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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Loewenstein, A. and Igner, D.(1991) 'Deuterium NMR studies of *n*-octyl α and β -glucopyranoside liquid-crystalline systems', *Liquid Crystals*, 10: 4, 457 – 466

To link to this Article: DOI: 10.1080/02678299108036435

URL: <http://dx.doi.org/10.1080/02678299108036435>

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Deuterium NMR studies of *n*-octyl α and β -D-glucopyranoside liquid-crystalline systems

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(Received 7 March 1991; accepted 5 May 1991)

Deuterium NMR measurements have been performed on mixtures of *n*-octyl- α -D-glucopyranoside (α OG) and *n*-octyl- β -D-glucopyranoside (β OG) with deuteriated water or benzene. The phase diagrams, at high α OG concentrations (lamellar phases), are similar to those reported previously for the β anomer. Deuterium NMR measurements of D₂O in mixtures with α OG or β OG at lower concentrations show the existence of additional hexagonal and isotropic (including possibly cubic) phases. Some differences were noted between the phase diagrams of α and β OG at these concentrations. The sign of the diamagnetic anisotropy, $\Delta\chi$, of the S_A lamellar phase of α OG/D₂O and α OG/C₆D₆ was found to be negative. Slow exchange between the sugar hydroxyl deuterons and water in α OG enabled us to measure their quadrupolar splittings at different temperatures. Using a simple model, where rotation of the polar head as a rigid unit around a single axis is assumed, we have calculated the direction of this axis relative to a molecular axis. The results show that this axis is approximately parallel to the C₄-C₈ axis.

1. Introduction

Studies of *n*-alkyl- β -D-glucopyranosides have shown that they can form thermotropic or lyotropic liquid-crystalline phases of the smectic A type and lamellar structure [1, 2]. These non-ionic amphiphiles dissolve both polar (e.g. water) or apolar (e.g. benzene) solutes, or both in significant quantities. Focher *et al.* have recently shown [3] that there exist considerable differences in the structural properties of dilute solutions of *n*-octyl- β -D-glucopyranoside (β OG) and its anomer, *n*-octyl- α -D-glucopyranoside (α OG). Chung and Jeffrey [4] have shown, by X-ray studies, the existence of additional cubic and hexagonal phases in mixtures of β OG and water at relatively low β OG concentrations and temperatures. Unfortunately however, due to the particular technique which was used, they were unable to specify the concentrations and temperatures in which these phases exist. Other related recent works are given in [5, 6]. These studies stimulated us to extend our investigations of the liquid-crystalline properties of both α OG and β OG solutions and compare them with those obtained earlier for β OG. The experimental technique that we have used was deuterium NMR, which has yielded most of the information in our previous studies.

One notable difference between the present results for α OG and our previous ones for β OG [1, 2] was the observation of five discrete doublets in the deuterium spectra of lamellar α OG-deuteriated water systems. These resonances belong to the water and the four hydroxyl groups of the sugar polar head. This implies that the exchange rate of the

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hydroxyl and water deuterons is slow compared to the inverse of the quadrupolar interaction in the temperature range of our studies. For β OG we had previously observed a single, relatively broad, doublet which indicated faster exchange between the hydroxyl deuterons and water. Since it seemed quite inconceivable that such a difference in the exchange rates would occur between the α and β anomers, we suspected that the commercial β OG used in our previous work [1,2] was contaminated with traces of acids or bases which catalysed the deuteron exchange reactions. Purification of β OG has indeed resulted in the observation of the discrete OD doublets in the lamellar phase of the β OG/D₂O system. These, however, are not always so well resolved as in α OG/D₂O and often exhibit incidental overlap. Discrete OD resonances were also observed in the hexagonal phases of α and β OG-water mixtures indicating that proton exchange is slow in these phases too. We may, conclude therefore, that the relatively broad resonances of the D₂O doublets in β OG-water samples reported in our previous work [1,2], should better be attributed to intermediate exchange rates caused by acidic or basic contaminations rather than to restricted motion of water molecules in a hydrogen bonded network as was suggested. The observation of the deuterium hydroxyl quadrupolar doublets in α OG/D₂O enabled us, using a simple model, to calculate the direction of the rotation axis (relative to a molecular frame) and the order parameter of the polar head group.

