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Liquid Crystals

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K. Praefcke[a]; P. Marquardt[ab]; B. Kohne[a]; Z. Luz[b]; R. Poupko[b]
[a] Institute of Organic Chemistry, Technische Universität Berlin, Berlin, Germany [b] The Weizmann Institute of Science, Rehovot, Israel

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Deuterium NMR studies of inositol liquid crystals [1]

by K. PRAEFCKE†*, P. MARQUARDT†‡, B. KOHNE†,
Z. LUZ‡ and R. POUPKO‡

† Institute of Organic Chemistry, Technische Universität Berlin,
D-1000 Berlin 12, Germany

‡ The Weizmann Institute of Science, Rehovot 76100, Israel

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Deuterium NMR investigations are presented on members of two new mesogenic series derived from the naturally occurring stereoisomers *myo*- and *scyllo*-inositol. Tetraethers of these two series exhibit thermotropic columnar phases in which the columns are apparently formed by stacked hydrogen bonded dimers of these molecules which chemically are vicinal diols. Deuterium NMR measurements were performed on the tetraoctyl homologues **2e** (a *cis* diol) and **3e** (a *trans* diol) of these series. We have investigated mixtures of these diols with small amounts of benzene-d_6 as probe molecules as well as samples of the neat diol compounds deuteriated at their hydroxyl groups. The results obtained show that the mesophases of both compounds are uniaxial and align partially in a magnetic field upon slow cooling from their isotropic liquids. The alignment is with the director parallel to the field direction indicating that the anisotropic magnetic susceptibility of this mesophase is positive. The deuterium quadrupole splitting of the benzene-d_6 probe in both systems is temperature dependent and in the *trans* diol **3e** it even changes sign. This is interpreted in terms of a model in which the benzene-d_6 probe equilibrates rapidly between two (or more) solvation sites with quadrupole splittings of opposite signs. The deuterium spectra of the neat deuterium labelled *cis* diol **2e** exhibit two different signals due to the two deuterons which are located at the axial and equatorial hydroxyl groups. This indicates that there is no fast intra- or intermolecular exchange of the hydroxyl hydrogens. The overall quadrupole splittings of the hydroxyl deuterons in this compound are highly reduced compared to their static values and this is interpreted in terms of motional modes involving both reorientation of the hydroxyl deuterons about their C–O axis and overall reorientation of the molecules (or pairs of molecules) around the columnar axes. The corresponding spectra of the neat deuteriated *trans* diol **3e** exhibit a single spectrum indicating that both hydroxyl deuterons in this compound are equivalent, or very nearly so. Within the mesophase region the spectrum undergoes gradual changes due to the increase in the molecular mobility, but the overall motional narrowing is less than in the *cis* isomer **2e**. Apparently due to stronger hydrogen bonding in the *trans* isomer **3e** the precession of the hydroxyl groups is hindered and a fast molecular reorientation is only possible at high temperatures.

1. Introduction

Although the formation of mesophases by non-calamitic compounds was discussed as early as 1923 [2] and studied theoretically by various authors since 1938 [3] it took more than 50 years until, in the late seventies, the first example of a discotic mesophase was realized [4]. This form of thermomesomorphism usually results in a spontaneous self-organization of disc-shaped [5] molecules into columnar structures, although in a

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* Author for correspondence.

few cases [6] nematic (N_D) phases are also observed. Studies of the mesomorphic properties of the di-isobutylsilanediol [7], a geminal diol, as well as of carbohydrate, inositol, inosose and phloroglucitol liquid crystals [8 (*a*–*d*)] show that a large number of these amphiphilic compounds form columnar mesophases consisting of hydrogen bonded multimers rather than of monomers as in the case of conventional discotic liquid crystals.

Here we describe NMR measurements on members of two new series of discotic liquid-crystalline compounds, viz. the *myo*- and *scyllo*-inositol tetraalkylether diol derivatives of type **2** and **3**, respectively.

As shown in scheme 1, the members of these two series are stereoisomeric with the *myo*-inositol series **2** having the two vicinal hydroxyl groups in a *cis* configuration and consequently one hydroxyl in the axial and the other in the equatorial position, whereas in the *scyllo*-inositol series **3** both hydroxyl functions are equatorially arranged in a *trans* configuration at the inositol ring. In a hitherto unpublished study [8 (*b*)] it was found that depending on the length of their alkyl side groups members of both series are thermotropic liquid-crystalline and exhibit columnar phases as differential scanning calorimetry (DSC), optical microscopy, and X-ray diffraction investigations revealed. As deduced from the X-ray results, a special feature of these mesophases is the fact that the discoid units which build up the columns consist of dimers, most likely formed by hydrogen bonding of the hydroxyl groups.

In general, the *myo*-inositol tetraethers investigated form mesophases solely of hexagonal symmetry (D_h) whereas most of the *scyllo*-inositol ones studied show polymorphism exhibiting a succession of mesophases with different structures.

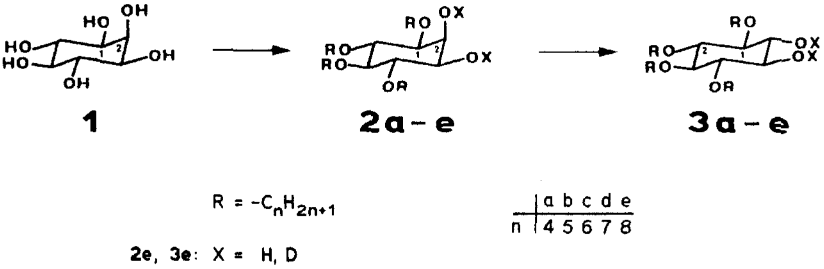
Here, we extend our earlier characterization [8 (*b*)] of these mesogenic inositol systems using deuterium NMR spectroscopy. In particular, we present results on the two stereoisomeric inositol tetraoctylethers **2e** (a vicinal *cis* diol) and **3e** (a vicinal *trans* diol) in which the four alkyl chains are in equatorial arrangements (cf. scheme 1). The phase sequence of the neat *cis* diol **2e** determined by DSC is

$$\text{Solid} \xrightarrow{37{\cdot}1^\circ\text{C}} D_{\text{ho}} \xrightarrow{44{\cdot}1^\circ\text{C}} \text{I}$$

whereas based on optical microscopy observations [8 (*b*)] that of the *trans* diol **3e** is

$$\text{Solid} \xrightarrow{42{\cdot}6^\circ\text{C}} D_1 \xrightarrow{55{\cdot}8^\circ\text{C}} D_2 \xrightarrow{69{\cdot}5^\circ\text{C}} D_3 \xrightarrow{78{\cdot}1^\circ\text{C}} D_{\text{ho}} \xrightarrow{91{\cdot}7^\circ\text{C}} \text{I}.$$

The three mesophase transitions ($D_1 \rightarrow D_2$, $D_2 \rightarrow D_3$, and $D_3 \rightarrow D_{\text{ho}}$) are observed as reversible and reproducible transformations of textural features, but they could not as



Scheme 1. Synthetic pathway for **2a–e** and **3a–e**.

yet be confirmed by other physical methods. In fact, no DSC peaks could be identified for these phase transitions and our powder X-ray measurements performed up till now [8 (*b*)] show the same pattern of hexagonal symmetry with very little changes in the lattice parameters through the whole mesophase region.

