumyantsev, *Mol. Cryst. Liq. Cryst.*, **150A**, 1 (1987).
26. A. Kumar, J. K. Sutherland and D. J. Thompson, *J. Chem. Soc., Perkin Trans. I.*, 445 (1987).
27. S. Yasui, M. Matsuoka, M. Takao and T. Kitao, *J. Soc. of Dyers and Colourist*, **104**, 284 (1988).
28. S. Yasui, M. Matsuoka and K. Kitao, *Shikizai Kyokai-shi*, **61**, 678 (1989).
29. S. Yasui, M. Matsuoka and T. Kitao, *Dyes and Pigments*, **11**, 81 (1989).
30. A. Bloom, P. L. K. Hung and D. Meyerhofer, *Mol. Cryst. Liq. Cryst.*, **41**, 1 (1977).
31. K. Toriyama, T. Ishibashi, K. Suzuki and M. Satoh, *IEEE Trans.*, **ED30**, 492 (1983).
32. N. Basturk, J. Cognard and T. H. Phan, *Mol. Cryst. Liq. Cryst.*, **95**, 71 (1983).
33. J. Cognard, T. H. Phan and N. Basturk, *Mol. Cryst. Liq. Cryst.*, **91**, 327 (1983).
34. S. Imazeki, *Mol. Cryst. Liq. Cryst.*, **140**, 119 (1986).
35. S. Imazeki, A. Mukoh, T. Yoneyama and M. Kaneko, *Mol. Cryst. Liq. Cryst.*, **145**, 79 (1987).
36. S. Imazeki, M. Kaneko, T. Ozawa and A. Mukoh, *Mol. Cryst. Liq. Cryst.*, **159**, 219 (1988).
37. S. Imazeki, H. Ono, M. Kaneko and A. Mukoh, *Mol. Cryst. Liq. Cryst.*, **162B**, 249 (1988).
38. S. Imazeki, A. Mukoh, T. Ozawa and M. Kaneko, *Mol. Cryst. Liq. Cryst.*, **170**, 107 (1989).
39. A. Saupe and W. Maier, *Z. Naturforsch.*, **16b**, 816 (1961).
40. T. Watanabe, M. Sukigara, K. Honda, K. Toda and S. Nagaura, *Mol. Cryst. Liq. Cryst.*, **31**, 285 (1975).
41. F. C. Saunders, L. Wright and M. G. Clark, in *Liquid Crystals and Ordered Fluids*, Vol. 4, A. C. Griffin and J. F. Johnson (ed.), Plenum Press, 1984.
42. H. G. Kuball, R. Memmber, A. Strauss, M. Junge, G. Scherowsky and A. Schoenhofer, *Liquid Crystals*, **5**, 969 (1989).
43. W. S. Park and T. Uchida, *Liquid Crystals*, **5**, 1405 (1989).
44. K. Araya and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **53**, 3079 (1980).
45. D. Demus, G. Pelzl, N. K. Sharma and W. Weissflog, *Mol. Cryst. Liq. Cryst.*, **76**, 241 (1981).
46. F. Schneider and N. K. Sharma, *Z. Naturforsch.*, **36a**, 1086 (1981).
47. Y. Matsunaga, *Materials Science*, **10**, 380 (1984).
48. R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).
49. M. J. S. Dewar and A. R. Lepley, *J. Amer. Chem. Soc.*, **83**, 4560 (1961).
50. S. Tokita, M. Matsuoka, Y. Kogo and H. Kihara, "*Molecular Design of Functional Dye—PPP Molecular Orbital Method and its Application*," Maruzen Co., Tokyo, 1989.