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Ultraviolet, Infrared and Magnetic Resonance Spectroscopy on Liquid Crystals†

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1. Introduction

Liquid crystals comprise the states of intermediate order that may have properties in common with normal isotropic liquids as well as with solid crystals and, for this and other reasons, provide a matrix for experiments on oriented molecules which has considerable advantages:

(1) With nematic liquid crystals and some smectic liquid crystals it is easy to obtain uniformly aligned samples corresponding to single crystals with solids.

(2) Nematic liquid crystals have solvent properties practically as good as isotropic liquids and there should be no difficulty to find a suitable solvent for nearly any organic compound.

(3) The combination of orientational order and of high molecular mobility which can be obtained with many nematic solvents is extremely useful in magnetic resonance studies. It provides us with a method for the study of molecular geometries.

Experiments with oriented molecules are only one aspect of spectroscopy in liquid crystals. We may use spectroscopical methods also to study the structure and the molecular order of the liquid crystal itself and draw conclusions on the molecular interactions connected with the formation of these states. Measurements of relaxation times in magnetic resonance experiments give in addition

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information on the dynamics of orientational fluctuations in these systems.

In recent years a large number of spectroscopical studies have been published, especially on magnetic resonance spectroscopy. Several review articles and a monograph covering the latter field are available.(1–4) The field is much too extensive for a comprehensive representation in a lecture. We regard, therefore, only some general features of spectroscopy in liquid crystals and discuss a few topics in more details which seem to me of special interest in connection with molecular structure and interactions in liquid crystals.

2. General Features and Comparison of UV, IR and Magnetic Resonance Spectra

With respect to their optical properties uniformly aligned nematic liquid crystals and smectic liquid crystals of type *A* are uniaxial. For a complete determination of their *UV* and *IR* absorption spectra measurements should be made with linear polarized light for the direction of polarization parallel and perpendicular to the optical axis.

These absorption measurements on liquid crystals are often difficult because the absorption may be very high and extremely thin layers may be needed. In the UV range it may be necessary to use layers as thin as 0.1 micron. The use of two polarizers, one in front of the layer and the second one as analyzer behind the layer, can be useful to suppress errors due to incomplete uniformity in alignment in such cases of high absorption.

Fortunately these difficulties do not arise when the liquid crystal is used as a matrix.(5–7) It can of course only be used in wavelength ranges when the absorption of the liquid crystal solvent itself is weak. The concentration of the solute molecules can always be kept low enough for a reasonably high transmission.

Many nematic liquid crystals can be relatively easily aligned in thin layers by surface action. Figure 1 shows, as an example, an aligned layer of nematic liquid MBBA (4-methoxybenzylidene 4-*n*-butylaniline) between crossed polarizers. The alignment was produced by rubbing the surfaces. The polarization of the incoming light is parallel to the direction of rubbing. The bright double lines follow inversion walls, which separate areas in which the preferred orientation differs 180°. In the center of the walls the molecules are preferably perpendicular to the direction of rubbing, while in the outside area they are preferably parallel to it. The preferred orientation changes continuously when we cross a wall until a complete turn of 180° is made and a physically equivalent orientation is regained. Inversion walls are common disturbances of alignment which are often difficult to avoid.