Two approaches were used in the NMR investigations of the inositol derivatives **2e** and **3e**. In one the mesogens were doped with small amounts of deuteriated benzene and the NMR of the latter measured within the mesophase region. These measurements provided information on the symmetry and alignment properties of the mesophases of **2e** and **3e** as well as on specific solute–solvent interactions.

An additional characterization of the mesomorphic states of **2e** and **3e** was achieved by direct investigation of these stereoisomeric diols deuteriated at their hydroxyl groups. These measurements revealed information on the modes of motion of these molecules (or pairs of molecules) in their mesophases.

2. Experimental

2.1. *Synthetic procedures*

A detailed description of the syntheses of the non-deuteriated *myo*- and *scyllo*-inositol tetraethers **2a–e** and **3a–e**, respectively, as well as a presentation of their phase transition data is given elsewhere [8 (*b*)]. The structures of all inositol derivatives **2a–e** and **3a–e** have been confirmed by IR and mass spectrometry, as well as ^1H and ^{13}C NMR spectroscopy [8 (*b*)]. In particular, the coupling constants of the cyclohexyl protons gained from ^1H NMR spectra prove the stereochemistry of these *myo*- and *scyllo*-inositol derivatives. Therefore, the axial or equatorial positions of substituents, respectively, on the cyclohexyl ring is defined unambiguously. In addition, correct C, H analyses have been obtained for all synthesized *cis* and *trans* diols **2a–e** and 3a–**e**, respectively, within the scope of the precision of the measurements.

2.1.1. *Preparation of the* myo-*inositol 1,4,5,6-tetraalkylethers **2a–e** (vicinal* cis *diols)*

The *cis* diols **2a–e** were obtained in a three step synthesis starting from commercially available *myo*-inositol (**1**):

(i) acetalisation of *myo*-inositol using cyclohexanone [9],
(ii) fourfold alkylation of this protected *myo*-inositol with the corresponding alkylbromides in the presence of powdered potassium hydroxide,
(iii) release of the *cis* diols **2a–e** by an acetal cleavage reaction.

Following this procedure the *cis* diols **2a–e** were obtained as highly viscous oils each of which solidified slowly to waxy crystals at room temperature. Their melting points (DSC) were: **2a** 44·8°C, **2b** ≈20·0°C, **2c** 27·7°C, **2d** 34·5°C and **2e** 37·1°C. The overall yields of these five compounds ranged between 16–41 per cent.

The compounds **2a** and mainly **2e** of this group of *cis* diols are the subject of investigation in this paper only.

2.1.2. *Preparation of the* scyllo-*inositol 1,2,3,4-tetraalkylethers **3a–e** (vicinal* trans *diols)*

The synthesis of the *trans* diols **3a–e** started from the corresponding *myo*-inositol tetraethers, the *cis* diols **2a–e**, and was performed in four steps:

(i) protection of the equatorial hydroxyl group in **2a–e** by selective benzylation using benzylchloride and powdered potassium hydroxide in benzene as solvent,

(ii) the remaining axial OH group was functionalized with methanesulphonyl chloride/pyridine,

(iii) addition of potassium superoxide [10] in dimethylsulphoxide and in the presence of small amounts of 18-crown-6 leading to the conversion of the configuration of the previous axial hydroxyl group into an equatorial one,

(iv) liberation of the benzyl protected equatorial hydroxyl group by catalytic hydrogenation (H_2, Pd/C) leading to the *trans* diols **3a–e**.

This synthetic scheme led to the *trans* diols **3a–e** as white crystals in overall yields of 13–33%. Their melting points (DSC) are **3a** 137·3°C, **3b** 117·5°C, **3c** 48·9°C, **3d** 39·6°C and **3e** 44·3°C.

As an example of this group of *trans* diols compound **3e** has been selected and studied only.

2.1.3. *Deuterium labelling of the* myo-*inositol 1,4,5,6-tetrabutylether* (***2a***), *the* myo-*inositol 1,4,5,6-tetraoctylether* (***2e***), *both* cis *diols, and of the* scyllo-*inositol 1,2,3,4-tetraoctylether, the* trans *diol* ***3e***

The tetraether diols **2a**, **2e** and **3e** deuteriated at their hydroxyl groups were prepared by exchange reactions with CH_3OD. About 250 mg of the dry diols **2a**, **2e** and **3e**, respectively, were dissolved in *c.* 5–10 ml of CH_3OD (99 at.%D) and stirred at 50°C for 10 min. The solvent was evaporated and collected, and the procedure repeated twice using fresh methanol-d_1. After the last exchange the mesogen was dried under vacuum, placed in a short 5 mm tube, vacuum sealed and allowed to crystallize before starting the NMR measurements. In one case (**2e** as an example) the degree of deuteriation was checked by proton NMR and found to be somewhat better than 70 at.%.

2.2. *NMR measurements*

The NMR measurements presented here were made on a Bruker CXP 300 spectrometer using the quadrupole echo technique with 2·5 μs $\pi/2$ pulses and time intervals between pulses of 15–20 μs. The delay time between quadrupole echo sequences was 0·2–4 s. The deuterium spectra of the probe molecules (C_6D_6) were recorded on a Bruker WH 270 using short single pulses. NMR rotation experiments were performed on a WH 90 spectrometer consisting of an electromagnet with a configuration suitable to rotate the sample.

For the measurements using benzene-d_6 as a probe in the mesophases of the considered inositol derivatives solutions of 0·5–0·8 wt % C_6D_6 in the mesogens **2e** or **3e** (in each case *c.* 250 mg) were prepared in standard 10 mm NMR sample tubes. In a typical experiment the solution was first heated to the isotropic liquid, shaken well and then allowed to cool outside the magnetic field to room temperature, yielding a supercooled C_6D_6 doped mesophase. The sample was then placed in the NMR spectrometer and spectra were recorded, first upon heating through the mesophase to the isotropic liquid and then on slow cooling.

