

## Ultraviolet and Visible Spectrophotometric Studies of Anthraquinone Derivatives in Nematic Solvents

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**Anthraquinone and eight derivatives of anthraquinone have been studied as guests in three different liquid crystal hosts by spectroscopic methods. All the compounds have their geometrical long axis preferably oriented along the director of the nematic samples, and the axis of highest polarizability normal to the director. Differences in the long axis order parameter  $S$  of the guests correlate very well with differences in anisotropic polarizabilities. The order parameter  $D$  of the guests is close to the theoretical values calculated from the shape biaxiality of the solutes. Anthraquinone itself shows anomalous behaviour, and possible sources of specific interactions are discussed.**

It has been discussed for a long time whether dispersion forces<sup>1-4</sup> or steric interactions<sup>5-8</sup> play the major role in orienting dissolved molecules in a liquid crystal solvent. In the Maier-Saupe (MS) theory, dispersion forces are regarded as the only orienting forces, and many properties of liquid crystals have been predicted with remarkable success. The MS theory is in principle correct for spherical molecules with an anisotropic point polarizability at the center of the molecule.<sup>9</sup>

Real nematogens are not spherically symmetrical. They have a pronounced shape anisotropy, with a long axis showing a preferred orientation parallel to the director of the nematic sample. It has been suggested<sup>10</sup> that the success of the MS theory is somewhat accidental, and that the anisotropy of dispersion forces is an order of magnitude smaller than required by the MS theory. Any interactions described by a second rank tensor will give the same temperature dependence as the MS theory. Therefore, other types of forces in addition to dispersion might contribute to the orientation of solutes in liquid crystals.

Fluorine and hydrogen have approximately the same covalent radii, therefore fluorine substituted benzenes have no preferred long axis, but can be considered as oblate molecules. A series of fluorine substituted benzenes were investigated in liquid crystals,<sup>11</sup> and the differences in their orientation correlated very well with variations in their anisotropic polarizability.

Sackmann and coworkers<sup>12,13</sup> found a larger scatter of experimental points in a plot of order parameter *versus* shape anisotropy than in a plot of order parameters *versus* anisotropic polarizabilities for a series of aromatic solutes. They concluded that the anisotropic polarizability is the main molecular property responsible for orienting a

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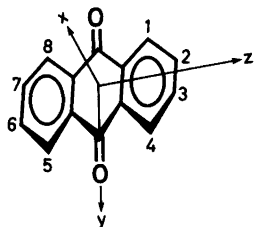


Fig. 1. Anthraquinones with the axis system used and the numbering of substituent positions.

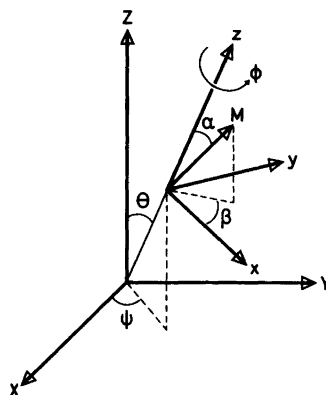


Fig. 2. Definitions of angles describing a transition moment  $M$  in the molecular frame  $x, y, z$ , and angles describing the molecular orientation in a laboratory fixed system  $X, Y, Z$ .

dissolved molecule in liquid crystals. It is, however, difficult to separate the shape anisotropy and the polarizability anisotropy in an aromatic compound, since the main polarizabilities are roughly proportional to the molecular dimensions.<sup>14</sup>

In most of the earlier work<sup>11-13</sup> the guest-host interactions were studied at one temperature only, and as much information as possible was extracted from the orientational behaviour under these conditions. In the present study, however, the investigations were carried out over the full nematic range of the liquid crystals used.

**Method.** In the present study we have used anthraquinone and various anthraquinone derivatives as solutes, or guests, in a liquid crystal host. In all these guests the longest

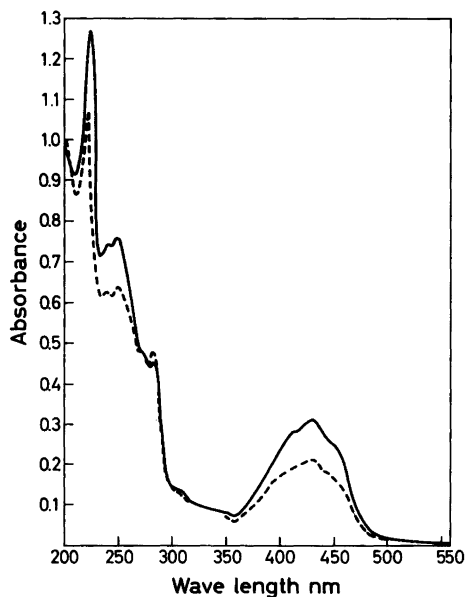


Fig. 3. Typical UV-visible spectrum showing 0.71 % of dye No. VIII in CCH-3 at 60° in a 12  $\mu\text{m}$  cell — 0V ---- 15 V. The 283 nm band is clearly y-polarized, but too close to z-polarized bands to determine any order parameter.

molecular axis ( $z$ ) is perpendicular to the axis of highest polarizability ( $y$ ) (see Fig. 1 for definition of axes). The molecular orientation of the guests is determined by two opposing forces, one resulting from the anisotropic polarizability and another due to the shape of the molecules.

A few investigations have considered deviations from cylindrical symmetry and how this will influence the observed order parameter.<sup>15-25</sup> To describe a biaxial molecule in a uniaxial nematic phase, a new order parameter  $D$  was introduced<sup>15</sup> as the differences in projections of the two short axes,  $x$  and  $y$  of a molecule onto the director of the nematic phase.

