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Order Parameters for Isomeric Phenyl Substituted Anthraquinone Dyes Dissolved in Nematic Liquid Crystals Mixtures—Influence of the Host

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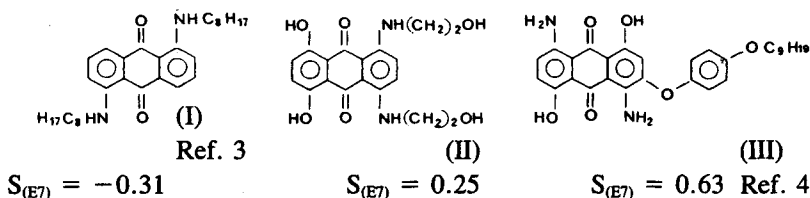
Substitution of the anthraquinone ring system has provided dyes suitable for guest-host applications. In general, one seeks to elongate the anthraquinonic system through a fourth ring. Different molecular structures have been proposed which all have similar ordering in the liquid crystalline host. Surprisingly, the 2-*p*-alkoxyphenyl substituted 1,5-dihydroxy-4,8-diaminoanthraquinones have a higher order parameter in liquid crystalline mixtures of positive dielectric anisotropy made from cyano substituted molecules. They lose this property in a system consisting of molecules without cyano groups at the termini of the molecular axes.

The properties of two isomeric substituted anthraquinone dyes in different hosts are compared in order to illustrate the considerable influence that dye-liquid crystal interactions may have on dye order parameter.

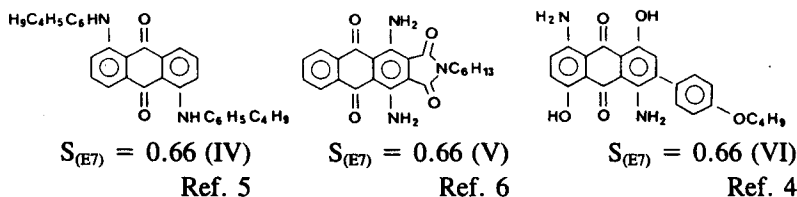
1. INTRODUCTION

Strong efforts have been made in display research to realize a product using dyes dissolved in a nematic liquid crystal host.¹ A major problem has been to find photostable dyes well oriented in the host. Substituted anthraquinones (A. Q.) have provided an acceptable solution for blue dyes. The contrast of a display strongly depends on the dichroic ratio (r) of absorbance of polarized light by the oriented dye (see experimental part). It has become usual to characterize a dye by an order parameter S related to r , and we will conform with this scientific practice. Dye order parameter (O. P.) generally depends on the dye shape as well as on the host transition

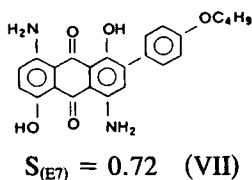
temperature.² In the particular case of anthraquinone dyes, substitution of the core may greatly modify the dye O. P. For instance, 1,5-dihydroxy-4, 8-diaminoanthraquinone (D. D. A.) has an O. P. $S_{(E7)} = 0.55$ in E7 (see experimental part for composition); substitution of the amino group will produce a dye with either a negative (-0.31) (I), or a small (0.25) (II), or a higher (0.65) (III) O. P.



Elongating the molecule notably increases the O.P., although most substituted A. Q. have similar OP values in a given L. C., i.e., 0.6-0.65 in E7. Formulae IV, V, and VI are given as examples.



Surprisingly, the 2-*p*-alkoxyphenyl substituted anthraquinone VII has a much higher (0.72) O. P. in E7 than its 3-substituted isomer VI.



The behavior of the two isomeric dyes in liquid crystalline solution, as well as the influence of the host will be reported.

2. RESULTS AND DISCUSSION

2.1. Influence of the molecular structure of the two isomers

The color of substituted anthraquinone dyes mainly depends on the substitution of the anthraquinone core in the 1-, 4-, 5-, and 8-positions. Derivatives of DDA are blue and the maximum absorption undergoes a blue shift of 20 nm on changing from CHCl_3 to E7; this results in a maximum absorption at $\lambda = 640$ nm using E7. The visible spectrum shows a vibrational structure consisting of two peaks (640; 598) and a shoulder (556 nm).