3. Results and discussion

3.1. *NMR of C_6D_6 doped* myo-*inositol tetraether* ***2e*** (*a* cis *diol*)

Because of the presence of the C_6D_6 probe molecules the clearing point is reduced by 5–6°C compared to the neat compound **2e** and the mesophase readily supercools to well below 0°C. Examples of spectra observed on heating the supercooled mesophase solution (0·5 wt %) of C_6D_6 in the *cis* diol **2e** are shown in the left hand series of figure 1.

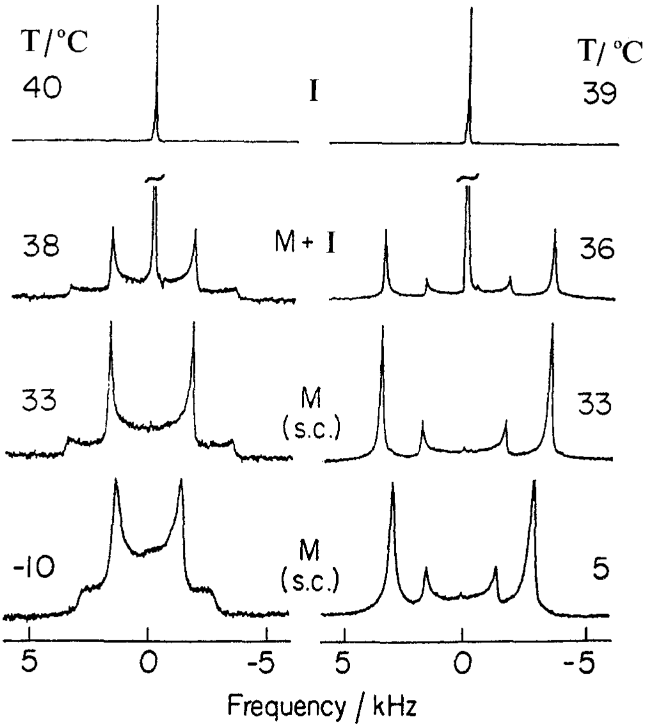


Figure 1. Deuterium NMR spectra of a 0·5 wt% solution of C_6D_6 in the *myo*-inositol tetraoctylether **2e** (a vicinal *cis* diol) in the mesophase region as a function of temperature. The spectra on the left hand side were obtained by heating a non-aligned supercooled solution through the mesophase to the isotropic region whereas the spectra on the right hand side were obtained on slow cooling of the sample (after several heating/cooling cycles through the clearing point). The signals due to the isotropic liquid in the biphasic region (M + I) have been truncated at about half their height.

At −10°C the spectrum is characteristic of a powder pattern of randomly distributed domains having uniaxial symmetry. The quadrupole interaction parameter ($\nu_{\parallel} = 2{\cdot}75$ kHz) is highly reduced with respect to the static value for aromatic deuterons [11] ($\nu_{\parallel} \approx 120$ kHz) indicating rapid reorientational diffusion of the probe molecules within the mesophase. On raising the temperature towards the clearing point the parallel features of the spectrum gradually sharpen, apparently due to the setting-in of some degree of alignment. Around 38°C the sample becomes isotropic as manifested by the appearance of a single peak. As the solution is cooled back to the mesophase region a completely different spectral lineshape is obtained; in particular the parallel features sharpen and increase in intensity. On cycling the temperature of the sample back and forth between the isotropic and mesophase through the clearing point the intensity of the parallel peaks continuously increases eventually resulting in a spectrum consisting of essentially a single doublet (see figure 2). Thus, although the bulk liquid-crystalline phase does not spontaneously orient itself in the magnetic field of the NMR spectrometer, it will align under the conditions just described during its formation from the isotropic liquid [12]. Moreover, these results show that the alignment of the director of this columnar phase is parallel to the field direction, i.e. the anisotropic magnetic susceptibility is positive ($\Delta\chi > 0$). This is in contrast to the situation in the

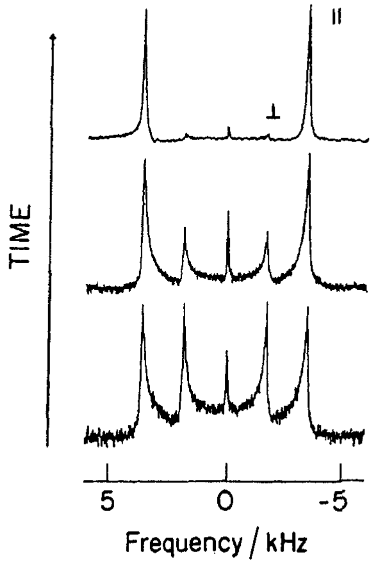


Figure 2. Deuterium NMR spectra of the same sample described in the caption of figure 1 in the mesophase region obtained on progressive temperature cycling through the clearing point. The outer peaks correspond to domains aligned parallel (||) to the magnetic field direction while the inner peaks are the perpendicular features (⊥) of the powder pattern due to the residual non-aligned part of the sample. On increasing the number of temperature cycles the latter signal gradually disappears.

mesophases of conventional discotics, for example derivatives of triphenylene or truxene, where $\Delta\chi$ is generally found to be negative. The different signs of $\Delta\chi$ reflect the opposite magnetic properties of the corresponding central cores of discogens; for aromatic rings $\Delta\chi$ is usually strongly negative whereas for aliphatic ones it is weakly positive. As we have indicated the uniaxial symmetry of the mesophase is reflected by the characteristic pattern observed in the non-aligned sample and by the exact ratio of 2:1 of the splittings of the parallel and perpendicular peaks observed in the aligned sample. Further confirmation comes from a rotation experiment performed on the Bruker WH 90 spectrometer (at 13·8 MHz). When a partially aligned sample, exhibiting spectra of the type shown in figure 2, is rotated by $\pi/2$ about an axis perpendicular to the field direction the intensity of the perpendicular features increases very strongly. This results from the fact that the aligned parallel domains are now oriented perpendicular to the field and overlap the perpendicular features of the powder to give very intense peaks.

The spectra on the right hand side of figure 1 were obtained on cooling a partially aligned sample where both the strong parallel features of the oriented domains and the perpendicular features of the residual non-oriented part of the sample are clearly seen. The splittings of the parallel features as a function of temperature are shown in figure 3. It may be seen that there is a slight increase in the splittings with increasing temperature, probably reflecting changes in the equilibrium distribution of the probe molecules between different solvation sites in the mesophase (see discussion in the next section).