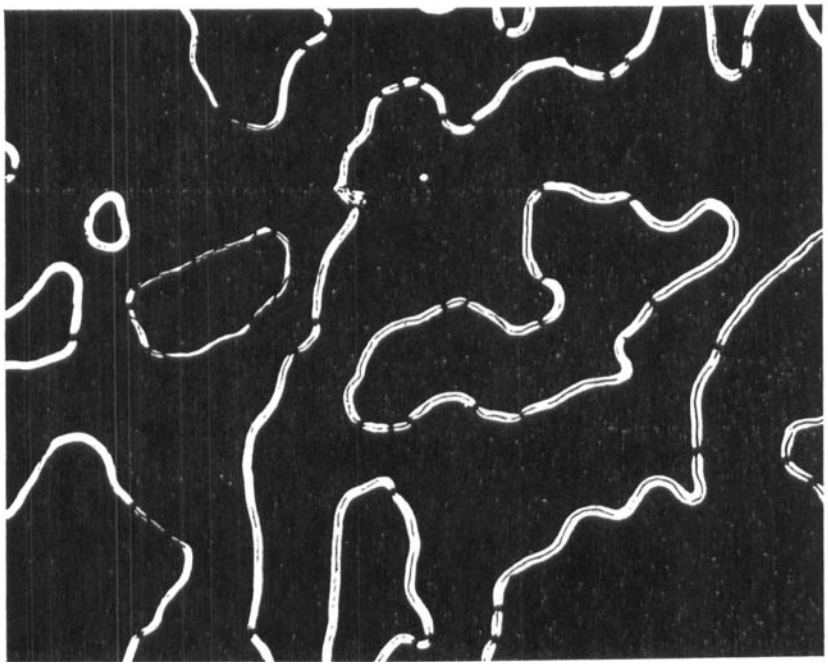


Figure 1. Surface aligned layer of nematic liquid 4-methoxybenzal-4-*n*-butylaniline, ca. 0.1 mm thick, crossed polarizers parallel and perpendicular to direction of rubbing.

Figure 2 shows the UV spectra of heptyloxyazoxybenzene in the isotropic liquid phase, the nematic liquid crystal state and the smectic state. Positions and intensities of the absorption bands are practically unchanged which demonstrates that no change of the π-electronic structure of the molecules is connected with these phase transitions.

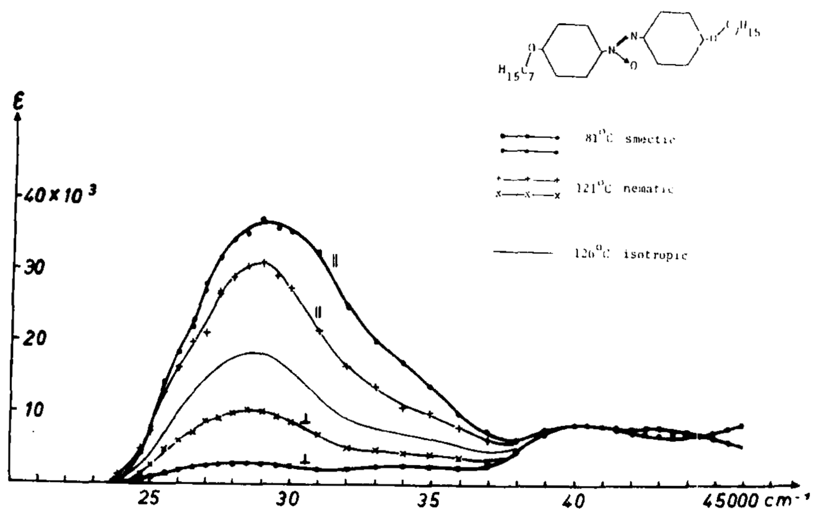


Figure 2. UV-absorption, molar extinction coefficient of 4,4′-di-*n*-heptyloxyazoxybenzene for linear polarized light, parallel (∥) and perpendicular (⊥) to optical axis. (According to Ref. 8).

The dichroism in the nematic phase is a function of the temperature it increases with decreasing temperature. In the smectic *C* phase, the dichroism is stronger than in the nematic phase and it shows only little temperature dependence.

There is a difficulty which should be mentioned here. Heptyloxyazoxybenzene forms a smectic phase of type *C* that is optically biaxial.(9) For the evaluation of the absorption measurements it has been treated as uniaxial which, however, is probably a fairly good approximation.

In Fig. 3 parts of the infrared absorption spectrum of undecadienic acid is reproduced. It demonstrates the similarity of line positions and intensities in the isotropic and nematic phase. The inner molecular vibrational frequencies are not noticeable shifted at the phase transition. The dichroism in the nematic phase is again larger at lower temperatures.

Figure 4 shows Raman lines of the normal isotropic liquid, the nematic liquid crystal and the solid crystalline phase of PAA (4,4′-di-methoxyazoxybenzene). The alignment of the nematic sample has not been specified. It is not uniform. The solid spectrum is taken with a polycrystalline sample.