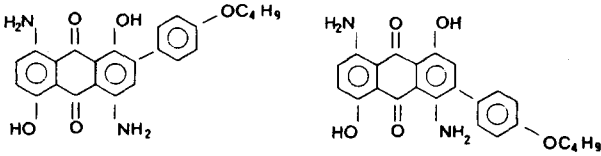
The absorption coefficients are 2.4×10^4 (cm^{-1} , moles $^{-1}$ l.) for both isomers; solubility varies with the host and is between 2–4%. The dissolution of the dye at 1% concentration does not significantly change the liquid crystalline host T_{NI} .

The conductivity of both solutions is higher than that of the host, staying around $\sigma \sim 10^{-10} \Omega^{-1} \text{cm}^{-1}$ for very pure dyes.

The results in Table I show how the order parameter of a 2-(*p*-alkoxyphenyl) substituted DDA increases from 0.63 to 0.75 as the

TABLE I

Order parameters of the two isomeric *p*-alkoxysubstituted anthraquinones (VII) and (VI) dissolved in nematic liquid crystal mixture E7. Only in the 2-substituted isomers does the O. P. increase with chain length.

		
R	O. P.	O. P.
H	0.63	0.64
CH_3	0.63	0.65
C_2H_5	—	0.67
C_3H_7	0.7	0.68
C_4H_8	0.72	0.66
C_5H_{11}	0.74	0.65
C_6H_{13}	—	0.65
C_7H_{15}	—	0.66
C_8H_{17}	0.75	0.67

alkoxy chain length increases while that of the homologous 3-substituted compounds remains around the 0.66 value. Among the numerous substituted anthraquinone dyes that we studied, only derivatives of structures VII show this strong dependence which indicates an interaction between the alkyl chains of both the dye and the liquid crystal.

2.2 Influence of the liquid crystalline host

2.2.1. The case of the 2-p-alkoxyphenyl substituted DDA

The importance of the host composition is exemplified by the behavior of compound (VII) in different L. C. matrices. Experimental results are shown in Table II. Comparing the order parameter of the dye dissolved in a host of different molecular composition, it becomes evident that the higher O. P.

TABLE II

Order parameters of 2-butoxyphenyl DDA (VII) in various hosts. Liquid crystals are designated by their central linkage. The higher order parameters are observed in mixtures of liquid crystals with the cyano group directed along the molecular axis. CB = cyano-biphenyls; CPy = cyanopyrimidines; CPCH = cyanophenylcyclohexane; CE = cyano-esters; PCH = phenylcyclohexane.

L. C. of POSITIVE DIELECTRIC ANISOTROPY

1) Mixtures of liquid crystals with the cyano-group along the molecular axis

Code	Comp.	T_{NI}	O. P.	D. A.	Source
E 7	CB	60	0,72	11	BDH
ROTN 43	CB;CPy	69	0,72	17,6	ROCHE
E 8	CB	70	0,74	18	BDH
Zli 1132	PCH	70	0,76	10,3	MERCK
ROTN 403	CB;CPy	82	0,76	19,3	ROCHE
E 9	CB	82	0,76		BDH
E 43	CB	84	0,76	12	BDH
Zli 1612	CPCH;CB	86	0,76	9,9	MERCK
E 63	CPCH;CB	89	0,77		BDH
Zli 1691	CPCH;CB	90	0,78	9,7	MERCK
ALP 1	CPCH;CB;CPy	94	0,77	14,2	ASULAB
ALP 2	CPCH;CB;CPy	105	0,77	13,9	ASULAB
ROTN 404	CPy;CB	105	0,77	21	ROCHE
ALP 10	CPCH;CPy	111	0,77	14,1	ASULAB
ALP 4	CPCH;CPy	115	0,79	13,7	ASULAB
ALP 14	CPCH;CPy	122	0,8	14,2	ASULAB
ALP 3	CPCH;CB;CPy	127	0,77	12,2	ASULAB
ALP 11	CPCH;CB;CPy	131	0,8	16,7	ASULAB

Table II (continued)

2) Addition of cyanophenyl benzoate (CE)