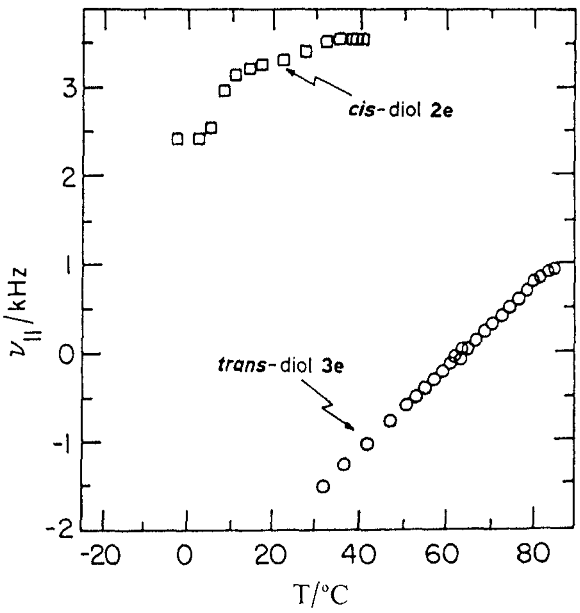


Figure 3. Plots of the quadrupole interaction parameter, $\nu_{\parallel}$ (half of the overall splitting of the parallel features) as a function of temperature observed in the mesophase regions of solutions of C_6D_6 in *myo*-inositol tetraoctylether **2e** (a vicinal *cis* diol, 0·5 wt%) and in *scyllo*-inositol tetraoctylether **3e** (a vicinal *trans* diol, 0·8 wt%), respectively. The sign of the splittings was arbitrarily taken as positive in the case of **2e** and to change from negative to positive upon increasing temperature in the alternative case of **3e**.

3.2. *NMR of C_6D_6 doped* scyllo-*inositol tetraether **3e** (a* trans *diol)*

The left hand row in figure 4 depicts spectra of a doped solution (0·8 wt %) of C_6D_6 in *trans* diol **3e** recorded on heating from room temperature. The low temperature spectra are characteristic of a uniaxial powder pattern, yielding at 32°C $\nu_{\parallel} = 1{\cdot}5$ kHz. On heating, the overall width of the spectrum decreases; it reaches zero at 63°C and then increases again on further heating up to the clearing point where it collapses to a single line. We interpret the gradual decrease of the splitting and its subsequent increase after passing through zero as a continuous (algebraic) change in the quadrupole interaction involving a change of signs at around 63°C. Similar observations of sign change have been made previously in solutions of probe molecules dissolved in discotic mesophases of triphenylene derivatives [13]. Following this work we interpret the results in terms of a model in which the guest molecules occupy two solvation sites involving (i) C_6D_6 molecules being intercalated between the inositol moieties and (ii) C_6D_6 molecules being dissolved in the aliphatic side chain region. It is reasonable to assume that the orientation of benzene in the two sites is quite different, for example parallel to the core moieties in site (i) and perpendicular to it, and consequently with local quadrupole interaction of opposite sign in site (ii). Assuming fast diffusion between these two sites the observed splitting is the weighted average of the splittings in both sites. A shift in the equilibrium population due to a variation of the temperature is reflected as a change in the average interaction.

The same model applies also to the temperature dependent splitting of the C_6D_6 probe in the *cis* diol **2e**. However, the effect is more conspicuous in the *trans* diol **3e** where the average splitting (accidentally) passes through zero.

As for the *cis* diol **2e** the *trans* diol **3e** mesophase could also be partially aligned by slow cooling through the clearing point within the magnetic field. In practice, the alignment was not as complete as for the *cis* isomer, but the preference of the director to align along the field direction is clearly manifested by the increase in the intensity of the parallel features observed on cooling the sample from the isotropic liquid (see the right hand series in figure 4). On further cooling within the mesophase the splitting pattern follows the same trend as observed on heating; it first decreases, passes through zero at 64°C and then increases again. Cooling to below 32°C results in crystallization and expulsion of the C_6D_6 probe (see the bottom right hand trace in figure 4).

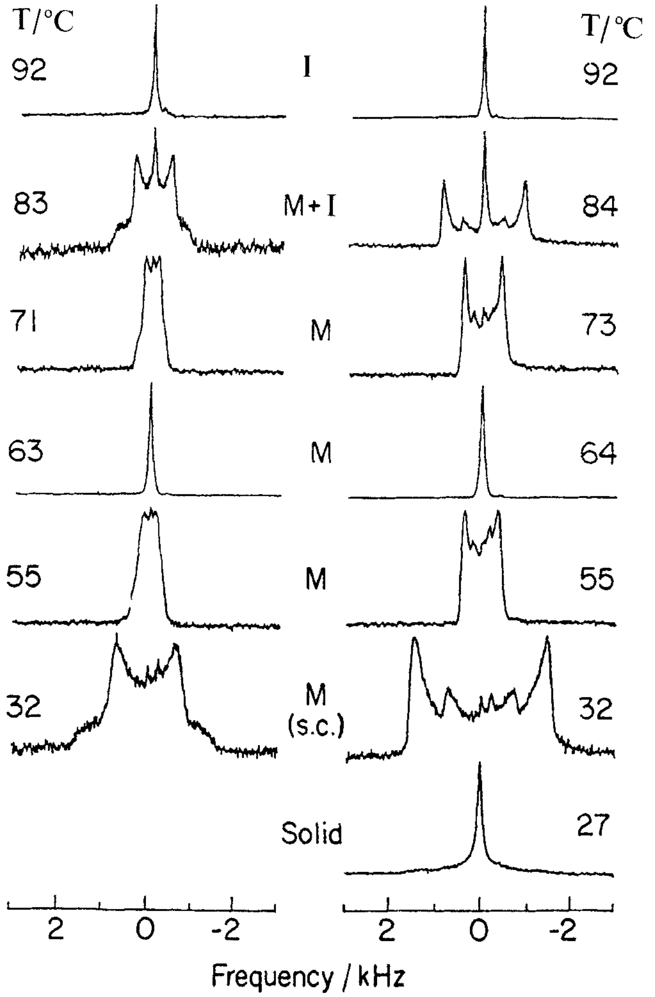


Figure 4. Deuterium NMR spectra for a 0·8 wt% solution of C_6D_6 in the *scyllo*-inositol tetraoctylether **3e** (a vicinal *trans* diol) as a function of temperature. The spectra on the left hand side were obtained on heating a non-aligned supercooled solution through the mesophase to the isotropic region. The spectra on the right hand side were obtained on slow cooling of the solution, after partial alignment by temperature cycling through the clearing point. Note, that both on heating and on cooling the splitting passes through zero at around 63–64°C. On cooling to below ≈30°C the sample solidifies and the probe benzene-d_6 is expelled.