The exact expression for  $D$  varies with a constant factor from one author to another. Here, the convention of van der Meer and Vertogen<sup>26</sup> will be used.

$$D = \overline{S_{xx} - S_{yy}} = \frac{3}{2} \sin^2 \theta \cos 2\phi \quad (1)$$

The bar indicates an average over all the molecules in the sample. The angles  $\theta$  and  $\phi$  and the axes are shown in Fig. 2.  $S_{xx}$  and  $S_{yy}$  are the order parameters of the two short axes relative to the director of the sample.

We are considering a rigid molecule with an axes system  $x, y$ , and  $z$ , in which  $z$  is the long axis of the molecule. A transition moment vector  $\mathbf{M}$  makes an angle  $\alpha$  with the  $z$ -axis. The projection of  $\mathbf{M}$  in the  $x, y$ -plane makes an angle  $\beta$  with the  $x$ -axis. It is previously shown<sup>27</sup> that:

$$2(A_p - A_h)/(2A_p + A_h) = \frac{1}{2}(3\cos^2\alpha - 1)S - \frac{1}{2}\sin^2\alpha \cos 2\beta D \quad (2)$$

Here  $A_h$  and  $A_p$  are the measured absorbances in the homeotropic and the planar orientations, respectively. The order parameter  $D$  is defined in eqn. (1), and the order parameter  $S$  in the following expression

$$S = \overline{\frac{1}{2}(3\cos^2\theta - 1)},$$

where the bar again indicates an average over the sample. If  $\alpha$  and  $\beta$  (Fig. 2) are determined for two or more separate absorption bands, with differently oriented transition moments,  $S$  and  $D$  can be calculated. Without knowing the angles  $\alpha$  and  $\beta$  we can still use the left hand side of eqn. (2) and obtain an observed order parameter  $S_{\text{obs}}$

$$S_{\text{obs}} = 2(A_p - A_h)/(2A_p + A_h) \quad (3)$$

This order parameter is a function of the angles  $\alpha$  and  $\beta$  and the order parameters  $S$  and  $D$ .

Table 1. Liquid crystal hosts employed.

Name	Code	Nematic range °C	Anisotropy	
			diel.	opt.
4-(4'-n-propylcyclohexyl)-cyanocyclohexane	CCH-3	58-80	4.5	+0.06
4-(4'-n-butylcyclohexyl)-cyanocyclohexane	CCH-4	54-79	4.5	+0.06
4-(4'-n-heptylcyclohexyl)-cyanocyclohexane	CCH-7	71-83	4.5	+0.06

**Table 2.** Guest molecules with substitution pattern and the reference numbers used in the text.

Name	No.	1 <sup>a</sup>	4	5	8
Anthraquinone	I	H	H	H	H
1-amino-anthraquinone	II	NH <sub>2</sub>	H	H	H
1,4-diamino-anthraquinone	III	NH <sub>2</sub>	NH <sub>2</sub>	H	H
1,5-diamino-anthraquinone	IV	NH <sub>2</sub>	H	NH <sub>2</sub>	H
1-hydroxy-anthraquinone	V	OH	H	H	H
1,4-dihydroxy-anthraquinone	VI	OH	OH	H	H
1,5-dihydroxy-anthraquinone	VII	OH	H	OH	H
1,8-dihydroxy-anthraquinone	VIII	OH	H	H	OH
1-amino-4-hydroxy-anthraquinone	IX	NH <sub>2</sub>	OH	H	H

<sup>a</sup> The numbers refer to positions in anthraquinone (Fig. 1).

Most liquid crystals contain one or more aromatic rings and hence absorb strongly in the ultraviolet region. Therefore the UV transition in the guest molecules cannot be observed since they are covered by the absorption of the much more abundant host molecules. Most cholesterics consist of a rigid cholesterol skeleton and do not absorb in the UV spectral range. By using compensated cholesteric liquid crystals a broader spectral range can be investigated. However, it is tedious to study compensated cholesteric liquid crystals over a wide temperature range, since a different proportion of the components must be employed at each temperature.<sup>13</sup>

Recently, a number of aliphatic liquid crystals based on cyclohexyl or bicyclooctane entities forming nematic phases have become commercially available.<sup>28</sup> They have no significant UV absorption and therefore allow the guest molecule to be studied over a wide spectral region, and in a continuous temperature range. Three different cyanobicyclohexyls have been employed as solvents for several anthraquinone guests. They have very low optical anisotropy, and are transparent above 200 nm. The properties of the solvents are summarized in Table 1.

We have used eqn. (2) to obtain the order parameters for anthraquinone (I), and eight anthraquinone derivatives (II–IX, Table 2). In some of the solutes the UV-visible bands are not well separated and only the long axis order *S* could be found.

## EXPERIMENTAL

The following liquid crystals were used:

- 4-(4'-n-propyl-cyclohexyl)-cyanocyclohexane, later to be called CCH-3,
- 4-(4'-n-butyl-cyclohexyl)-cyanocyclohexane (CCH-4) and
- 4-(4'-n-heptyl-cyclohexyl)-cyanocyclohexane (CCH-7).

All of these were commercial products from Merck. The anthraquinone derivatives were obtained from the K & K Laboratories, Merck, Aldrich, and Baker, and used without further purification; they are numbered I–IX (Table 2).

Solutions of all the anthraquinones in the cyanobicyclohexyls were prepared by weighing approximately 100 mg of the liquid crystals, which are all crystalline at room temperature, and adding enough of the anthraquinones dissolved in chloroform to make a 0.4–1.0 % solution. The chloroform was evaporated under reduced pressure, or at elevated temperature. The guest concentrations were low in order to minimize any disturbing effects on the liquid crystal hosts, but were high enough to obtain UV-visible absorption spectra of reasonable absorbance. The concentrations used were all below the saturation points of the anthraquinone derivatives in the liquid crystals chosen.