We have studied the D₂O resonances in phases with relatively low α OG and β OG concentrations. Our spectra conform with the existence of three types of phases: a hexagonal phase, a phase which exhibits a single NMR resonance which we denote as isotropic or cubic and a lamellar phase. Some differences between the behaviour of the α and β anomers were noted.

2. Experimental

2.1. Materials

α and β OG were obtained from Sigma. Some α OG was dried by distillation with dry benzene followed by drying under vacuum for several days. The dried material contained less than 0.15 wt% of water. Otherwise α OG was vacuum pumped for several days but this operation does not remove all of the water and the product remains as the hemihydrate. β OG was purified by passing a methanolic solution through a column containing Amberlite MB-1A above some Amberlite XAD-2. The methanol was distilled and the material dried under vacuum for several days. Samples were prepared by weighing and mixing the components in 5 mm NMR tubes which were then sealed and heated for further equilibration. Most measurements were made during slow cooling (1 K/120 s) from the isotropic melt.

2.2. NMR measurements

The NMR measurements were performed on a Bruker AM400WB NMR spectrometer operating at 61.4 MHz for deuterium. The temperature was controlled by a flow of heated air or cooled nitrogen over the sample. Temperature precision and stability varied from ± 2 K at the highest or lowest temperatures to ± 0.5 K near room temperature. Samples were not spun in the magnetic field.

3. Results and discussion

3.1. Phase diagrams

Within the limits of experimental error there are no significant differences between the phase diagrams of α OG-water or α OG-benzene at high α OG concentrations

($x_{OG} > 0.25$ where x_{OG} indicates the mole fraction) as compared to the corresponding diagrams for β OG [2]. The transition temperatures of the phases could not be determined with high precision because of the temperature instability and inaccuracy at elevated temperatures.

We performed a detailed study of the α and β OG-D₂O systems as a function of the temperature in the concentration range of $0.07 < x_{OG} < 0.22$. Below x_{OG} of about 0.07 the system seems to exist as a micellar solution (a single resonance) at all temperatures. The results are shown schematically in figures 1 and 2 for α OG and β OG respectively. Before discussing these figures in detail it should be noted that all of the transition temperatures can be affected by supercooling. It is very difficult, without waiting for very long times, which is impractical, to determine the true transition temperatures by the method we used. Nevertheless, the general picture is reproducible and provides reliable information about the systems under study. Also, the quantitative ratio between the phases in biphasic regions are not shown in figures 1 and 2; this ratio varies with the temperature in the expected way.

Both α and β anomers show at least three types of characteristic spectra with features which correspond to the lamellar, hexagonal and isotropic or cubic phases. The NMR technique is incapable of the determination of the phase structure and consequently we rely on the X-ray measurements [4] for tentative identification. Spectra which show two coexisting phases (biphasic) are often observed, with the exception of the lamellar-hexagonal biphasic system.

Typical spectra for some of the regions shown in figures 1 and 2 are given in figures 3 and 4. Spectra of lamellar phases are characterized by doublets (of the D₂O or OD

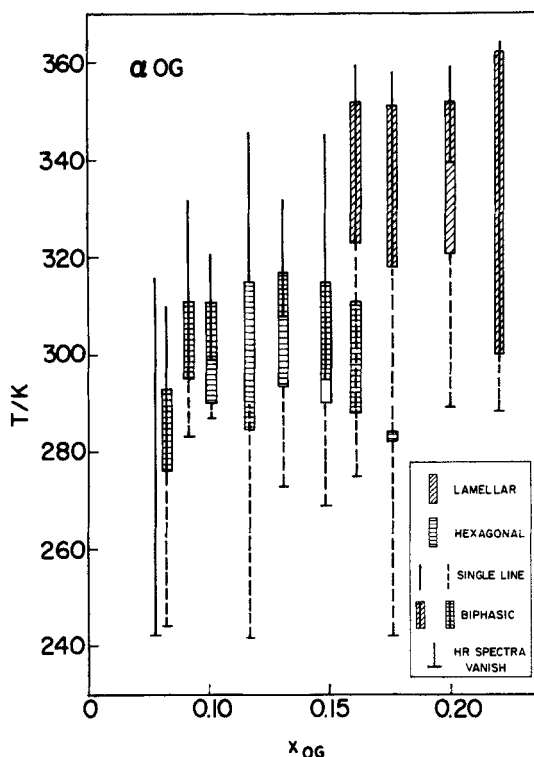


Figure 1. Schematic phase diagram for α OG. The notation is explained in the insert.