3.3. *NMR of neat* myo-*inositol tetraether* **2e** (*a* cis *diol*)

For the interpretation of the results described here it is necessary to know the parameters of the quadrupole interaction tensor of the deuterium nucleus in a static O–D bond of the inositol molecule. In addition, for deriving these parameters from the spectra of solid *cis* diol-d_2 **2e** and *trans* diol-d_2 **3e** we have also measured the deuterium NMR spectrum of the monotropic liquid-crystalline *myo*-inositol tetraether **2a**, labelled at its hydroxyl groups. This compound is solid at room temperature and its deuterium NMR spectrum yields the quadrupole interaction parameters, $\nu_{\parallel}^{st} = 160\,\mathrm{kHz}$, $\eta^{st} = 0{\cdot}11$ where we associate the principal value of this tensor with the direction of the O–D bond and the superscript st refers to the parameters for static molecules. Similar parameters have been determined for other hydroxyl deuterons in solids where no molecular motion takes place [11, 14]. As shown later, these parameters are also very close to those determined in the crystalline state of *cis* diol-d_2 **2e** and of *trans* diol-d_2 **3e**.

Spectra of *cis* diol-d_2 **2e** obtained on heating from the crystalline state through the mesophase are shown in figure 5. The solid state spectrum at low temperatures ($< -45^{\circ}\mathrm{C}$) is similar to that of *cis* diol-d_2 **2a** and is characterized by the quadrupole tensor parameters $\nu_{\parallel}^{st} = 168\,\mathrm{kHz}$ and $\eta^{st} \approx 0{\cdot}1$. On heating to above $-45^{\circ}\mathrm{C}$, but still in the solid phase, there is a gradual change in the lineshape and a very significant reduction in the signal to noise ratio. Both these effects clearly indicate the setting-in of motion; the decrease in sensitivity reflects the shortening of T_2 due to motion, and when the rate of this motion becomes of the order of the quadrupole interaction the overall lineshape is modified. Just around the melting point (see traces at 33°C and 38°C in figure 5) this motion is sufficiently fast to give a well-defined motionally narrowed spectrum which remains essentially unchanged in the mesophase region. The lineshape in this region can be interpreted in terms of a superposition of two, equally intense, axially symmetric powder patterns with motionally average quadrupole interaction parameters, $\nu_{\parallel}^{1} = 43\,\mathrm{kHz}$ and $\nu_{\parallel}^{2} = 21\,\mathrm{kHz}$ (see the left hand series of figure 6). We shall shortly discuss the possible origin of these two types of spectra. Beforehand, we wish to comment on the spectrum obtained on partial alignment.

Recalling from the experiments with doped *cis* diol **2e** that around the clearing temperature the mesogen aligns parallel to the field direction we have attempted to align the neat sample under similar conditions as used previously. The resulting spectra obtained on slow cooling from the liquid are shown in the right hand series of figure 5. Indeed, in the mesophase region two doublets are observed which correspond to the parallel feature of two powder patterns obtained in the non-aligned sample. In fact these partially aligned spectra can be simulated applying the same magnetic parameters used to calculate the powder pattern (see the right hand traces in figure 6). Note that relatively large linewidths were required for the simulation reflecting the fact that the alignment is not perfect. Further cooling into the solid phase results in a gradual line broadening and eventually in a rigid powder pattern. However, its shape is different from that of the original solid sample (of the bottom two traces in figure 5) apparently reflecting some alignment introduced in the mesophase from which it was formed.

The two components observed in the spectra of *cis* diol-d_2 **2e** (cf. figure 5) are almost certainly due to the inequivalence of the axial and equatorial hydroxyl deuterons in this compound. To interpret the splittings of the two subspectra we considered several dynamic processes keeping in mind that the mesogen molecules are arranged in coplanar dimers within the columns and that no exchange between the axial and equatorial deuterons takes place on the NMR time scale.

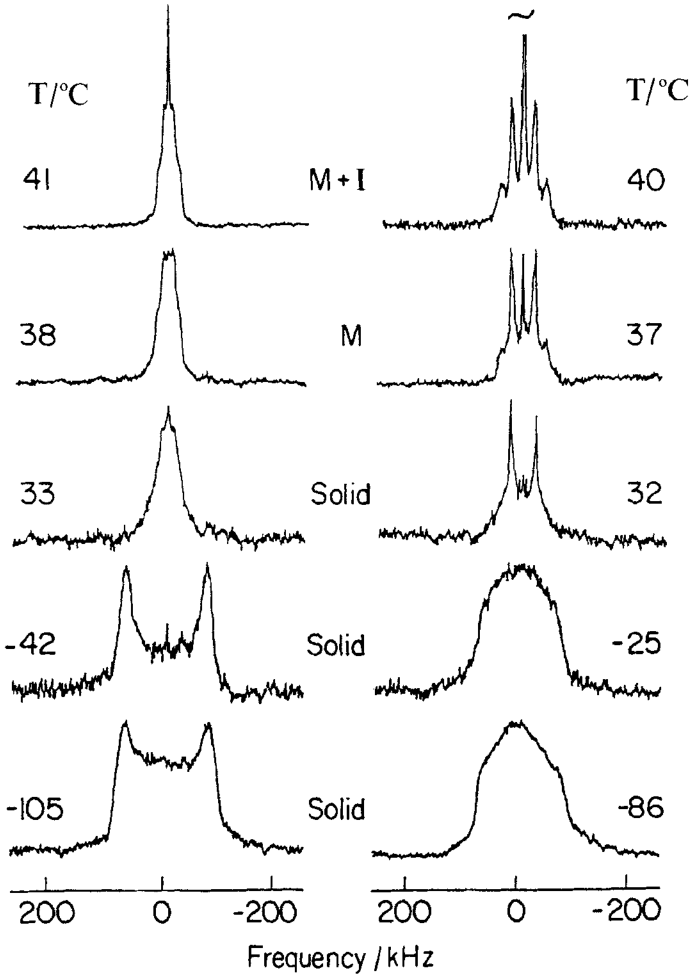


Figure 5. Deuterium NMR spectra of neat *myo*-inositol tetraoctylether **2e** (a vicinal *cis* diol-d_2) deuteriated at the hydroxyl groups in the solid and mesophase region as a function of temperature. The spectra on the left hand side were recorded on heating the crystalline sample. Those on the right hand side were obtained by cooling from the isotropic liquid after several temperature cycles around the clearing point in order to align the sample. The spectra in the mesophase region consist of a superposition of two powder patterns (left) or two doublets (right).