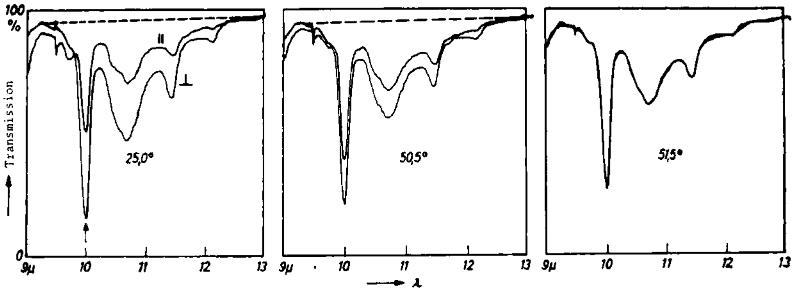


Figure 3. Sections of the infrared spectra of 2,4-nonadienic acid with linear polarized light, parallel (||) and perpendicular (⊥) to optical axis; nematic phase at 25 and 50.5 °C and normal liquid at 51.5 °C. (According to Ref. 10).

Again the nematic spectrum is very similar to the spectrum of the isotropic phase. There are, however, additional features which indicate that the absorption peaks of low frequency vibrations where the molecules react approximately like rigid bodies are somewhat better defined in the nematic phase. In the solid crystal, these frequencies are fairly sharp and can be well observed in the 50 to 100 cm^{-1} region. Also a splitting of the inner molecular vibration frequencies can be observed.

As we have seen, the frequencies and intensities of the electronic transitions and between molecular vibrational states are about the same in the nematic liquid crystalline state as in the isotropic liquid state and the spectrum of the different states are very similar. This is completely different for magnetic resonance spectroscopy. Especially proton magnetic resonance spectra change dramatically at the normal liquid to liquid crystal phase transition.

Figure 5 shows as an example the proton magnetic resonance spectrum of PAA in different states: normal liquid, nematic liquid crystal and solid crystal. The absorption curve is shown for the isotropic liquid. The nematic spectrum and the solid spectrum is for technical reasons represented by the derivative curves of the absorption. The changes in the spectra are due to changes in the molecular orientation and molecular mobility. They are not due and do not indicate changes of the molecular structure at the phase transitions.

The resonance frequencies of the nuclei are in the first place determined by the Zeeman splitting of the spin levels in the applied