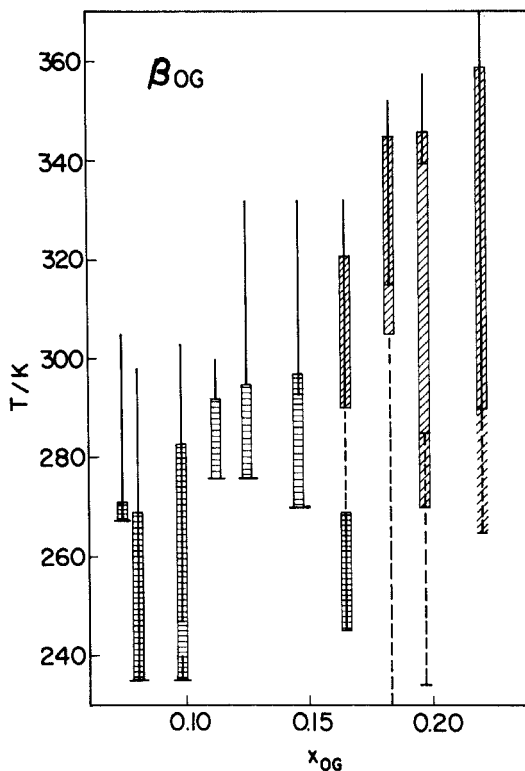


Figure 2. Schematic phase diagram for β OG. The notation used is the same as those in figure 1.

resonances) with symmetric line shapes. Hexagonal phases show spectra with two doublets differing in their frequency separation by a factor of two (corresponding to the parallel and perpendicular components) and lineshapes similar to those obtained in polycrystalline samples (sharp ascent and slow descent). At high OG concentrations, $x_{OG} > 0.17$ in both α and β OG, the only ordered phase is the lamellar phase while at low OG concentrations the only ordered phase is the hexagonal phase. At a rather narrow concentration range ($x_{\alpha OG}$ and $x_{\beta OG}$ about 0.165) we observed both lamellar and hexagonal phases separated by an intermediate, presumably cubic, phase. The overall picture shows some notable features for the behaviour of the α and β anomers.

- (1) The transition temperatures to the lamellar and particularly to the hexagonal phases are lower for the β anomer.
- (2) Upon cooling the α anomer the spectra of the hexagonal phase change into a singlet (presumably from an isotropic phase). Upon further cooling this singlet abruptly vanishes (due to excessive broadening) at a certain temperature. The β anomer behaves differently; no isotropic phase exists below the hexagonal phase. At some temperature the spectra of the hexagonal phase broaden to such an extent that they cannot be observed by our technique. Some differences are noted also by a visual observation. The α samples, at low temperatures, are white and opaque while the β samples are clear and transparent. We are unable to determine, from the NMR measurements, whether the isotropic phase lying below the hexagonal phase is a cubic or another type of an isotropic phase. Complementary X-ray measurements are essential to solve this problem.

- (3) In the concentration and temperature ranges shown in figures 1 and 2, for both α or β OG, the pure hexagonal phase exists in a rather narrow region. At high α or β OG concentration the lamellar phase exists over a broad range of concentrations and temperatures.

In the spectra for the highest α or β OG concentrations shown in figure 1 and 2 ($x_{OG} = 0.22$), we observed what seems to be a splitting of the D_2O line into two unequal components with a separation (about 600 Hz for β OG and 1000 Hz for α OG) that increases as the temperature is lowered. We are unable to find an explanation for this unusual feature which was not observed below or above this particular concentration.

3.2. The sign of the diamagnetic anisotropy ($\Delta\chi$)

The sign of the diamagnetic anisotropy for α OG, in the lamellar phase, with water or benzene as solutes was determined using two methods. In one two small tubes (length 17 mm, o.d. 5 mm, i.d. 4 mm and sample height c. 5 mm) containing α OG- D_2O ($x_{OG} = 0.34$) or α OG- C_6D_6 ($x_{OG} = 0.55$) were prepared. These tubes were inserted vertically, coaxial with the magnetic field, supported by a teflon cylindrical ring, in a 20 mm NMR tube. The samples were heated in the magnetic field to the isotropic phase and then cooled to 320 K and 310 K for water and benzene solutions, respectively.