Optical cells were made from two quartz plates coated with a thin (approximately 13 nm) tin-indium oxide electrode layer (Merck substance E). The plates were rubbed with tissue paper to give a hopefully completely planar orientation.<sup>29</sup> A 12  $\mu\text{m}$  thick mylar spacer was used to keep the cell walls apart, and the quartz plates were subsequently clamped together. No sealing was necessary, so the quartz plates could easily be reused many times.

No apparent deterioration of the filled cells after one week's of storage at ambient temperature was detected, but all the measurement were performed within 48 h after the cells were made.

The spectra were recorded on a Cary 14 Recording Spectrometer with a water-heated sample compartment thermostatted to  $\pm 0.3$  °C. An empty cell was placed in the reference beam. A 15 V a.c. voltage was applied across the cell to give homeotropic orientation (12.5 kV/cm).

In principle, an infinite voltage must be applied to achieve a perfect homeotropic orientation. In practice no change was observed in the absorption and hence in the orientation above 15 V for the systems studied.

Because the y-polarized bands in I, VI and IX at 274, 280 and 277 nm, respectively, are close to the z-polarized bands it was necessary to correct for the background. A symmetrical shape was supposed for all the bands. A few of the spectra were analyzed carefully, and it was found that the background corresponds closely to the absorption at 300 nm for I. The background was subtracted from the peak absorbance before the order parameters were calculated. The probable error of  $S_{yy}$  is of the order 0.01. For VI and IX the backgrounds were close to zero and no additional corrections were made. The probable error due to this is of the order 0.003 units in  $S_{yy}$ .

### CALCULATION OF ANISOTROPIC POLARIZABILITIES

Molecular polarizabilities can be regarded as a sum of bond polarizabilities, which are considered to be cylindrosymmetric. Let us consider a bond  $i$  that makes an angle  $\theta_i$  with the z-axis of a molecule and whose projection in the  $x,y$ -plane of the molecule makes an angle,  $\phi_i$  with the x-axis. Referring to Fig. 2, the bond  $i$  is equivalent to the M vector, and  $\theta_i$  and  $\phi_i$  are equivalent to  $\alpha$  and  $\beta$ , respectively.

The diagonal elements of the polarizability tensor will be:<sup>30</sup>

$$\begin{aligned} a_{zz} &= \sum_i [\alpha_{ii} \cos^2 \theta_i + \alpha_{ti} \sin^2 \theta_i] \\ a_{yy} &= \sum_i [(\alpha_{ii} \sin^2 \theta_i + \alpha_{ti} \cos^2 \theta_i) \sin^2 \phi_i + \alpha_{ti} \cos^2 \phi_i] \\ a_{xx} &= \sum_i [(\alpha_{ii} \sin^2 \theta_i + \alpha_{ti} \cos^2 \theta_i) \cos^2 \phi_i + \alpha_{ti} \sin^2 \phi_i] \end{aligned} \quad (4)$$

Table 3. Values of the bond polarizabilities and angles used.

Bond	$\alpha_{ii}^a$	$\alpha_{ti}^a$	$\theta_i^b$	$\phi_i^c$	Ref. <sup>d</sup>
C-H	7.9	5.8	90	90	32
C-O	22.5	4.8	90	90	30
C <sub>ar</sub> -N	7.8	6.1	90	90	33
O-H	10.0	5.0	161	90	34
N-H <sub>in</sub> <sup>e</sup>	5.8	8.4	162	90	32
N-H <sub>out</sub> <sup>e</sup>	5.8	8.4	36	148	32

<sup>a</sup> Polarizabilities in  $10^{-25}$  cm<sup>3</sup>,  $\alpha_{ii}$  along the bond axis,  $\alpha_{ti}$  perpendicular to the bond axis. <sup>b</sup> The angle between the bond and the long (z) molecular axis. <sup>c</sup> The angle between the bond and the short (x) molecular axis. The axes are shown in Fig. 2. <sup>d</sup> Giving the values for the bond polarizabilities. <sup>e</sup> in: In-plane; out: Out-of-plane.

Table 4. The polarizability components ( $\alpha_{zz}$ ,  $\alpha_{yy}$ ,  $\alpha_{xx}$ ) for the anthraquinone derivatives. Values for the relative anisotropy ( $\Delta\alpha/\Sigma\alpha_{ii}$ ) and the biaxiality ( $\lambda_\alpha$ ).

Compound <sup>b</sup>	Polarisability components <sup>a</sup>			Relative anisotropy <sup>c</sup>	Biaxiality $\lambda_\alpha$
	$\alpha_{zz}$	$\alpha_{yy}$	$\alpha_{xx}$		
I	258.2	263.0	141.6	9.52	1.33
II	279.1	276.9	157.5	8.56	1.18
III	290.0	290.8	173.4	7.94	1.24
IV	290.0	290.8	173.4	7.94	1.24
V	266.7	283.1	145.6	10.98	1.61
VI	275.2	303.2	149.6	12.47	1.93
VII	275.2	303.2	149.6	12.47	1.93
VIII	275.2	303.2	149.6	12.47	1.93
IX	282.6	297.0	161.5	10.11	1.56

<sup>a</sup> In  $10^{-25}$  cm<sup>3</sup>. <sup>b</sup> The substances are given in Table 2. <sup>c</sup>  $10^{-2}$ .

Here  $\alpha_{ii}$  and  $\alpha_{\perp i}$  are the parallel and perpendicular components of the  $i$ 'th bond polarizability. The summations span over all the bonds  $i$  in the molecule.

The  $y$ -axis lies in the plane of the anthraquinones coinciding with the two carbonyl groups. The  $z$ -axis is perpendicular to the  $y$ -axis in the plane of the molecules and will be the geometrical long axis of the anthraquinones. The  $x$ -axis is perpendicular to the plane (see Fig. 1).