An exact quantitative analysis of the observed deuterium splittings in the mesophase of the diol **2e** requires knowledge of the exact structure of the dimers. For lack of sufficient information on this point, and in fact because of the limited experimental data, we need to make certain approximations. In particular, we consider the simplified case that each dimer has cylindrical planar symmetry and is rapidly reorienting about an axis normal to its plane (cf. figure 7 (*a*)). In addition, we assume that the O–D bonds undergo a fast symmetric cone-like precession about their corresponding C–O bonds (cf. figure 7 (*b*)). The combination of this precessional motion, the fast reorientation of the dimers, and the wobbling motion of the axis

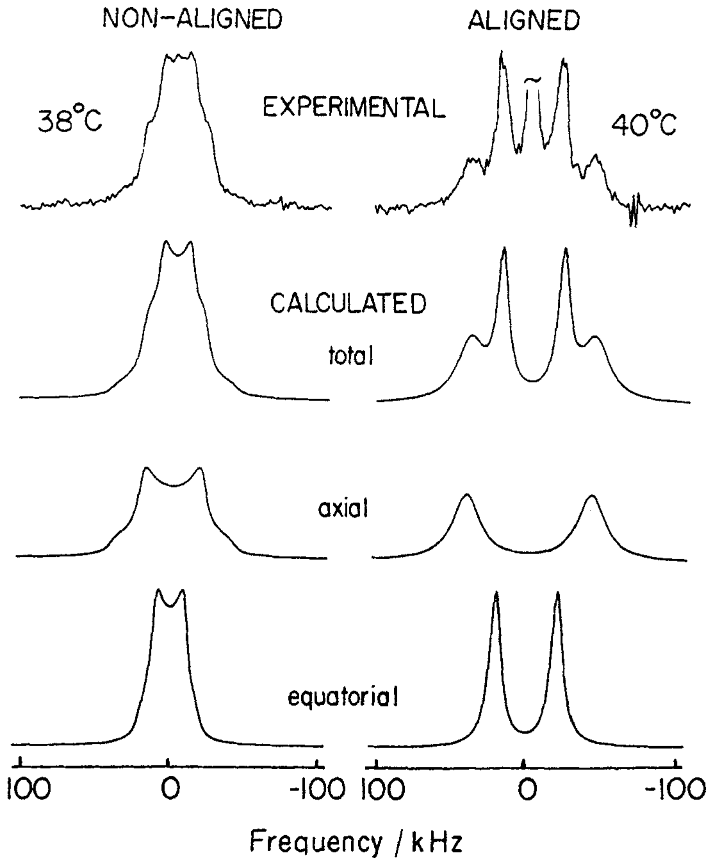


Figure 6. Experimental (at 38°C and 40°C from figure 7) and calculated deuterium NMR spectra of the hydroxyl deuterons in the mesophase region of *myo*-inositol tetraoctylether **2e** (a vicinal *cis* diol-d_2). The spectra are assumed to consist of two equally intense uniaxial components due to the axial and equatorial hydroxyls. The spectra on the left hand side correspond to a non-aligned sample while those on the right hand side to a sample aligned with the director parallel to the magnetic field direction. The parameters used in the calculation were $\nu_Q^1 = 20{\cdot}5\,\mathrm{kHz}$, $\nu_Q^2 = 41{\cdot}5\,\mathrm{kHz}$, $1/T_2^1 = 3{\cdot}2\,\mathrm{kHz}$ and $1/T_2^2 = 4{\cdot}3\,\mathrm{kHz}$ for the non-aligned sample, while for the aligned sample the same ν_Q^i were used but with $1/T_2^1 = 4{\cdot}8\,\mathrm{kHz}$ and $1/T_2^2 = 11{\cdot}1\,\mathrm{kHz}$.

normal to the dimer results in an average quadrupole interaction for the O–D deuterons given by

$$\langle \nu_Q \rangle = S_{zz} 1/2(3\cos^2\gamma - 1) 1/2(3\cos^2\alpha - 1)\nu_Q^{st}.$$

In this expression S_{zz} is the orientational order parameter of the normal axis, γ is the angle between this axis and the C–O bond direction and α is the C–O–D bond angle (cf. figure 7 (*b*)). Inserting $\nu_Q^{st} = 168\,\mathrm{kHz}$, $\alpha = 107°$, $\gamma_{ax} = 0$, and $\gamma_{eq} = 109{\cdot}5°$, yields for the axial and equatorial deuterons, respectively: $|\langle\langle \nu_Q^{ax} \rangle\rangle| = 62\,\mathrm{kHz}$ and $|\langle\langle \nu_Q^{eq} \rangle\rangle| = 20{\cdot}6\,\mathrm{kHz}$. These results must be compared with the experimental splittings of 43 kHz and 21 kHz for the two subspectra. Thus, we may safely identify the observed larger and smaller splitting with the axial and equatorial hydroxyl deuterons of **2e**, respectively, and derive an average orientational order parameter of $S_{zz} = 0{\cdot}84 \pm 0{\cdot}15$. The large

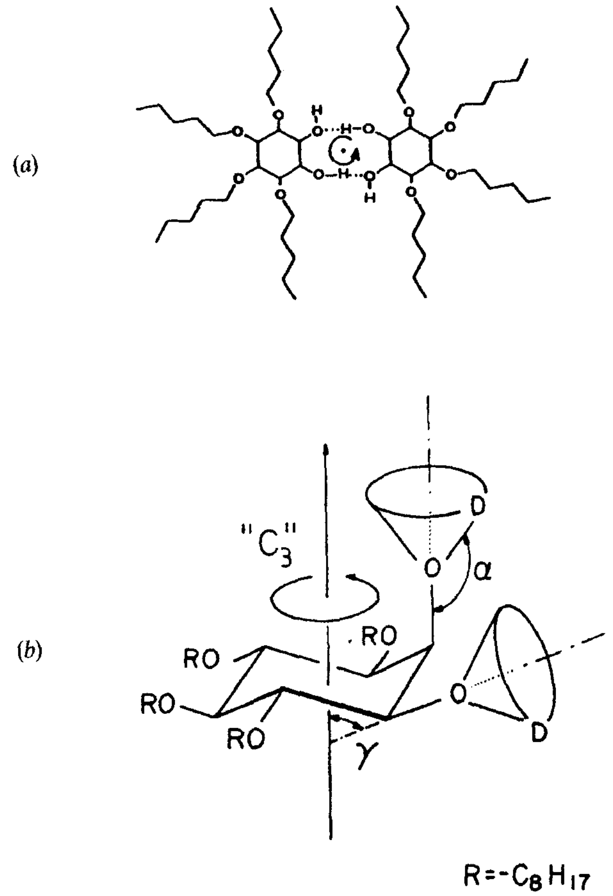


Figure 7. The molecular structure, the geometrical parameters and modes of motions assumed for the *myo*-inositol tetraoctylether **2e** (a vicinal *cis* diol-d_2) in the solid and liquid-crystalline mesophase, respectively: (a) reorientation of a dimeric unit of **2e** around an axis perpendicular to the common plane of the hydrogen bonded dimer, (b) cone-like precession of the deuterons in the hydroxyl groups.

difference in S_{zz} obtained from the two deuterons ($S_{zz(\mathrm{ax})} \approx 0{\cdot}7$ and $S_{zz(\mathrm{eq})} \approx 1{\cdot}0$) reflect, of course, the crude approximation made in the analysis, in particular, in assuming cylindrical planar symmetry for the dimer. A better fit would be obtained by including the biaxial order parameter, S_{xx}–S_{yy}, in the analysis, but the crudeness of the model does not justify such an analysis.