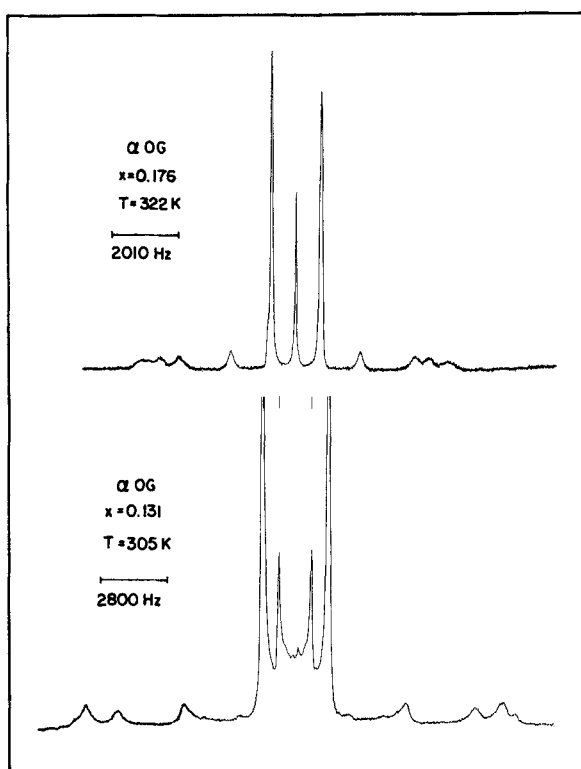


Figure 3. Typical spectra of α OG related to figure 1. Upper spectrum: lamellar-isotropic biphasic system. The central peak is due to an isotropic phase. The high intensity doublet is due to D_2O and four broad OD resonances are observed. Lower spectrum: hexagonal phase, outer peaks belong to OD.

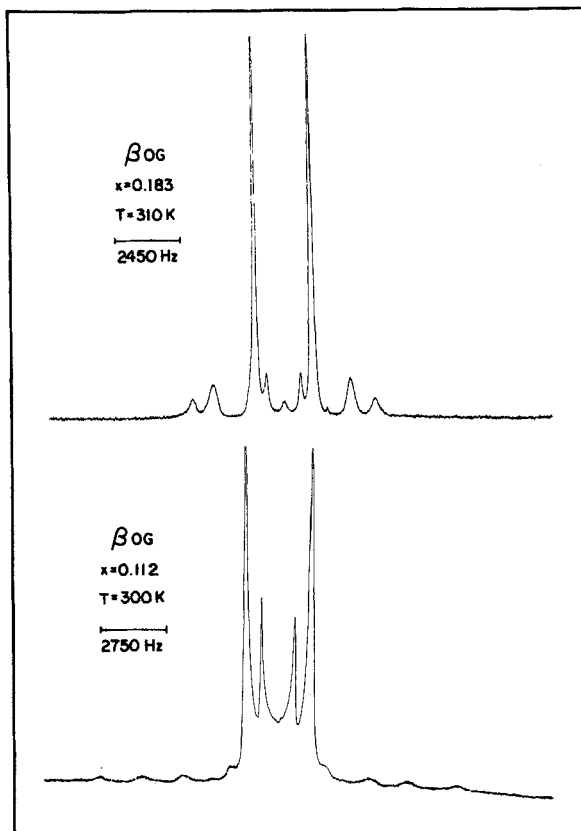


Figure 4. Typical spectra of β OG related to figure 2. Upper spectrum: mostly lamellar with a small isotropic component in the centre. The high intensity doublet is due to the D_2O . Other peaks are due to OD with two OD resonances overlapping. Lower spectrum: hexagonal phase, outer peaks belong to OD.

Their spectra exhibited the expected quadrupolar doublets for oriented solutions, i.e. the director was either parallel or perpendicular to the magnetic field. The samples were then dropped to horizontal position by removing the teflon ring *in situ*. After this operation we were unable to observe any spectra from these samples. This result shows that for the horizontal position the director is distributed evenly in any plane parallel to the magnetic field resulting in a spectrum with no sharp features. Hence, in the vertical position, the director is distributed uniformly in all directions perpendicular to the magnetic field which implies that $\Delta\chi < 0$. In the second method the sample containing benzene was heated in the magnet to 325 K. The observed spectrum exhibited a typical polycrystalline powder pattern with parallel and perpendicular components (differing in their spacing by a factor of 2), which corresponds to non-aligned samples. The sample was then heated in the magnetic field to the isotropic state and cooled slowly back to 325 K. The spectrum obtained was of an ordered material, i.e. a doublet with a spacing equal to the perpendicular (smaller) component in the spectrum of the non-aligned sample. This experiment proves again that $\Delta\chi$ is negative. This experiment cannot be performed conveniently with the α OG-water sample because of the large number of lines in the spectra.