Code	Comp.	T_{NI}	O. P.	D. A.	Source
ROTN 101	CE	71	0,56	17,6	ROCHE
ROTN 103	CE;CPy	81	0,69	25,6	ROCHE
ALP 13	CE;CPy;CPCH	150	0,73	13,7	ASULAB

3) Addition of compounds of negative dielectric anisotropy

Code	Comp.	T_{NI}	O. P.	D. A.	Source
3.1) Dialkyl P.C.H.					
Zli 1565	CPCH;PCH	87	0,71	6,0	ROCHE
ALP 18	CPCH;PCH	89	0,72	10,2	ASULAB
ALP 16	CPCH;PCH	90	0,72	8,9	ASULAB
Zli 1694	CPCH;PCH	90	0,74	6,5	MERCK
3.2 Esters (E)					
E 55	CB;E		0,61		BDH
E37	CB;E	89	0,72		BDH
Zli 1344	PCH;E	90	0,75	10,8	MERCK
Zli 1221	PCH;E	90	0,74	8,0	MERCK
Zli 1291	PCH;E	107	0,74	8,6	MERCK

L. C. of NEGATIVE DIELECTRIC ANISOTROPY

Code	Comp.	T_{NI}	O. P.	D. A.	Source
EN 24	ESTER	65	0,52	-5,6	CHISSO
ALN 8	ESTER	66	0,52	-8,0	ASULAB
ALN 1	ESTER	80	0,61		ASULAB
Zli 1275	ESTER	80	0,55	-0,8	MERCK
ALN 52	PCH	64	0,43	-0,7	ASULAB
NP 5	AZOXY	73	0,39	-0,2	MERCK
MBBA	SCHIFF'S BASE	47	0,31	-0,55	ASULAB

are measured for mixtures of highly positive L. C. * Particularly high values are measured for mixtures that contain only L. C. compounds having both the following properties:

- a cyano group oriented in the direction of the molecular long axis.
- a direct carbon-carbon linkage between the two organic rings. Such compounds are, for instance, C. B., CPy, etc.

Among the hosts having these requirements, the order parameter increases as their transition temperature T_{NI} increases. This trend is very pronounced in the case of compounds of class VII.

*Positive (negative) L. C. stands for L. C. of positive (negative) dielectric anisotropy (D. A.).

The formulation of a host from compounds which do not have the above characteristics results in lower O. P. for the same T_{NI} value: the compound VII ($R = C_4H_9$) has an O. P. of 0.77 in E9 (C. B. mixture of $T_{NI} = 82^\circ\text{C}$), but its O. P. drops to 0.69 in ROTN 103 (CB, CE mixture of $T_{NI} = 81^\circ\text{C}$) which contains some cyano esters.

In a mixture composed purely of C. E. such as ROTN 101 ($T_{NI} = 71^\circ\text{C}$), the O. P. for compound VII is only 0.56.

This adverse influence is not restricted to esters, but extends to compounds with azoxy or Schiff's base linkages.

Also, the use of compounds without terminal cyano substitution lowers the apparent dye O. P. as is observed with compositions containing dialkyl PCH's or alkoxyphenyl benzoates.

In a mixture of negative dielectric anisotropy, the order parameter of dyes of class VII is also very low.

Figure 1 illustrates how the dichroic ratio of VII is affected by the host composition for different molecular structures.

2.2.2. Comparison of the behavior of both isomers

The increase in order parameter value mentioned in the case of compound VII is also observed for its isomer VI, although to a smaller extent: while the O. P. of compound VII rises from 0.7 to 0.8 as T_{NI} goes from 60° to 122° , the increase in O. P. for compound VI is only from 0.68 to 0.7 (Table III). The incorporation into the mixtures of compounds without a cyano substituent directed along the molecular axis does not affect the O. P. of compound VI as it does for compound VII.

With negative mixtures, which are necessary to realize dichroic displays with dark figures on a clear background (7) and which are composed only of this type of L. C. compound, the relative order of the S value of both isomers is reversed, and the 3-phenyl substituted anthraquinone has the higher O. P. value.

Mixtures of highly negative L. C.'s such as EN17 and EN24 are obtained by including dicyano substituted phenyl benzoates (7) in an ester matrix. In these mixtures the O. P. of compound VII is so low that it is not useful for practical applications.