The polarizability components of the parent compound anthraquinone (I) were given<sup>31</sup> as:

$$\alpha_{zz}=258.2 \times 10^{-25} \text{ cm}^3 \quad \alpha_{yy}=263.0 \times 10^{-25} \text{ cm}^3 \quad \text{and} \quad \alpha_{xx}=141.6 \times 10^{-25} \text{ cm}^3$$

For the other guest compounds in this study, which are substituted anthraquinones (see Table 2), the polarizabilities are unknown. Using eqn. (4) and adopting bond polarizabilities given in the literature,<sup>30,32-34</sup> the polarizability components were calculated for all the guest molecules. In these calculations the bond from the 1,4,5 and 8 positions in anthraquinone were regarded as parallel with the  $y$ -axis, meaning that both  $\theta_i$  and  $\phi_i$  are  $90^\circ$ , regardless of which atom is bonded to the carbon. Due to hydrogen bonding to the carbonyl oxygen, the hydrogen atom of the hydroxy groups and a hydrogen atom of the amino groups are presumably situated in the plane of the molecule, *e.g.* the O-H and N-H bonds are normal to the  $x$ -axis. The C-O-H, C-N-H and H-N-H angles were considered to be  $109^\circ$ ,  $108^\circ$  and  $106^\circ$ , respectively.

In Table 3 the bond polarizabilities and the angles employed in the calculations are summarized, while the results of the calculations are listed in Table 4. These values are not very sensitive to changes in the bond angles. Additional results for relative anisotropies ( $\Delta\alpha/\Sigma\alpha_{ii}$ ) and biaxiality ( $\lambda_\alpha$ ) calculated from polarizabilities are also given in Table 4 (for definitions of  $\Delta\alpha$  and  $\lambda_\alpha$ , see below).

For (II), (IV), (V) and (VII) the polarizability main axes will not coincide with the long axis defined in Fig. 1. Calculations of the full polarizability tensors<sup>35</sup> and subsequent diagonalization showed that the axis of highest polarizability and the  $z$ -axis were tilted less than  $0.8^\circ$  with respect to each other. The values of the diagonal elements given in Table 4 did not vary when our coordinate system and the coordinate system defined by the polarizability main axes were interchanged.

Polarizabilities are in principle solvent dependent<sup>36</sup> but usually the changes are ignored when values found in the vapour phase or in unpolar solvents are considered to be valid also in liquid crystals. Most nematogens are polar molecules, although this is not a necessary condition for making a liquid crystalline phase.

Sackmann and coworkers<sup>12</sup> give the anisotropy ( $\Delta\alpha$ ) as:

$$\Delta\alpha = 2\alpha_i - \alpha_j - \alpha_k \quad (5)$$

where  $i$  is the axis of highest,  $j$  of medium and  $k$  of lowest polarizability. For elongated solutes in liquid crystals they found that the long axis order is proportional to the anisotropy. Other workers<sup>37</sup> have used the scaled anisotropy  $\Delta\alpha/\Sigma\alpha_{ii}$  instead of  $\Delta\alpha$  directly when discussing the properties of liquid crystals, and find a good correlation between this term and the long axis orientational order.

It is known that even for simple isotropic liquids the structure will mostly be determined by repulsive forces.<sup>38</sup> Also in liquid crystals these forces are expected to play an important role. The order parameter of a solute will also depend on the solvent properties and usually diminishes when the order of the solvent liquid crystal decreases. When low concentrations of similar solutes are investigated in liquid crystals, the order parameter and other physical properties of one solvent will be the same for all solutes.

The anisotropy of a molecular property cannot be described by one single number. Analogous to eqn. (5) the shape anisotropy ( $\beta$ ) can be approximately expressed by:  $\beta \sim (2I_z - I_x - I_y)$ , where  $I_x$ ,  $I_y$  and  $I_z$  are the lengths of the molecular axes. This equation depends only upon the maximum dimensions of the molecule and not how well it "fills the corners". Recently, a shape tensor has been defined,<sup>25</sup> this procedure gives a better description of the shape of a molecule.

The biaxiality ( $\lambda$ ) of a molecule has been defined<sup>26</sup> as

$$\lambda = 6^{1/2}(\gamma_{jj} - \gamma_{ii})/4(\gamma_{kk} - \frac{1}{2}\gamma_{ii} - \frac{1}{2}\gamma_{jj}) \quad (6)$$

where  $\gamma$  is a molecular tensor property, and  $\gamma_{nn}$  are the components of the diagonalized tensor.  $\gamma_{kk}$  is the component along the preferred oriental axis of the molecule, whereas  $\gamma_{ii}$  and  $\gamma_{jj}$  are the components along the short and medium transverse axis, respectively. Using polarizabilities as the molecular tensor property, the  $\lambda$  values of Table 4 have been calculated.

The angles and bond lengths of anthraquinone are known from X-ray studies.<sup>39</sup> When these distances were employed and the atoms regarded as spheres with fixed diameters, the following dimensions of anthraquinone were obtained:  $I_z = 1020$  and  $I_y = 680$  pm. The "thickness" of an aromatic ring is *ca.* 370 pm. With bond lengths equal to 128, 140, 100 and 100 pm for C-O, C-N, O-H and N-H, respectively, together with the bond angles given earlier, the largest dimensions of all the guest molecules can be calculated. The data are listed in Table 5, together with relative anisotropies  $\Delta/\Sigma I_i$  and biaxialities ( $\lambda_i$ ) calculated from their dimensions.

## RESULTS

*Anthraquinone* ( $I$ ) belongs to the symmetry point group  $D_{2h}$  and the absorption bands must be either  $x$ ,  $y$ , or  $z$ -polarized. Nepras and coworkers<sup>40</sup> have used configurational analysis

Table 5. The dimensions of the anthraquinone derivatives ( $I_z$ ,  $I_y$  and  $I_x$ ) together with the relative anisotropy ( $\Delta_I/\Sigma I_i$ ) and biaxiality ( $\lambda_I$ ).