3.3 Hydroxyl quadrupolar splittings

The spectra of a mixture of α OG and D_2O , in the lamellar phase (for a relatively high α OG concentration), at several temperatures, are shown in figure 5. Similar spectra were measured for other concentrations in the lamellar phase region. The temperature dependence of the OD quadrupolar splittings for a particular α OG concentration are shown in figure 6. The spectra in figure 5 contain five doublets of which the innermost belongs to D_2O (this was easily proven through the addition of water) and the others belong to the four ODs in positions 2, 3, 4, and 6 of the sugar (cf. figure 7). It should be noted that the centres of the different doublets do not coincide, being shifted up to about 2 ppm. These shifts must be due to the chemical shift anisotropy which, unfortunately, cannot be evaluated because of the large experimental errors. The differences in the isotropic chemical shifts, which were measured in CD_3OH , are of the order of 0.5 ppm.

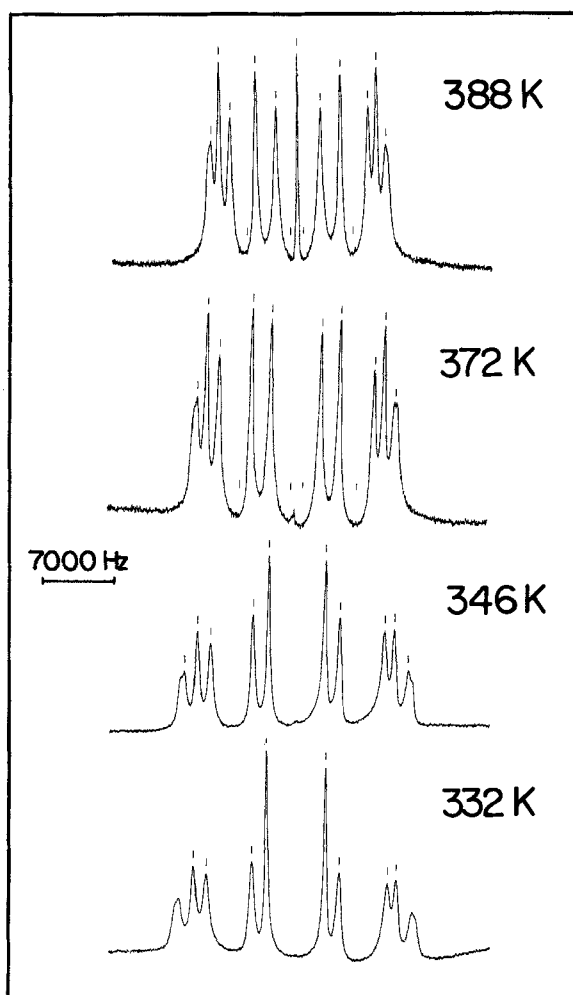


Figure 5. Deuterium NMR spectra in the lamellar phase of α OG- D_2O solutions ($x_{\alpha OG} = 0.42$) at different temperatures. The central doublet belongs to D_2O . In the upper spectrum the system is biphasic and shows the central resonance of the isotropic phase.