This inversion phenomenon, sketched in Figure 2 is neither accompanied by a change in optical properties nor by a variation of the L. C. T_{NI} value.

In a particularly useful mixture (ALN76, $T_{NI} 80$; $\Delta\epsilon \approx -3.9$) developed in this laboratory for the inverse guest-host display, reasonably high order parameters are obtained with 3-substituted phenyl AQ which give a weak,

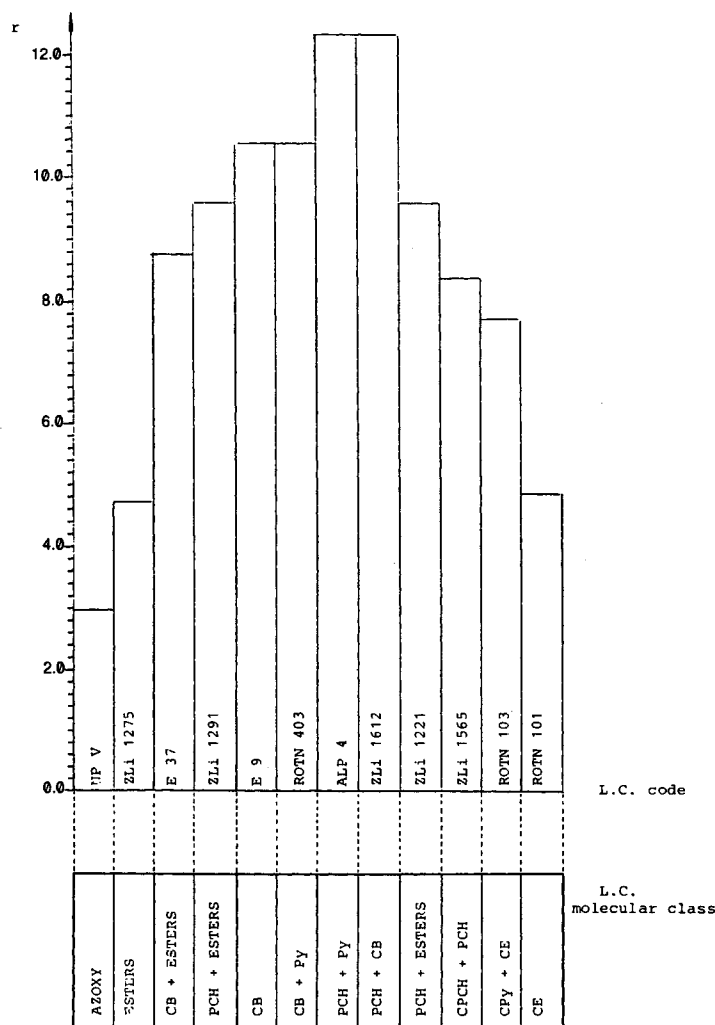


FIGURE 1 Dichroic ratios for compound VII ($R = C_4H_9$) in L.C. mixtures of various molecular types. L.C. code numbers are indicated in the Figure while the corresponding molecular compositions are framed below. See Table V.2 for definition of molecular class code letters. *p*-Cyano compounds lead to higher dichroic ratios.

but definite alternation effect depending on the number of carbon atoms in the chain (Table IV).

By choosing a compound with an even number of carbon atoms, one reaches an order parameter of 0.7 which is useful for many applications.

TABLE III

Order parameter of 2-(VII) and 3-(VI) substituted anthraquinones as a function of increasing T_{NI} ($R = C_4H_9$). The O. P. of both dyes increases but compound VII reaches higher values.