It is interesting to note that whatever motions are present in the mesophase of compound **2e** they are evolving gradually, as a function of temperature. As far as their rate is concerned they do not exhibit a discontinuity within the solid or at the solid to mesophase transition. If any discontinuous change does occur it must be within the sensitivity of the NMR method. Indeed, the melting enthalpy of this diol (3·9 kJ mol^{-1}) is unusually low and quite similar to that of the clearing transition (5·6 kJ mol^{-1}). Apparently, the dominant endothermic effect of the solid to mesophase transition involves, besides the change in packing energy, only small additional contributions due to chain melting. It would be interesting to check this point by ^{2}H NMR using samples of **2e** specifically deuteriated at the side chains.

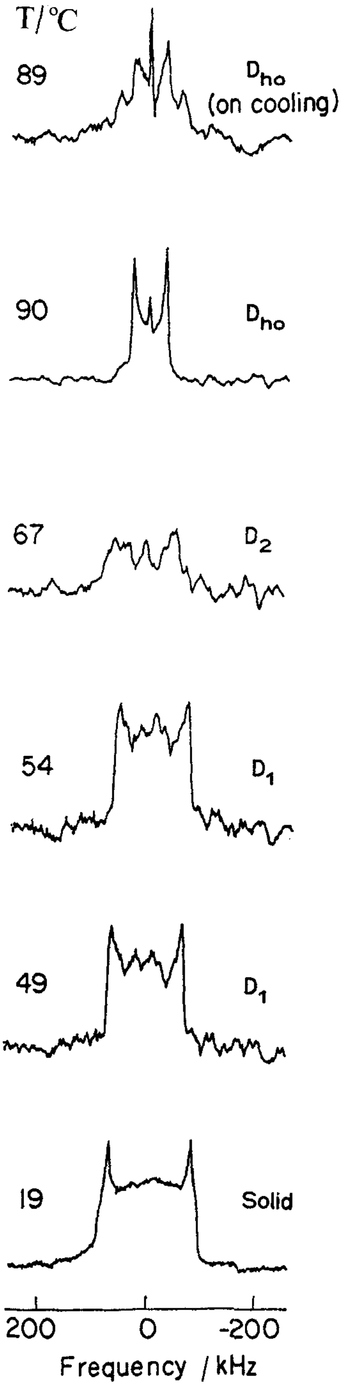


Figure 8. Deuterium NMR spectra of neat *scyllo*-inositol tetraoctylether **3e** (a vicinal *trans* diol-d_2) in the solid and mesophase region as a function of temperature as indicated. The spectra were recorded by heating a non-oriented sample from the solid through the mesophase region except for the top trace which was recorded on cooling from the isotropic liquid. The labelling of the phases is based on tentative identification made by polarizing optical microscopy.

3.4. *NMR of neat* scyllo-*inositol tetraether 3e* (*a* trans *diol*)

In figure 8 deuterium NMR spectra of the hydroxyl deuterons in a sample of neat *trans* diol d_2 **3e** are shown in the solid (lower trace) and the mesophase (remaining traces) region. The solid spectrum is similar to that found in the crystalline states of the *cis* diols **2a** and **2e** indicating that in this phase the hydroxyl groups are rigid. The quadrupole interaction parameters for these deuterons are $\nu_Q^{st} = 169$ kHz and $\eta^{st} \approx 0{\cdot}08$ in the solid at 18°C and remain essentially unchanged until the melting temperature (≈ 43°C). At this point a discontinuous change takes place in the lineshape yielding a uniaxial spectrum with a quadrupole parameter of $\langle \nu_Q \rangle = 137$ kHz (cf. the trace at 49°C). This reduction in the quadrupole interaction indicates that the hydroxyl deuterons undergo some kind of fast motion which, however, cannot be attributed to the cone-like precession discussed previously (see figure 7) since such a process would lead to a much larger reduction of the quadrupole interaction parameter than the 20 per cent observed experimentally. Rather, we must assume the presence of a local, more restricted motion that results in an axial (or nearly axial) averaged quadrupole tensor. The spectrum observed on melting remains unchanged until about 20°C above the melting temperature. It then undergoes a gradual change in its lineshape as well as a loss of intensity (see the trace at 67°C in figure 8). These changes indicate the onset of a new mode of motion. However, the rate of this motion is apparently of the order of the quadrupole splitting and not sufficiently fast to yield a motionally averaged spectrum as observed for the *cis* diol **2e**. Consequently, there is a loss of intensity in the NMR spectrum resulting in poorly defined lineshapes. Thus, the deuterium NMR spectra do not support the existence of distinct D_1, D_2, and D_3 phases as found by optical microscopy (cf. Introduction), although they also do not refute their occurrence. Therefore, the phase labelling in figure 8 refers only to the temperatures at which D_1 and D_2 were identified by polarizing optical microscopy.

Above about 75°C the spectrum intensity increases again yielding an axially symmetric quadrupole tensor with $\langle \nu_Q \rangle = 62$ kHz which remains essentially unchanged until the clearing temperature. We associate this spectrum with the mesophase D_{ho} in the optical microscopy phase sequence. The value of 62 kHz may be compared with the value of 21 kHz measured for the equatorial hydroxyl deuterons of *cis* diol-d_2 **2e**. This relatively large value measured in the high temperature mesophase (D_{ho}) of *trans* diol-d_2 **3e** indicates a much more restricted motion than in the isomeric compound **2e**. Specifically, it is possible that the dimers undergo fast reorientation within the molecular plane, but no cone-like motion of the hydroxyl groups takes place. This different behaviour compared to the stereoisomer **2e** may be associated with the relative configuration of the two vicinal hydroxyl groups in **3e**. It is very likely that such a precessional motion will be strongly hindered when both hydroxyl groups are equatorial (as in the *trans* isomer **3e**), whereas, when one group is axial and the other equatorial (as in the *cis* isomer **2e**) there is much less interference and both hydroxyl groups can precess freely.