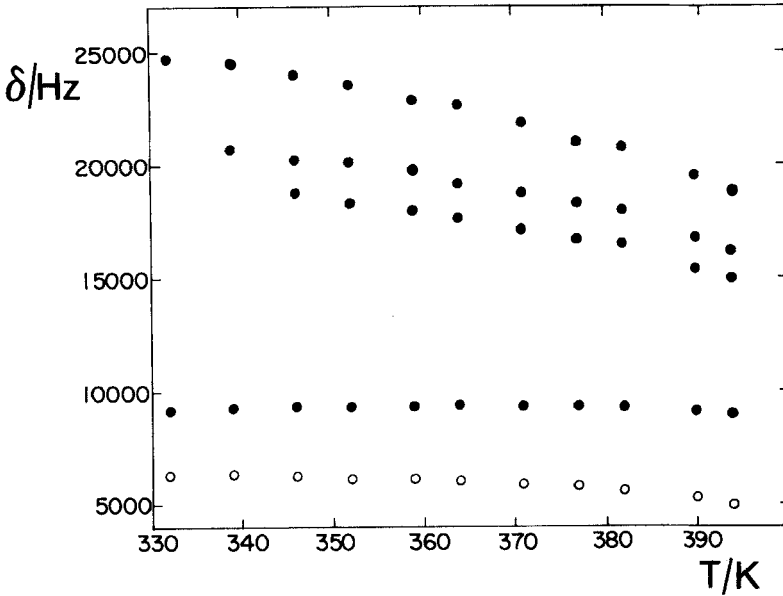


Figure 6. Quadrupolar splittings of the four OD groups (full circles) and D₂O (open circles), in a α OG-D₂O solution ($x_{\alpha\text{OG}}=0.55$) as a function of the temperature.

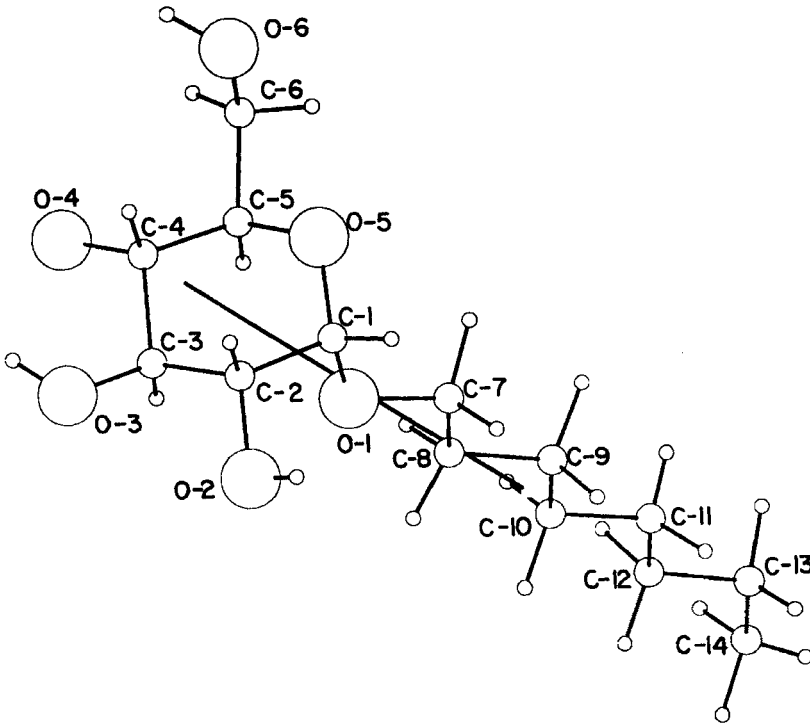


Figure 7. Drawing of the α OG molecule with the rotation axis [10]. The axis is drawn through the centre of mass of the molecule.

A simple model permits us to calculate the orientation of the rotation axis of the polar head group from the measured four hydroxyl doublets. A similar procedure was used by Prestegard *et al.* [7, 8]. This procedure, as applied to our case, is now described. We assume that the sugar ring is a rigid entity and undergoes fast reorientational diffusion around a single axis whose direction we seek to find. Furthermore we assume that each OD group rotates freely around its OC axis and that its average orientation coincides with the direction of the particular CO bond to which it is attached. The molecular geometry was taken from X-ray data for the solid α OG monohydrate [9]. For each quadrupolar doublet belonging to a particular OD, the quadrupolar splitting, δ_i , is given by

$$\delta_i = 3/2(QCC)S\langle(3 \cos^2 \alpha_i - 1)/2\rangle, \quad (1)$$

where S is an order parameter for the rotation axis and is assumed to be the same for all of the hydroxyl groups, α_i is the angle between the OC bonds and the axis of rotation and QCC is the averaged quadrupole coupling constant for the OD bond taken as 200 kHz. Assuming free rotation of the O_6C_6 bond around the C_5C_6 axis equation (1) must be multiplied by $(3 \cos^2 \beta - 1)/2$ for the O_6D doublet where β is the angle between the C_5C_6 and C_6O_6 bonds. It should be noted that equation (1) does not contain the expected temperature or concentration dependence of α . Further temperature dependence of δ_i is expected since the OD chemical exchange rates vary with temperature.