<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <chem>Nc1ccc2c(c1)c(=O)c3c(O)c(N)cc(=O)c3cc2c1=O</chem> </div> <div style="text-align: center;"> <chem>Nc1ccc2c(c1)c(=O)c3c(O)c(N)cc(=O)c3cc2c1=O</chem> </div> </div>			
L. C.	TNI	O. P.	O. P.
E 5	50	0.71	0.64
E 7	60	0.71	0.66 ($R = C_3H_7$)
E 8	70	0.74	0.68
E 43	84	0.76	0.68 ($R = CH_3$)
ALP-1	94	0.77	0.70
ROTN 404	105	0.77	0.70
ALP-4	115	0.79	0.70 ($R = CH_3$)
ALP-14	122	0.80	0.70

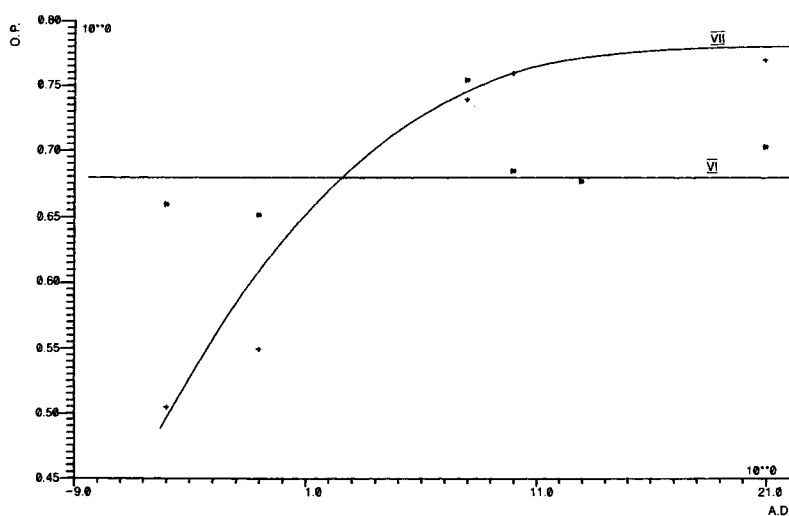
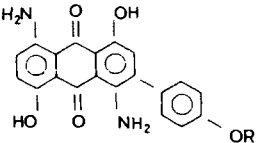


FIGURE 2 While the O. P. of compound VII increases as the host changes from negative to positive dielectric anisotropy, that of compound VI remains invariant.

TABLE IV

Order parameter of compound VI in a typical negative mixture ALN76. The alkyl chain length causes an alternating effect. In this mixture, compound VII has an O. P. of 0.55.

	
R	O. P.
H	—
CH ₃	0.68
C ₂ H ₅	0.70
C ₃ H ₇	0.68
C ₄ H ₉	0.70
C ₅ H ₁₁	0.67
C ₆ H ₁₃	0.70
C ₇ H ₁₅	0.67
C ₈ H ₁₇	0.70

3. EXPERIMENTAL

3.1 Syntheses of the dyes

The isomers VI and VII, and the compounds VIII and IX have been prepared by a slight modification of the methods described by Venkataraman.⁹ In this same article, the authors have verified unambiguously (by NMR spectroscopy and the preparation of derivatives) the substitution position of the alkoxyphenyl group in compounds VI and VII.

All the compounds described gave satisfactory microanalytical results.

3.1.1. Preparation of 4,8-diamino-1,5-dihydroxy-2-(p-alkoxyphenyl) anthraquinones (VIII)

1,5-Dihydroxy-4,8-dinitroanthraquinone (8.25 g) was dissolved in a mixture of boric acid (13 g) and concentrated sulphuric acid (190 ml). The solution was cooled to -8°C . The appropriate alkoxybenzene (0.05 mole) was added dropwise, keeping the mixture at this temperature for one hour.

The reaction mixture was poured onto crushed ice (200 g) and the resultant suspension heated under reflux for 4 hours to destroy the boric ester. The precipitate was collected, washed with water until neutral, and dried.

The crude product thus obtained was reduced by boiling for two hours in a solution containing sodium sulphide (50 g), water (250 ml), and ethanol (32 ml). The mixture was filtered while hot and the precipitate washed with water until neutral. The moist precipitate was boiled in 10% hydrochloric acid (300 ml) for another hour. The precipitate was collected, washed with water until neutral, and dried in vacuum. The dried product was treated by Soxhlet extraction with chloroform. Evaporation of the chloroform and recrystallization of the residue from chlorobenzene gave a product which was finally purified by column chromatography on silica gel.