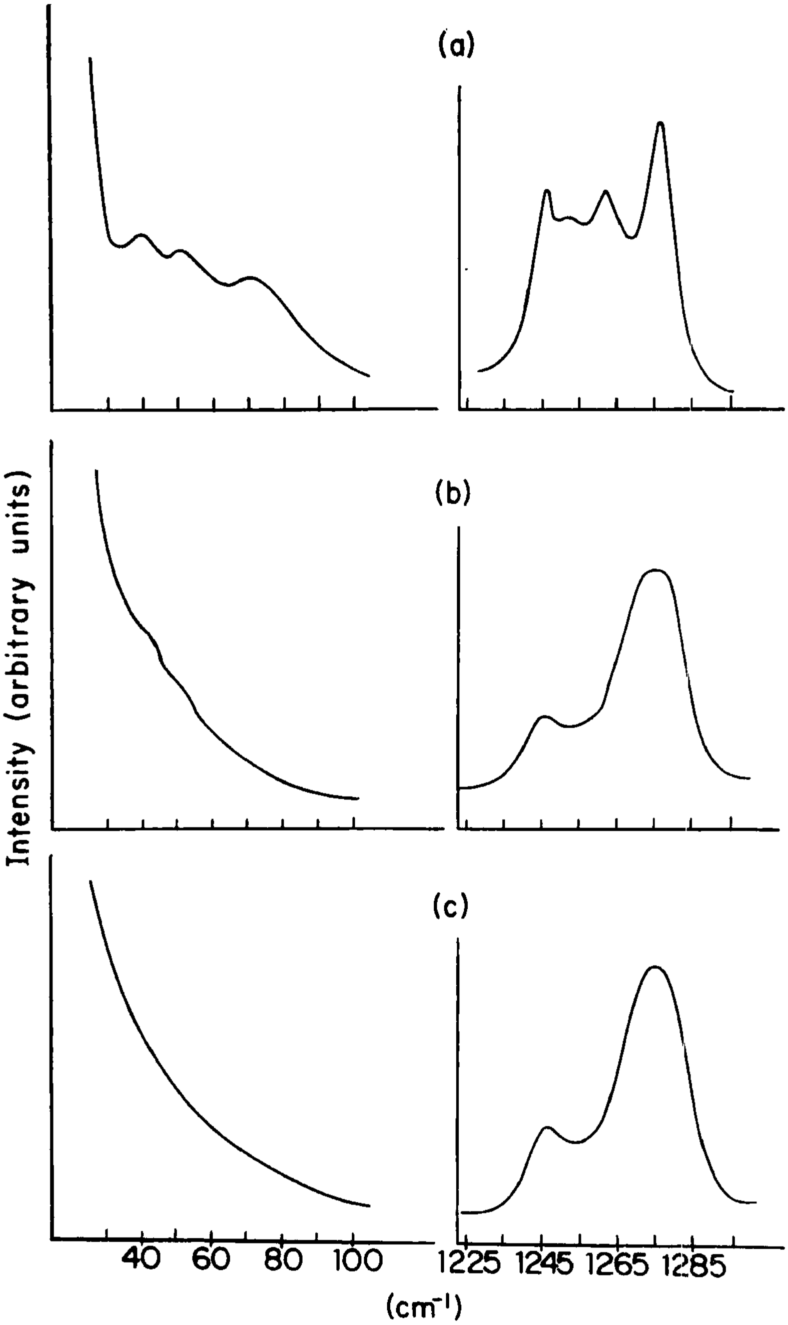


Figure 4. Sections of Raman spectra of 4,4′-dimethoxy-azoxybenzene, (a) solid, (b) nematic, (c) normal liquid. (According to Ref. 11).

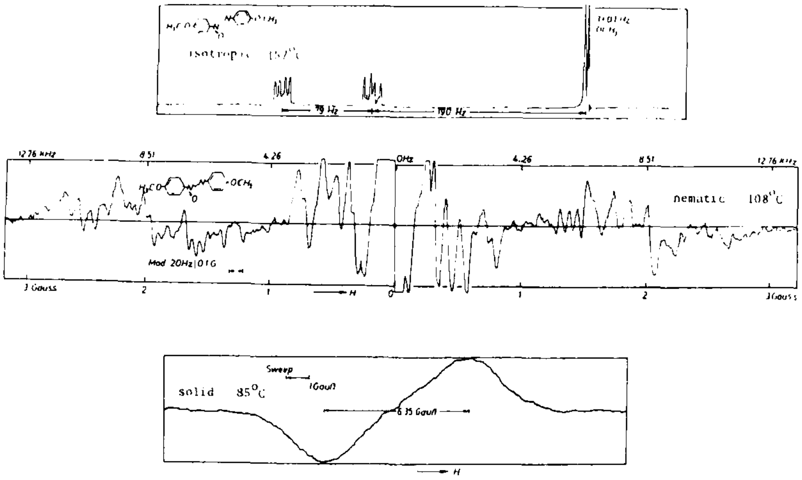


Figure 5. PMR spectra of 4,4′-dimethoxy-azoxybenzene. (According to G. Englert, see Ref. 12).

strong magnetic field. The local fields differ somewhat for different protons because of the screening by the surrounding electron clouds.

In the spectrum of the isotropic liquid phase these differences in screening or, in other words, the chemical shifts determine the overall splitting of about 270 Hz at the resonance frequency of 60 MHz. The overall splitting in the liquid crystal is nearly two orders of magnitude larger. In the solid crystal it is another factor 2 larger. While in the nematic phase a detailed fine structure is observed, there is only a broad band without structure in the solid.

The large splitting in the nematic and the solid phase is due to the direct magnetic interaction between the protons, which in normal liquids with a high molecular mobility reduces to zero. The fine structure is lost in the solid for two reasons:

(1) The solid sample was a polycrystalline sample and not uniformly aligned, contrary to the nematic liquid crystal which is aligned by the magnetic field.

(2) The molecules in the solid have little mobility and therefore the intermolecular spin–spin interactions are effective.

The fine structure in the nematic phase is not always observable. It disappears with molecules that have many more protons than PAA because there are too many interacting nuclei. When nematic liquids are used as solvents for NMR experiments this is an advantage because the resonance lines of the solute can then be observed on a smooth background.

3. Orientational Order and S-Matrix

The dichroism in UV and IR spectra, the direct magnetic couplings and quadrupole splitting observable in magnetic resonance experiments are all due to the orientational order of the molecules in liquid crystals. To characterize this orientational order for spectroscopic purposes it is useful to introduce a set of average values of spherical functions of second order (see for information References 1–4 or 13). This set of values can be written as a matrix which transforms by a change of the molecular coordinate system as a second rank tensor.