We have, therefore, four equations for the splittings of the O_2D , O_3D , O_4D and O_6D doublets. The α_i are known functions of Θ and ϕ , the polar angles which determine the direction of the axis of rotation of the sugar group in the cartesian crystal system based upon the crystal coordinates defined in [9]. As we have three unknowns (Θ , ϕ and S) and four experimental splittings ($\delta_a, \delta_b, \delta_c$ and δ_d), the problem is overdetermined. The best values for the unknowns were computed using equation (1); the fit between the calculated and measured δ_i s was better than 1 per cent. The results for $\delta_{\text{calculated}}$, δ_{measured} , Θ , ϕ and S at several concentrations and temperatures are given in tables 1 and 2 for some of our measurements. For all cases the rotation axis is oriented approximately (within 3°) parallel to the C_4C_8 axis. Figure 7 shows this axis drawn upon the X-ray structure [9]; for convenience the axis in this figure passes through the centre of mass of the molecule.

In principle this model calculation should enable us to assign unequivocally each δ_i to a particular OD group in the molecule by comparing the calculated quadrupolar

Table 1. Experimental and calculated deuterium quadrupolar splittings of the OD groups at some concentrations and temperatures for α OG-D₂O solutions.

X_{OG}	T/K	δ_a/Hz		δ_b/Hz		δ_c/Hz		δ_d/Hz	
		Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.
0.625	383	19430	19460	16900	17005	15660	15530	9205	9210
0.625	346	23780	23730	20430	20450	18980	19070	9200	9165
0.545	390	19540	19530	16770	16750	15390	15360	9100	9130
0.545	346	24055	24055	20240	20175	18800	18845	9360	9370
0.416	383	18360	18450	16560	16490	14480	14370	8640	8700
0.416	364	20990	20950	18540	18550	16210	16200	8835	8850
0.416	332	23120	22950	20020	20210	17940	17950	8650	8620
0.312	359	20230	20320	18040	17930	15380	15400	8160	8160
0.312	327	22030	21780	18760	19075	16650	16530	8010	8025

Table 2. Values of Θ , ϕ and *S* calculated from the data given in table 1.

X_{OG}	<i>T</i> /K	$\Theta/^\circ$	$\phi/^\circ$	<i>S</i>
0.625	383	51.7	174.2	0.41
	346	48.8	171.3	0.35
0.545	390	51.6	174.0	0.40
	346	49.3	171.5	0.37
0.416	383	50.7	176.1	0.35
	364	49.1	175.3	0.33
	332	46.8	173.9	0.29
0.312	359	48.3	175.0	0.30
	327	46.4	174.0	0.27

splittings obtained from the solutions of equation (1) to the measured values. This turned out to be impossible in practice. The equations have, within reasonable differences between the calculated and experimental values, two sets of solutions (with very similar Θ and ϕ values) which correspond equally well to the experimental results (within their errors), but differ in the relative magnitudes of the calculated δ_i s. Thus, the tentative assignments of the OD resonances are $\delta_4 > \delta_3 > \delta_2 > \delta_6$ for two (high concentration) α OG solutions and $\delta_3 > \delta_2 > \delta_4 > \delta_6$ for the other two (low concentration) solutions. The indices refer to the particular OD groups as shown in figure 7. Furthermore, the basic assumptions of the model are too crude to enable this assignment. Hence, we are unable to provide an unambiguous assignment to the hydroxyl groups, except for the O_6D group which has the smallest splitting.

It should be noted (see figure 6) that δ_6 is essentially temperature independent while the rest decrease slightly with increasing temperature as might be expected. This phenomenon was observed for all α OG solutions that were studied and can be attributed to the additional flexibility of the O_6D group as compared to other OD groups. Similar behaviour was observed for the terminal methyl group of the octyl chain in β OG [2]. In addition, the order parameters, *S*, given in table 2 are somewhat larger than those deduced for the chain methylenes in pure β OG [2] and tend to decrease with increasing water concentration. These results are expected for a smectic A phase with a layered structure which is bound more tightly in the polar group region.

A. L. acknowledges support from the Fund for Promotion of Research at the Technion.

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