3.1.2. Preparation of 4,8-diamino-1,5-dihydroxy-3-(*p*-alkoxyphenyl) anthraquinones (VI)

4,8-Diamino-1,5-dihydroxyanthraquinone-2, 6-disulphonic acid (4.0 g) was dissolved in a hot solution (80°C) of boric acid (2.0 g) in concentrated sulphuric acid (30 ml). The blue solution was cooled to 5°C and added dropwise to the appropriate alkoxybenzene (0.0184 mole). The mixture was stirred well in order to keep the reaction temperature around 5°C. The blue color changed to brownish-red. The mixture was then stirred for a further two hours at 5°C, when it was poured onto crushed ice. The resulting suspension was boiled for four hours to destroy the boric ester. After being cooled, the precipitate was collected and washed with water.

The moist precipitate was dissolved by heating in a mixture of 33% ammonia (24 ml) and water (160 ml). Sodium dithionite (2.2 g) was then added in portions, and the mixture was stirred at 95°C for two hours. After being cooled, the precipitate was collected, washed with water until neutral, and dried in a vacuum. The product was then extracted by Soxhlet extraction with chloroform. Evaporation of the chloroform and recrystallization of the residue from benzene gave a product which was finally purified by column chromatography on silica gel.

3.1.3. Preparation of 1,5-dihydroxy-2-(*p*-alkoxyphenyl) anthraquinones (VIII)

Compound VII (0.0088 mole) was dissolved in dimethylformamide (140 ml) at 40°C, followed by dropwise addition of *n*-pentyl nitrite (0.0535 mole) and stirring at this temperature for two hours. The blue color turned to brown. The reaction mixture was poured into brine (250 ml). The product

was filtered off and washed with water. Purification was effected by column chromatography on silica gel, with chloroform as eluent.

3.1.4. Preparation of 1,5-dihydroxy-3-(*p*-alkoxyphenyl) anthraquinones (IX)

The dye IX was obtained by deamination of compound VI as described for the preparation of compound VIII.

3.1.5. Preparation of 1,4,5,8-tetrahydroxy-2-(*p*-alkoxyphenyl) anthraquinones (X)

A mixture of VI (0.0053 mole), sodium hydroxide (0.71 g) and sodium dithionite monohydrate (1.58 g) in water (40 ml) was boiled for four hours. The cooled reaction mixture was poured into 10% hydrochloric acid (150 ml). The solid was filtered off, washed with water, and dried in vacuum. The dried solid was heated for two hours at 165°C in nitrobenzene (40 ml) to which were added a few drops of piperidine. The nitrobenzene was removed by distillation and the residue washed with hexane. The product was purified by column chromatography on silica gel with chloroform as eluent. The compound X could also be obtained by using VII instead of VI as the starting material.

3.2. Order parameter measurement

In a 30 μ -thick glass cell, the inner surface of which was covered with an aligning layer (tangentially evaporated SiO_x/rubbed polyimide), was introduced a 0.5% solution of a dye dissolved in a liquid crystal mixture.

The absorbance of this solution in polarized light was recorded at its maximum wavelength of absorption, with the direction of the polarizer parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the alignment direction. The two orientations were obtained by rotation of the cell, the polarizer being fixed. The order parameter is calculated from the relation:

$$S = \frac{r - 1}{r + 2}$$

where r is the dichroic ratio, A_{\parallel}/A_{\perp} .

All the values reported come from our own measurements for the purposes of comparison.

3.3. Liquid crystal composition and physical properties

Both commercial and proprietary (ALN; ALP) mixtures were used. A useful experimental description is difficult. We have attempted to summarize in Table V.2 the single components used and in Part V.1 the com-

TABLE V

Compositions and formulae of the commercial mixtures used in this work.