Let ξ, η, ζ, denote the axes of a molecular cartesian coordinate system and θ_ξ, θ_η, θ_ζ, the angles between these axes and the symmetry axis of the nematic liquid crystal. Then the elements of the matrix are given by:

$$S_{lk} = 1/2\langle 3 \cos\theta_l \cos\theta_k - \delta_{lk}\rangle,$$
$$l, k = \xi, \eta, \zeta. \qquad (1)$$

The trace $\sum S_{ll}$ is zero and there exists always a principle molecular coordinate system where the matrix is diagonal.

It is convenient to refer to the diagonal elements S_{ll} as degree of order or S-value of the corresponding axis. When β_ξ, β_η, β_ζ are the direction cosines of a given molecular axis p, q in the ξ, η, ζ-system then its S-value can be expressed by the elements of the S-matrix

$$S_{pq} = \sum_{l,k} \beta_l \beta_k S_{lk}. \qquad (2)$$

Since the S-matrix has only five independent elements, more than five S-values are always linearly dependent on each other. These considerations are, however, only valid for rigid molecules. The number of independent S-values is reduced in the case of symmetrical molecules. It reduces to one when the molecule has a three or more fold symmetry axis. The relation between the S-values is of major importance. It is, for instance, essential for geometrical structure determination of molecules by NMR studies.

The S-matrix contains all information on molecular orientational order that we may obtain from infrared and UV-spectroscopical studies as well as from the analysis of magnetic resonance spectra, provided in the latter case that the molecular mobility is high so that effective coupling constants obtained by averaging over the molecular motions may be used.

When we regard an absorption band of a linear polarized electronic or vibrational transition, then the degree of order of the transition axis determines the dichroism. We have the relation

$$S_{\mathrm{tr}} = \frac{f_1 - f_2}{f_1 + f_2} \tag{3}$$

which allows to calculate the S-value of the transition axis out of the integrated intensities f_1 and f_2 of the absorption band measured with linear polarized light, polarized parallel and perpendicular to the optical axis.

In ESR experiments information on the orientation of the radical in the liquid crystal can be obtained from the change of the hyperfine coupling. The hyperfine coupling constants are changed because of the direct magnetic interaction between the nuclei and the electron. The change of the coupling constant is given by

$$\delta A = \sum_{ij} S_{ij} A_{ij} \tag{4}$$

where A_{ij} are the components of the coupling tensors in the molecular coordinate system. It is assumed here that the magnetic field is parallel to the symmetry axis of the nematic liquid. When the coupling tensor has a rotational symmetry as it is the case for many interesting radicals, we can write

$$\delta A = S_{\mathrm{sym}} \Delta A. \tag{5}$$

Here S_{sym} is the degree of order of the axis of the coupling tensor and $\Delta A = A_{\parallel} - A_{\perp}$ the difference between its principle values parallel and perpendicular to the symmetry axis.

In case of electric quadrupole interactions of the nucleus with the electron cloud we have again equations analogous to (4) and (5) for the resulting quadrupole interaction constant.

The coupling constant for the direct magnetic coupling between two nuclei p and q may be defined as

$$B_{pq}^{\text{dir}} = -\frac{h}{8\pi^2}\gamma_p\gamma_q\left\langle\frac{3\cos^2\theta_{pq}-1}{r_{pq}^3}\right\rangle \tag{6}$$

where h is Planck's constant, γ denotes the gyromagnetic ratio. r_{pq} is the distance between the two nuclei and θ_{pq} the angle between the nuclear axis and the magnetic field. The angle brackets indicate that the average over the molecular orientational motion has to be taken. Here it has to be assumed that the molecule has a sufficiently high mobility.

For rigid molecules when the expectation value $\langle r_{pq}^{-3}\rangle$ is independent of θ_{pq} we have

$$B_{pq}^{\text{dir}} = -\frac{h}{4\pi^2}P_2(\alpha)\gamma_p\gamma_q\frac{1}{\mathbf{r}_{pq}^3}S_{pq}. \tag{7}$$

$\mathbf{r}_{pq}$ may be defined as the NMR distance between the nuclei and S_{pq} is the degree of order. We have included here the case that the magnetic field is not parallel to the nematic symmetry axis. α denotes the angle between the magnetic field and this symmetry axis and

$$P_2(\alpha) = \tfrac{1}{2}(3\cos^2\alpha - 1) \tag{8}$$

is the spherical function of second order. It is equal to 1 for $\alpha = 0$.