Compound <sup>a</sup>	Dimensions <sup>b</sup>			Relative anisotropy	Biaxiality $\lambda_I$
	$I_z$	$I_y$	$I_x$		
I	1020	680	370	0.239	0.38
II	1020	700	370	0.232	0.42
III	1020	720	370	0.225	0.45
IV	1020	720	370	0.225	0.45
V	1020	690	370	0.236	0.40
VI	1020	690	370	0.236	0.40
VII	1020	690	370	0.236	0.40
VIII	1020	690	370	0.236	0.40
IX	1020	710	370	0.229	0.43

<sup>a</sup> The substances are given in Table 2. <sup>b</sup> In pm.

and theoretically calculated the polarizations of the eight  $\pi$ - $\pi^*$  transitions with the longest wavelengths for this compound and for (II), (III) and (IV) together with several other amino anthraquinones. Some of these bands are poorly separated and cannot be used directly. However, the 312 nm band, which is z-polarized, and the y-polarized 274 nm band, are well separated from the other bands and were used in this study.

*1-amino-anthraquinone (II)* belongs to the point group  $C_s$ . The transition moment directions for the eight longest wavelength transitions of this compound have been calculated.<sup>40</sup> The experimental wavelengths of the various transitions observed in the three hosts are in good agreement with the theoretical calculations. The longest wavelength band at 460 nm is used in this study to give the order parameter  $S$  only, the other bands were too close together to be sufficiently resolved. The 460 nm band is due to a  $\pi$ - $\pi^*$  transition and will therefore be in the molecular plane. The transition moment makes an angle of  $12^\circ$  with the z-axis.

*1,4-diamino-anthraquinone (III)* has  $C_{2v}$  symmetry and the absorption bands must be x-, y-, or z-polarized. Theoretical calculations have given the polarization of the eight longest wavelength  $\pi$ - $\pi^*$  transitions.<sup>41</sup> Among them the longest (590 nm) wavelength band is determined to be z-polarized, and to lie in the molecular plane. Other bands are too poorly separated, to allow a determination of the  $D$  order parameter.

*1,5-diamino-anthraquinone (IV)* belongs to the  $C_{2h}$  symmetry group. The transition moment corresponding to the band at 468 nm was found to make an angle of  $18^\circ$  with the z-axis of the molecule, and lies in the y,z-plane.<sup>41</sup>

*1-hydroxy-anthraquinone (V)*. Because of the low symmetry of this molecule, an independent determination of the transition moment directions is necessary. It is known<sup>42</sup> that amino- and hydroxy substituents have approximately the same influence on the transition moment directions in anthraquinones, hence an angle of  $12^\circ$  as in (II) was adopted for calculating the  $S$  order parameter.

*1,4-dihydroxy-anthraquinone (VI)* has  $C_{2v}$  symmetry like dye (III). In compound (VI) all the bands are displaced somewhat compared to (III). The long wavelength bands were shifted towards shorter wavelengths and the short wavelength bands towards longer wavelengths. The same polarization directions are assumed as for (III). This assumption is consistent with the measured positive and negative order parameters. Two bands well



Table 6. The observed and calculated electronic transitions for anthraquinone and substituted anthraquinones.

Compound <sup>a</sup>	obs. (nm)	calc. (nm)	Ref.	$\alpha^b$
I	312	311	39	0°
	274	285	39	90°
II	460	461	39	12°
III	590	515	40	0°
IV	468	468	40	18°
V	406			12° <sup>c</sup>
VI	477			0° <sup>c</sup>
	280			90° <sup>c</sup>
VII	420			18° <sup>c</sup>
VIII	433			0° <sup>c</sup>
IX	531			0° <sup>c</sup>
	277			0° <sup>c</sup>

<sup>a</sup> Substances are given in Table 2. <sup>b</sup> The angle between the long molecular axis (*z*) and the transition moment. <sup>c</sup> Values taken from the corresponding amino-derivatives.

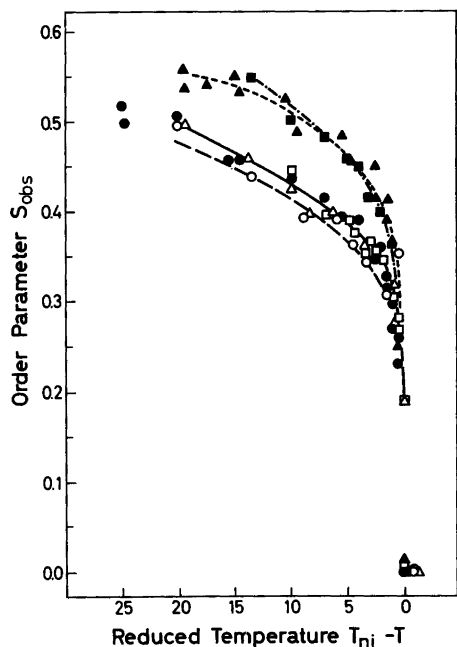


Fig. 4. Observed order parameters for the longest wavelength absorption bands of dye Nos. II (460 nm) and IV (468 nm) in three different nematic solvents. Circles in CCH-4, squares in CCH-7, and triangles in CCH-3. Filled symbols IV, open symbols II.

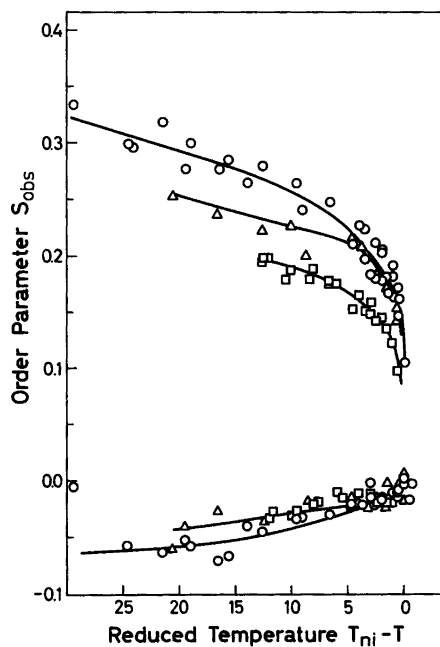


Fig. 5. Observed order parameters of two bands from VI in three different solvents. Circles CCH-4, triangles CCH-3 and squares CCH-7. Upper curves 477 nm band. Lower curves 280 nm band.

separated are found at 477 and at 280 nm, and the *S* and *D* order parameters are calculated.