TABLE V.1

L. C. commercial mixtures (from our chromatographic analysis)

Code	Composition	T_{NI} °C	Source
Zli 1132	0.15 BCH-5; 0.24 PCH-3; 0.36 PCH-5 0.25 PCH-7	70	Merck
EN 24	0.8 HPE; 0.2 dicyano PCHE	66	Chisso
E7	0.51 K 15; 0.25 K 21; 0.16 M 24; 0.08 T 15	59.8	BDH
ROTN 103	0.05 PEPN 4; 0.24 PEPN 5; 0.13 PEPN 6 0.18 PEPN 7; 0.12 P ₃ 5; 0.08 P ₃ 7; 0.20 T P ₃ 4	81.4	Roche
ROTN 404	0.31 M 15; 0.14 M 24; 0.14 T 15; 0.09 P ₃ 5 0.18 P ₃ 7; 0.14TP ₃ 4	105	Roche

Merck: Frankfurter Str. 250 D-6100 Darmstadt 1; BDH: Poole Dorset BH 124 NN England; Roche: Liquid Crystals group RA/LC CH-4002 Basel; Chisso: 7.3 Marunouchi 2 Chome CHIYODA-KU Tokyo.

TABLE V.2

L. C. formulae.

K-15		PEPN 4	
K-21		PEPN 5	
M-15		PEPN 6	
M-24		PEPN 7	
T-15		P3 5	
BCH-5		P3 7	
PCH-3		TP3 4	
PCH-5		HPE-33	
PCH-7		PCHE	

positions and sources of mixtures, when known. Compositions of the various hosts studied are directly indicated in Table II.

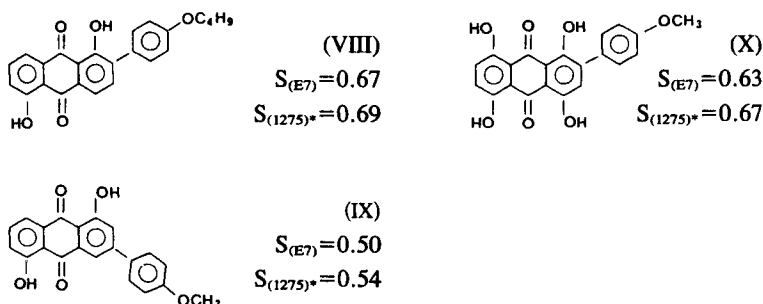
4. DISCUSSION

2-*p*-Alkoxyphenyl substituted DDA have a high order parameter in mixtures of liquid crystals of positive dielectric anisotropy composed of molecules having a cyano group lying in the direction of their long axes as in cyanobiphenyls, cyanophenylcyclohexanes or cyanopyrimidines.

This O. P. is lower when the mixture contains compounds devoid of the cyano substituent.

In a negative liquid crystalline mixture, the O. P. is very low, being a minimum in azoxy mixtures where $\Delta\epsilon \sim 0$.

This property is not shared by the isomer substituted in the 3-position, or by the 2- or 3-*p*-alkoxyphenyl-1, 5-dihydroxy-anthraquinones (VIII, IX) or by the 1,4,5,8-tetrahydroxy-2-*p*-alkoxyphenylantraquinones (X) the O. P. of which is nearly independent of the nematic host.



This seems to be the first reported case of such a strong interaction between a dissolved dye and the nematic host.

The increase in the order parameter of the dye of structure VII relative to that of its isomer must be related to a dipole-dipole interaction between the liquid crystal molecule and the dye, both in its ground and its excited state; this effect cannot change the energy level as there is no shift in the maximum absorption wavelength. It also depends upon the volume really occupied by the L. C. molecule: taking into account molecular deformations, the volume occupied by an aromatic ester is nearly the double that of a biphenyl due to the rotation about the ester linkage (Figure 3).

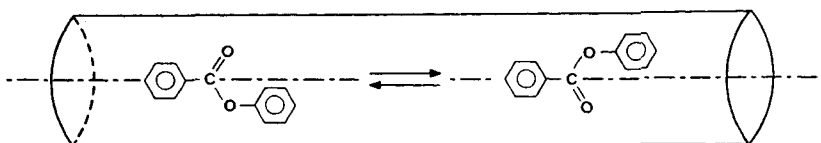


FIGURE 3 The volume of the cavity left by an ester molecule is higher than is suggested by its formula, due to the rotation about the ester linkage.

CONCLUSIONS

We have shown that the order parameter of AQ dyes in E7 is similar to that of the liquid crystal (0.65)* and that only in the case of favorable interactions between the host and the dye are higher values observed.

These high values will only arise if the L. C. molecular composition preserves these interactions; then the observed dye O. P. may increase to 0.8.

Acknowledgment

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