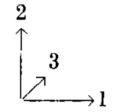
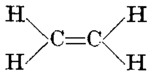
4. Orientation and Interactions

The information on molecular orientations that we obtain by spectroscopical measurements allows us to study the interactions that determine the molecular orientational order. By what factors this orientation is determined depends much on the kind of liquid crystal under consideration.

The orientation, for instance, that was found for the solvent molecules of nematic liquid polypeptide solutions is supposed to be due to associations of the small solvent molecules with the oriented polymers. The comparison of the orientation found for dimethyl formamide in different nematic polypeptide solutions supports this assumption.(14) The orientation varies considerably and depends, therefore, obviously on specific solute solvent interactions.

In lyotropic systems, e.g. in soap water solutions, it is of importance whether a molecule dissolved in such a system stays preferably in the water or prefers to stay inside the aggregates formed by the amphiphilic compounds. Benzene, for instance, is hydrophobic and it has been found to have an orientation in these systems comparable in extent to that in thermotropic liquid crystals.(15) For hydrophilic compounds which stay outside the aggregates one expects, on the other hand, only very little orientation.

TABLE 1 Orientation of acetylene and ethylene in nematic solution. The first column indicates the position of the molecular coordinate system. (See Refs. 16 and 17).

	S_{11}	S_{22}	S_{33}
$H—C\equiv C—H$	-0.014	0.007	0.007
	0.064	-0.033	-0.031

The discussion of the orientation in thermotropic liquid crystals is in some respects less complicated than in the above systems since here we have not only macroscopically but also microscopically homogeneous systems and specific intermolecular interactions seem to be less important. It is often assumed that the molecular shape is the dominating factor for the orientation in thermotropic liquid crystals. And indeed for larger molecules it has always been found that they follow this assumption. An elongated molecule always orients preferably with the long molecular axis parallel to the optical axis of the liquid. The long axis has accordingly the largest positive S-value. On the other hand, the shortest axis has the most negative S-value. With small molecules the rule does not always hold.

In Table 1 it can be seen that, contrary to the expectations, the symmetry axis of acetylene has a negative S-value. Ethylene is also an exception. The axis 3, normal to the molecular plane, which corresponds to the shortest molecular dimension has an S-value slightly less negative than that of axis 2. The examples show that the geometrical molecular shape can not explain the observation quantitatively.

For a more detailed and more quantitative discussion of the molecular orientation in thermotropic liquid crystals we regard the free energy of the molecule as a function of its orientation.

$$F = F(\theta_1, \theta_2, \theta_3). \tag{9}$$

It is defined so that $e^{-F/kt}$ gives the Boltzmann factors or statistical weight for an orientation characterized by the values θ_1, θ_2 and θ_3. We expand F into a power series of $\cos\theta_i$. In the principle coordinate system where S_{ik} is diagonal, this gives up to terms in third order

$$F = -(a_0 + a_1 \cos^2\theta_1 + a_2 \cos^2\theta_2). \tag{9'}$$

If we use (10) the measured S-values allow us to determine the coefficients a_1 and a_2 and, therefore, in our approximation the explicit expression for the orientation dependent part of the free energy.

It is on the other hand possible to estimate theoretically the relative values of the energy coefficients of similar molecules. This has been done for instance for fluorobenzene derivatives.(13)

It was assumed that the difference of the coefficients of different fluorobenzenes is due only to the changes in dispersion forces. With additional assumptions and simplifications, it becomes possible starting from the experimental values of one fluorobenzene to derive the coefficients and calculate the S-values of other fluorobenzenes in the same solution.

Table 2 gives the experimental results and the comparison with calculated values obtained in both solvents by adapting the coefficients a_1 and a_2 for 1,4 fluorobenzene.

It is especially interesting to compare the orientation of ortho- and meta-difluorobenzene. Both molecules have a permanent electrical dipolemoment, but for ortho difluorobenzene the axis 2 which is the axis with the highest S-value is parallel to the dipolemoment while for meta-fluorobenzene it is perpendicular to the dipolemoment. According to the theoretical estimation, both molecules should orient equal and it turns out that they indeed orient very similar. It demonstrates that the permanent dipolemoment is of minor importance for the molecular orientation.