*1,5-dihydroxy-anthraquinone* (VII): The same transition moment directions were assumed as determined for (IV).

*1,8-dihydroxy-anthraquinone* (VIII) like (III) and (VI) belongs to the point group  $C_{2v}$ , but has the *y*-axis as its  $C_2$ -axis. For compound (VIII) the longest wavelength band showed positive order, and was considered to be *z*-polarized. In 1,8-diamino-anthraquinone the longest wavelength band is known to be *z*-polarized.<sup>41</sup>

*1-amino-4-hydroxy-anthraquinone* (IX) belongs to the point group  $C_s$ . Since the amino- and hydroxy-substituents have about the same influence on the transition moment directions in anthraquinone (see above), it is reasonable to suppose that the band with largest dichroism is *z*-polarized, and the bands with largest negative dichroism are *y*-polarized. This assumption gave the same sequence of *z*- and *y*-polarized bands as for dye (III).

The calculated and observed wavelengths employed in this work together with the transition moment directions are summarized in Table 6. A typical UV-visible spectrum is shown in Fig. 3. From these spectra the observed order parameters are calculated according to eqn. (3) for the bands shown in Table 6. The observed order parameters are plotted against reduced temperature ( $T_{ni}-T$ ), and smooth best fit curves are drawn. Examples are shown in Figs. 4-7.

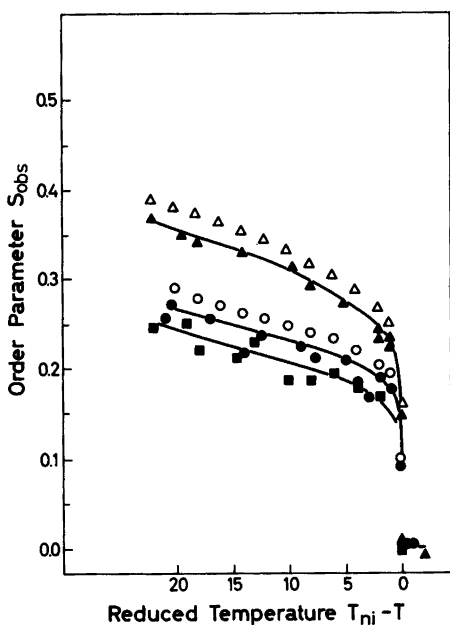


Fig. 6. Order parameters for three hydroxy-substituted anthraquinones, in CCH-3 triangles V, circles VII, squares VIII. Filled symbols observed for longest wavelength absorption, open symbols derived for the long axis of the molecules. For (VIII) the absorption is along the *z*-axis and the observed and derived values are identical.

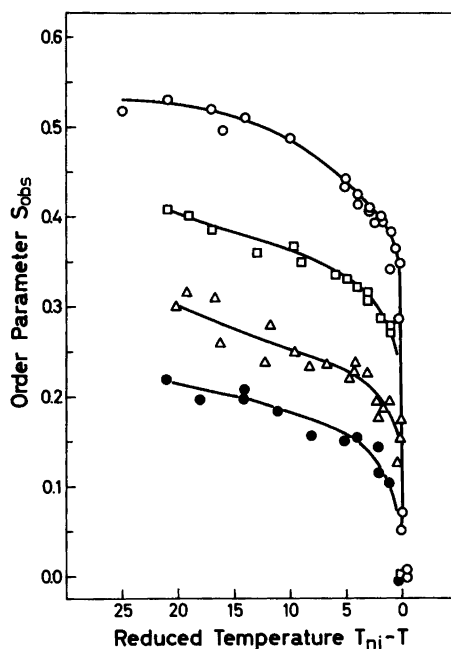


Fig. 7. Order parameter for 1,4-disubstituted anthraquinones in CCH-3. Meaning of curves: ● I, ○ III, △ VI, □ IX.

For the dyes (IV), (V) and (VII) the angle  $\alpha$  for the longest wavelength transition is different from zero, but only one transition moment can be clearly resolved and in principle neither  $S$  nor  $D$  can be determined. Setting  $D$  equal to zero,  $S$  is derived using the  $\alpha$  values from Table 6. These calculations probably yield  $S$  values that are too low by 0.01–0.02 units.

The compounds (III) and (VIII) have their longest wavelength bands  $z$ -polarized and the  $S$  order parameters are obtained directly. A plot of the  $S$  order parameter versus the anisotropic polarizabilities are shown in Fig. 8 for different solutes.

With  $\beta=90^\circ$  for the in-plane bands of anthraquinones and  $\alpha$  having the values listed in Table 6, eqn. (2) was used to calculate the  $S$  and  $D$  order parameters of (I), (VI) and (IX). Plots of the  $D$  order parameter versus the  $S$  order parameter are shown in Figs. 9–11. The full line in these plots are theoretical values for different values of  $\lambda$  and were obtained using the theory of Luckhurst *et al.* The biaxiality,  $\lambda$ , measures the deviation from cylindrical symmetry of the potential of mean torque and depends on properties of both solute and solvent.

However, if dispersion forces only are considered responsible for the long range order, it has been shown<sup>23</sup> that  $\lambda$  will depend only on the polarizability of the solute, as given by eqn. (7) and be independent of the solvent used.