Finally, we comment on the alignment of the mesophase by the magnetic field. We have seen where the spectrum of the C_6D_6 probe dissolved in *trans* diol **3e** was used to monitor the effect of the magnetic field, that partial alignment of the mesophase could be achieved by slow cooling of the sample within the magnetic field across the clearing temperature. This was also observed in the heat sample but in a less pronounced way. In the upper trace of figure 8 the spectrum of the neat sample of **3e** is shown as obtained after slow cooling from the isotropic liquid. It clearly does not correspond to a fully aligned sample, but it nevertheless shows a marked increase in the intensity of the parallel features thus confirming the previous conclusion that $\Delta\chi$ is positive for this mesophase.

4. Conclusions

The deuterium NMR results presented for the two liquid-crystalline *myo*- and *scyllo*-inositol derivatives **2e** and **3e**, differing structurally in the stereochemistry of their vicinal diol situation only, are consistent with the columnar structure determined for their mesophases by X-ray studies and confirm their axial symmetry. The results also show that the anisotropic magnetic susceptibility of these mesophases is positive as expected for columnar phases exhibited by discotic liquid-crystalline compounds with saturated cores. Measurements on the thermomesomorphic diols **2e** and **3e** deuteriated at their hydroxyl groups provided information on possible modes of molecular motions. At sufficiently high temperatures, reorientation of the molecules or molecular dimers about the columnar axis appears to be fast on the NMR timescale in both compounds. However, the two stereoisomers differ in two aspects:

(i) In the *cis* isomer **2e**, in which one hydroxyl group is axial and the other equatorial, the molecular reorientation motion remains fast even upon cooling into the solid phase whereas in the *trans* isomer **3e** in which both hydroxyl groups are equatorial the motion already freezes out well above room temperature.

(ii) In the *cis* isomer there is an additional motional averaging process involving a cone-like precession of the hydroxyl deuterons which does not take place in the *trans* isomer.

Both effects can be related to the different configuration of the hydroxyl groups in the two stereoisomers by assuming less interference and weaker intermolecular hydrogen bonding between the hydroxyl groups in the *cis* isomer as compared to the *trans* case. More details about the motional characteristics in the various mesophases of **2e** and **3e** can perhaps be derived from deuterium NMR measurements on other selectively deuteriated mesogens, in particular mesogens specifically deuteriated at the cyclohexane ring and at various positions of the side chains.

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K.P. wishes to dedicate this paper to OStR *Bodo Michels* to mark the occasion of his retirement in August 1991 from his teaching position in chemistry at the Goethe-Oberschule, formerly Gymnasium Friderico Francisceum, Bad Doberan in Mecklenburg-Vorpommern in Germany.

References

[1] Part LVII in the series of liquid-crystalline compounds; part LVI: PRAEFCKE, K., KOHNE, B., SINGER, D., DEMUS, D., PELZL, G., and DIELE, S., 1990, *Liq. Crystals*, **7**, 589. This topic has been the subject of presentations at numerous international meetings between August 1988 and March 1990.

[2] VORLÄNDER, D., 1923, *Z. phys. Chem.*, **105**, 211.

[3] (a) LANGMUIR, I., 1938, *J. chem. Phys.*, **6,** 873. (b) ONSAGER, L., 1949, *Ann. N.Y. Acad. Sci.*, **51,** 627; 1949, *Chem. Abstr.*, **43,** 7292b. (c) ISIHARA, A., 1951, *J. chem. Phys.*, **19,** 1142. (d) RUNNELS, L. K., and COLVIN, C., 1971, *Molec. Crystals liq. Crystals*, **12,** 299.

[4] CHANDRASEKHAR, S., SADASHIVA, B. K., and SURESH, K. A., 1977, *Pramana*, **9,** 471. The discogenic peresters of hexahydroxybenzene studied here were already known in the literature since BAKER, H. J., and VAN DER BAAN, SJ., 1937, *Recl. Trav. chim. Pays-Bas*, **56,** 1161. Surprisingly, these authors completely overlooked the liquid-crystalline properties of their compounds at that early time. The only evidence for mesophase formation by disc-shaped molecules was that during the carbonisation of graphitizable organic materials, see BROOKS, J. D., and TAYLOR, G. H., 1965, *Carbon*, **3,** 185.

[5] An expression obviously introduced by Langmuir [3(a)].

[6] PRAEFCKE, K., KOHNE, B., and SINGER, D., 1990, *Angew. Chem.*, **102,** 200; 1990, *Angew. Chem. Int. Ed. Engl.*, **29,** 177. KOHNE, B., and PRAEFCKE, K., 1987, *Chimia*, **41,** 196. See also references of other research groups given in these two papers.

[7] BUNNING, J. D., LYDON, J. E., EABORN, C., JACKSON, P. M., GOODBY, J. W., and GRAY, G. W., 1982, *J. chem. Soc. Faraday Trans. I*, **78,** 713.

[8] (a) ECKERT, A., KOHNE, B., and PRAEFCKE, K., 1988, *Z. Naturf.* (b), **43,** 878. PRAEFCKE, K., LEVELUT, A.-M., KOHNE, B., and ECKERT, A., 1989, *Liq. Crystals*, **6,** 263. (b) PRAEFCKE, K., KOHNE, B., MARQUARDT, P., STEPHAN, W., LEVELUT, A.-M., and WACHTEL, E., *Molec. Crystals liq. Crystals* (in the press). MARQUARDT, P., PRAEFCKE, K., KOHNE, B., and STEPHAN, W., *Chem. Ber.* (submitted). PRAEFCKE, K., MARQUARDT, P., KOHNE, B., and STEPHAN, W., *J. Carbohydr. Chem.* (submitted). MARQUARDT, P., 1990, Ph.D. Thesis, Technische, Universität Berlin. (c) PRAEFCKE, K., KOHNE, B., ECKERT, A., and HEMPEL, J., 1990, *Z. Naturf.* (b), **45,** 1084. (d) LATTERMAN, G., and STAUFER, G., 1989, *Liq. Crystals*, **4,** 347.

[9] ANGYAL, S. J., TATE, M. E., and GERO, S. D., 1961, *J. chem. Soc.*, p. 4116.

[10] PRAEFCKE, K., and STEPHAN, W., 1987, *Liebigs Ann. Chem.*, p. 645.

[11] BARNES, R. G., 1974, *Advances in Nuclear Quadrupole Resonance*, Vol. 1, edited by J. A. S. Smith (Heydon), p. 335. RINNE, M., and DEPIREUX, J., *Ibid.*, p. 357.

[12] GOLDFARB, D., LUZ, Z., and ZIMMERMANN, H., 1983, *Isr. J. Chem.*, **23,** 341.

[13] GOLDFARB, D., LUZ, Z., and ZIMMERMANN, H., 1982, *J. Phys.*, **43,** 421 and 1255.

[14] BERSON, R., 1960, *J. chem. Phys.*, **32,** 85. PYYKKÖ, P., 1967, *Ann. Univ. Turk. A1*, p. 13.