The general agreement is an argument for the importance of dispersion forces. The differences of the experimental results in the different solvents show also clearly that a simple interaction model which does not take into account specific solvent properties can only give a rough approximation and cannot explain finer details of orientation effects. It indicates that in the discussion of molecular structure and crystallinity specific intermolecular interactions have to be considered at least when smaller shifts in clearing temperatures are discussed.

5. The Orientational Distribution Function

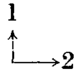
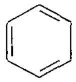
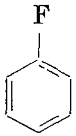
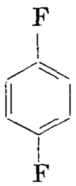
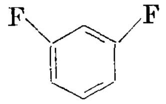
The expression for the free energy used in the previous calculations give us, by definition, the complete orientational distribution function. It is, of course, of interest to compare the theoretical distribution function as given in the approximation (10) with the actual distribution in a nematic solvent.

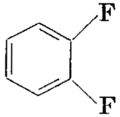
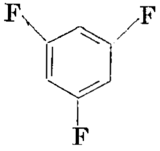
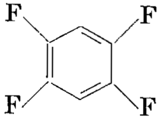
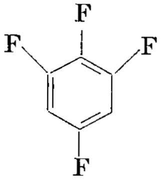
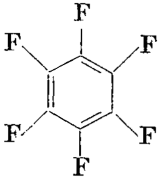
The distribution function can in some cases in fact be experimentally determined by magnetic resonance spectroscopy as first shown by Schwerdtfeger and Diehl.(19) When the viscosity of the liquid crystal is very high, the mobility of the molecules becomes too low for the use of an effective spin-Hamiltonian in ESR experiments.

Instead of averaging over the molecular motion, we have to consider the other extreme that each radical has a quasi-fixed orientation and that all motion can be neglected. When measurements are made under these conditions at different angles between magnetic field and symmetry axis of the liquid it becomes possible to evaluate numerically the distribution function.

Only one radical, vanadyl-acetylaceton has so far been studied in a suitable high viscosity nematic solvent.(19,20) Unfortunately, the experiment gives only the distribution function of the symmetry axis of the coupling tensor. The radical has however no three or more fold symmetry axis which coincides with the axis of the coupling tensor and for that reason a direct check of the approximation (10) is not possible by these results.

TABLE 2 Experimental and calculated S-values and energy coefficients (according to Ref. 18). The position of the molecular coordinate system is indicated in the first column. Values in parenthesis are calculated with parameters adapted for 1,4-difluorobenzene. Solvent I 4,4′-di-n-hexyloxyazoxybenzene, solvent II 3:2 mixture of 4-heptanoyloxy- and 4-hexanoyloxy-4′-ethoxyazobenzene

	Solvent I				Solvent II			
	S_1	S_2	a_1/kT	a_2/kT	S_1	S_2	a_1/kT	a_2/kT
	0.05	0.05	0.82	0.82	0.05	0.05	0.82	0.82
	(0.05)	(0.05)	(0.81)	(0.81)	(0.04)	(0.04)	(0.55)	(0.55)
	0.10	0.01	1.09	0.70				
	(0.11)	(0.01)	(1.25)	(0.81)	(0.12)	(−0.01)	(1.11)	(0.55)
	0.18	−0.03	1.68	0.81	0.20	−0.06	1.66	0.55
	(0.18)	(−0.03)	(1.68)	(0.81)	(0.20)	(−0.06)	(1.66)	(0.55)
	0.02	0.10	0.83	1.17	0.00	0.14	0.88	1.47
	(0.02)	(0.13)	(1.03)	(1.46)	(0.00)	(0.13)	(0.83)	(1.39)

	0.03 (0.02)	0.11 (0.13)	1.03 (1.03)	1.36 (1.46)	0.03 (0.00)	0.11 (0.13)	1.03 (0.83)	1.36 (1.39)
	0.08 (0.08)	0.08 (0.08)	1.41 (1.46)	1.41 (1.46)	0.08 (0.08)	0.08 (0.08)	1.41 (1.39)	1.41 (1.39)
	0.00 (−0.02)	0.18 (0.21)	1.23 (1.24)	1.95 (2.12)	0.01 (−0.04)	0.17 (0.23)	1.28 (1.11)	1.92 (2.22)
	0.14 (0.15)	0.04 (0.04)	1.82 (1.90)	1.42 (1.46)	0.15 (0.16)	0.04 (0.02)	1.95 (1.94)	1.52 (1.39)
	0.14 (0.11)	0.14 (0.11)	3.10 (2.12)	3.10 (2.12)	0.14 (0.11)	0.14 (0.11)	3.10 (2.22)	3.10 (2.22)

6. Thermal Fluctuations and Spin-Lattice Relaxation Times

In nematic solutions of low viscosity the positions of the magnetic resonance lines are given by an effective Hamiltonian obtained by averaging over the molecular orientational motion. It gives us the orientation parameters. Measurements of the spin-lattice relaxation times give us some information on the motion itself.