## DISCUSSION

*The S Order Parameter.* The  $S$  order parameter of the different solutes are plotted in Fig. 8. It can be seen that the points – within experimental error – fall on a straight line when the

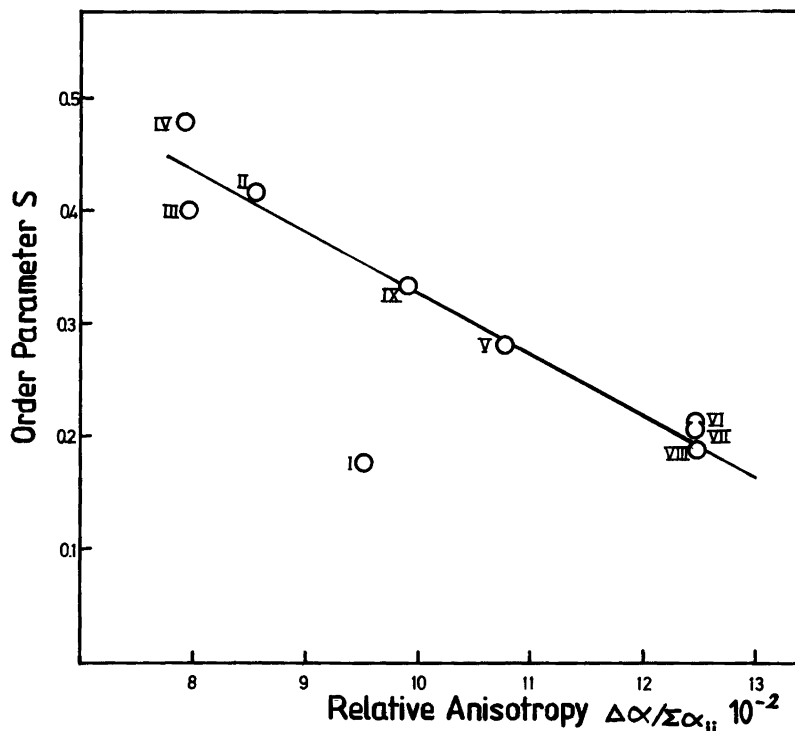


Fig. 8. Order parameters in CCH-3 versus anisotropic polarizabilities. The values shown are at a reduced temperature of 5 K. Roman numerals identify the compounds.

order parameters are plotted *versus* the relative anisotropy in polarizability ( $\Delta\alpha/\Sigma\alpha_{ii}$ ). A serious exception to this regularity is provided by the parent compound anthraquinone. The values given in the present work are somewhat lower than the values given earlier for (II), (III) and (IV) in a cyanobiphenyl-cyanoterphenyl mixture<sup>43</sup> and for (III) and (IX) in cyanoesters.<sup>44</sup> The reason for this discrepancy is probably that our measurements – although they were carried out over the full nematic temperature range of the hosts – never are done more than 25 K below the nematic-isotropic transition, while the previous data are recorded 40–60 K below the phase transition. When the experimental points are plotted as in Fig. 8 they can easily be fitted to a straight line. We obtain a slope of the straight line equal to  $-5.24$  at the reduced temperature ( $T_{ni}-T$ ) of 5 K in CCH-3. This value decreases to  $-5.76$  and to  $-6.02$  at the reduced temperatures 10 and 20 K, respectively. The correlation is better than 0.98 at all temperatures if the values for anthraquinone itself is disregarded.

In CCH-7 values of  $-5.04$  and  $-5.58$  are found for the slopes at the reduced temperatures 5 and 10 K, respectively.

In the anthraquinones the longest axis of the molecules and the axis of highest polarizability are normal to each other, and two different forces try to orient the molecules in opposite directions. In all our compounds the transition moments of lowest energy are parallel or nearly parallel to the geometrical long axis, and perpendicular to the axis of highest polarizability. If the molecules have their geometrical long axis oriented along the director of the nematic sample, the angle  $\alpha$  in eqn. (2) is zero for (I), (III), (VI) and (VIII) or near zero for (II), (IV), (V), (VII) and (IX) and the observed order parameter will be positive. If, on the other hand, the molecules have the axis of highest polarizability oriented along the director, the angle  $\alpha$  will be  $90^\circ$  or near  $90^\circ$ , hence the observed order parameter will be negative.

The observed order parameter was positive for our substances, and it is clearly seen that the geometrical long axis is preferentially oriented. But even for the geometrical dimensions of the molecules there seems to be an inverse correlation between the observed order and the anisotropy. This probably occurs because the amino group is larger than the hydroxy

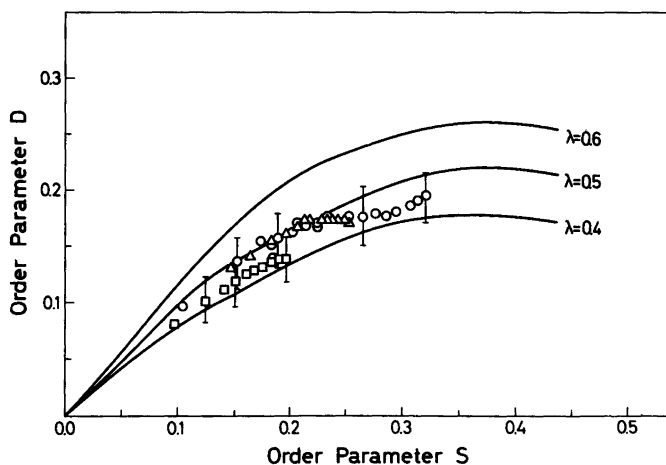


Fig. 9. Order parameter  $D$  versus  $S$  for (VI) in three different solvents. For clarity, error bars are omitted from most of the points. Theoretical curves for three different values of  $\lambda$  are shown. The  $\lambda$  value from anisotropic polarizability is 1.93, from the molecular dimensions it is 0.40. Meaning of curves:  $\Delta$  CCH-3,  $\circ$  CCH-4,  $\square$  CCH-7.

group, and increases  $l$ , slightly more, while at the same time the amino group have a smaller effect on the polarizability.

Solutes (II) and (V) behave as expected from the theory and show nearly the same long axis order parameter in all the three solvents. For the substances (III), (IV), (VII) and (VIII) the order depends to some extent on the solvent used, and not only on the properties of the solutes.

For substances (I), (VI) and (IX) there are much larger variations in the long axis order from one solvent to another. It is noteworthy that the ordering ability of the solvents are not the same for all the solutes. While compound (VI) has the highest order in CCH-4 and lowest in CCH-7, compound (IX) shows the highest order in CCH-7 and lowest in CCH-4. Even in related solvents like the three present cyanobicyclohexyls, there is a marked variation in the solute ordering. Therefore, the solute polarizability cannot be the only factor determining the orientational order.

*The order parameter D.* In eqn. (7) an expression was derived for the biaxiality, or deviation from cylindrical symmetry of a molecule. Van der Meer and Vertogen<sup>14</sup> considered the molecular dimensions of the solute to be the molecular tensor property  $\gamma$ . Luckhurst *et al.*<sup>18</sup> derive the same expression, but they use the polarizability as the property  $\gamma$ .

The order parameters  $D$  are plotted *versus* the order parameters  $S$  in Figs. 9–11 for the three compounds in which both parameters are determined. Even in the three closely related solvents the biaxiality seems to depend upon the solvent used to a certain extent. Compound (VI), however, had large variations in the  $S$  order in the three solvents (Fig. 5), but the biaxiality seems nearly independent of the solvent (Fig. 9). For dye (IX) the biaxiality as well as the long axis order are highest in CCH-7. The biaxiality in anthraquinone (I) varies from 0.0 to 0.25 depending on the host liquid. It is clearly seen that the intermolecular potential must vary from one liquid crystal to another. Thus, the dispersion forces alone cannot be responsible for the long range order in the liquid crystal guest-host system.

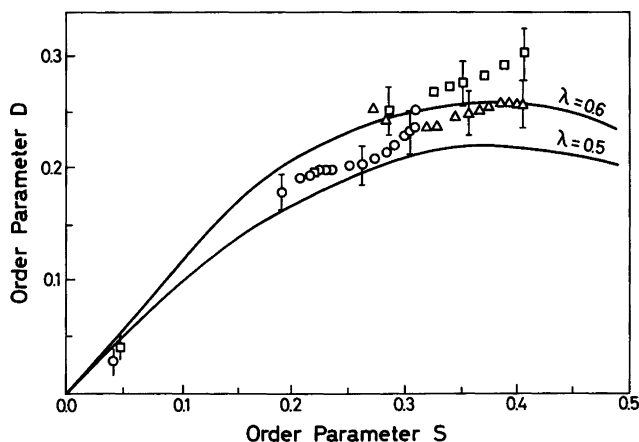


Fig. 10. Order parameter  $D$  versus order parameter  $S$  for (IX) in three different solvents. For clarity error bars are omitted from most of the points. Theoretical curves for two different values of  $\lambda$  shown. The  $\lambda$  calculated from polarizability is 1.56. From the molecular dimension a value of 0.46 is obtained. Curves as in Fig. 9.

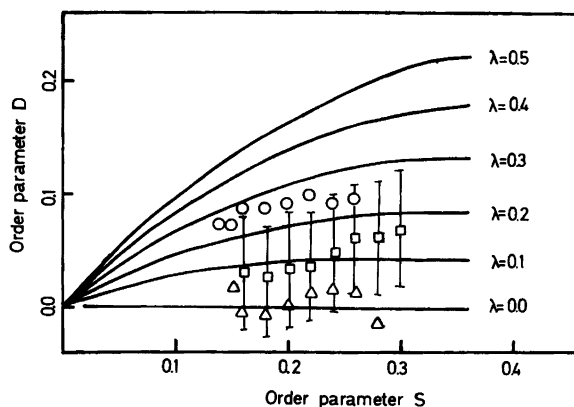


Fig. 11. Order parameter  $D$  versus  $S$  for I in three liquid crystals. Theoretical curves for different values of  $\lambda$  are shown. The values found from polarizability and shape are 1.33 and 0.38, respectively. Curves as in Fig. 9.

The order parameter  $D$  for (VI) is given in Fig. 9 for different  $S$  values. The theoretical  $\lambda$  value from the shape biaxiality is 0.40, which is in good agreement with the experimental data. A much higher value of  $\lambda$  equal to 1.93 was obtained from the polarizability. The value of  $\lambda$  found experimentally for (VI) is slightly lower than the values 0.54–0.61 found by NMR spectroscopy in a number of solvents.<sup>45</sup>

In Fig. 10 we have plotted the data for (IX). The theoretical  $\lambda$  value from shape biaxiality is 0.46, which is slightly less than the value found experimentally. If the biaxiality is calculated from the polarizability, we get  $\lambda$  equal to 1.56.

For both (VI) and (IX) the biaxialities found experimentally agree well with the ones calculated from the dimensions of the molecules, whereas calculations based on the polarizabilities of the molecules yielded a value three or four times larger than the experimental value.

The values for the parent compound anthraquinone are plotted in Fig. 11. These points show  $D$  values that are lower than expected from the shape biaxiality (0.38), whereas compounds (VI) and (IX) gave values slightly higher than expected from the shape alone. It was shown earlier that anthraquinone also gave anomalous results for the  $S$  order parameter. These features strongly suggest that there are some kind of specific interactions between anthraquinone and cyanobicyclohexyl. A possible explanation might be hydrogen bonding between the somewhat acidic hydrogen on the same carbon as the cyano group and the oxygen of anthraquinone. In the substituted anthraquinone on the other hand, the oxygen would already be engaged in an intramolecular hydrogen bonding.

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