It is known from light scattering and other optical observations that in nematic liquid crystals strong thermal fluctuations of relatively long wavelengths are present. It can, therefore, be expected that there are low frequency components in the molecular orientational motion which will lead to unusual effects in the spin-lattice relaxation times.

A first theoretical treatment was made by Pincus.(21) His starting point is the general relation for T_1 valid in the case of two interacting nuclei of spin 1/2 at a fixed distance r

$$\frac{1}{T_1} = \frac{9}{8}\gamma^2 \frac{h^2}{4\pi^2 r^2}\left[\zeta_1(\omega) + \zeta_2(2\omega)\right]. \tag{10}$$

$\zeta_1(\omega)$ and $\zeta_2(2\omega)$ are Fourier transforms of orientational correlation functions for the motion of the nuclear axis.

For the calculation of the Fourier transforms, Pincus used the theory of thermal fluctuations as developed by de Gennes and coworkers.(22) He assumed that the axis of the considered pair is parallel to the long axis of the molecule and assumed further that this can be identified with the director **L** used in the continuum theory. Including possible effects due to diffusion this leads to

$$\frac{1}{T_1} = \frac{9}{16\sqrt{2}\pi^3}\cdot\frac{\gamma^2 h^2}{r^6} - \frac{kT}{(\kappa/\eta + D)^{1/2}}\cdot\frac{1}{\kappa\omega^{1/2}}. \tag{11}$$

Here κ, η, and D denote mean values for an elastic constant, a viscosity coefficient and a diffusion constant.

The frequency dependence predicted by Pincus was in fact found experimentally. The temperature dependence, however, turned out to be not at all in agreement with (11). There is an obvious objection against the treatment by Pincus. It is not justified to identify the momentary orientation of the molecule with the director **L** which is defined as the preferred orientation.

Doane and Johnson(23) avoided this difficulty in their treatment. They introduced a local coordinate system in which one axis coincides with the preferred orientation as obtained by averaging over a sufficiently large area surrounding the considered molecule. The orientational fluctuations of the molecule in this local coordinate system are assumed to contribute nothing to the frequency dependence of T_1. The latter is determined, therefore, by the orientational motions of the local coordinate system which can be described by de Gennes theory. The final expression is

$$\frac{1}{T_1} = \frac{9}{16\sqrt{2}\pi^3} \cdot \frac{\gamma^2 \hbar^2}{r^6} \cdot \frac{kT}{(\kappa/\eta + D)^{1/2}} \cdot \frac{S^2}{\kappa\omega^{1/2}}. \tag{12}$$

It differs from the previous one only by the factors S^2. The frequency dependence is unchanged, but the temperature dependence is different. In agreement with the experiment, Eq. (12) gives little temperature dependence, because the ratio S^2/κ has been found to be nearly temperature independent. The problem is, however, still not yet solved satisfactorily. Other difficulties in the explanation of T_1 experiments have turned up (see Ref. 24).

Finally it is interesting to mention that pretransitional effects near the normal liquid to nematic liquid transition point have also observable effects on relaxation times and line widths in the normal liquid. This has first been noticed by Blinc *et al.*(25) Very recently, careful line width measurements for N^{14} resonances have been made with PAA by Cabane and Clark.(26)

They find a temperature dependence of the line width which agrees very good with the much earlier studies of magnetic birefringence in PAA.(27) The Cotton–Moutton constant has a very similar temperature dependence as the line width, and by extrapolation it is found that both go to infinity at a temperature which is a few degrees lower than the transition temperature. It confirms that the transition is of first order although in many respects it is not very far from a second order transition. Correlations between pretransitional effects have been discussed theoretically some time ago by de Gennes(28) and these experimental results confirm his predictions.

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