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On the structure of the thermotropic cubic mesophases

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Two new substances, glycosides, with an optically isotropic mesophase were investigated. Using measurements of the refractive index, the optical isotropy of the thermotropic phases was proved. X-ray diffraction experiments provided information about the structure of the cubic mesophase. Similarly to the lyotropic cubic phases, here too structures of space group 1a-3d are present.

1. Introduction

Although the thermotropic cubic mesophase was discovered more than 25 years ago [1, 2] there is very little knowledge about the actual structure of this phase. The thermotropic cubic phase was called originally the 'smectic D' phase, but investigations of the refractive index [3] and initially X-ray diffraction experiments [4] showed that there is no layered structure present. The structure was discovered to be optically isotropic and hence to have a cubic lattice. Cubic structures of several types are well known in lyotropic liquid crystalline systems and their structure was elucidated by extensive studies [5–7]. However very few investigations were performed to study the structures of thermotropic cubic phases. One major reason is that there are only a few substances which display a cubic phase; that is, only a few substances of this type are known [8], and structural investigations of these substances have been performed only in some cases [4, 8–16]. There are some, partially controversial proposals for the structures of these mesophases, but up to now there is no general picture established about the structures of thermotropic cubic phases.

This work will introduce two new substances that show a thermotropic cubic phase [17]. These substances are two glycosides (see figure 1): substance **1**: *n*-dodecyl-α-gentiobioside and substance **2**: 1.1-di-(*β*-D-glucosyloxymethyl)pentadecane. It is already known that carbohydrate liquid crystal materials display not only the smectic A phase, but also that rectangular and discotic phases have been reported [18–20]. Now the variety of phases of this class of compounds has been extended again. We support the optical isotropy of the newly observed phase by measurements of the refractive index, and several X-ray diffraction techniques have been used to obtain information about the structure of this cubic phase.

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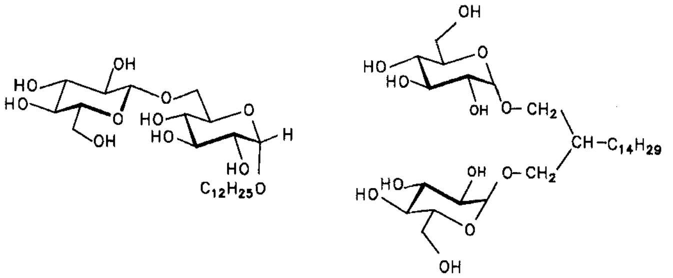


Figure 1. Structural formulae of the substances investigated.

2. Experimental

The synthesis of the compounds used in this study is described elsewhere [17]. To guarantee the thermotropic behaviour, it is essential to dry the substances carefully prior to use. Both compounds are strongly hygroscopic, and therefore they were dried for 24 h under a pressure of 1 Pa in an Abderhalden drying apparatus before any experimental work was performed. The thermal behaviour was investigated using a Perkin–Elmer DSC 7. Polarized light microscopy studies were performed using a Boetius hot stage or a Linkam THM 600 hot stage attached to a Zeiss microscope. X-ray diffraction patterns were taken with a Guinier film camera from Huber Diffraction Technik GmbH, a flat film camera, a Rigaku Denki small-angle camera or a Siemens X-1000 area detector. Ni-filtered or monochromatic CuK_α-radiation was used. Oriented samples were prepared using a magnetic field of about 0·8 T. The investigations of the refractive index were performed with an Abbé refractometer according to the procedure described in [3].

3. Results and discussion

Optical investigation using the polarizing microscope (POM) showed no birefringence either for substance **1** or substance **2**. Variation of temperature did not cause any birefringence, so that the melting point could not be determined by POM. However, the transition mesophase → isotropic melt was detectable by a change in the viscosity of the investigated substances. The mesophase displays a rather high viscosity, almost plasticity, and the substances do not flow. This behaviour changes dramatically with the transformation into the isotropic phase. The substances then begin to flow.

The thermal properties were investigated using the differential scanning calorimeter.

Substance **1** C-75°C-cub-162°C-I.

Substance **2** C-111°C-cub-205°C-I.

Both substances display a similar behaviour. Only in the first heating run do they show a transition crystalline → mesophase (see figure 2). A noticeable crystallization could not be observed on cooling on 0°C, using different cooling rates, and although the substances crystallize eventually, this occurs, very slowly after several weeks.

To exclude the possibility that the mesophase observed in the optical and thermal analysis experiments is a pseudoisotropic orientation of an anisotropic mesophase, instead of a truly isotropic mesophase, experiments to elucidate the refractive indices were performed (see figure 3). Both substances showed no splitting of the incoming beam into an ordinary and an extraordinary ray, and hence the mesophase observed must

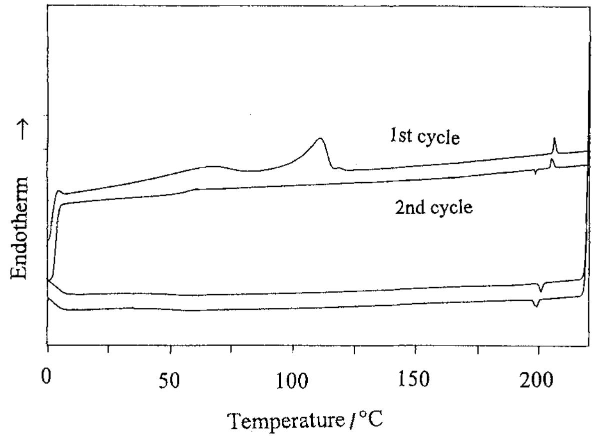


Figure 2. DSC traces of substance **2**—first and second cycle; scan rate 10 K min^{-1}.

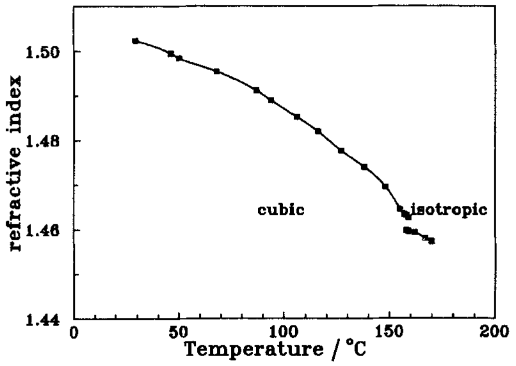
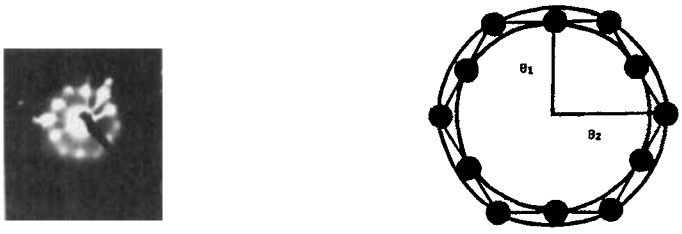


Figure 3. Refractive index of substance **1** as a function of temperature.

θ and d-spacing values for the Guinier reflections in the cubic mesophase.

Substance 1		Substance 2	
$\theta_1 = 1{\cdot}35°$	$d_1 = 32{\cdot}7$ Å	$\theta_1 = 1{\cdot}24°$	$d_1 = 35{\cdot}7$ Å
$\theta_2 = 1{\cdot}55°$	$d_2 = 28{\cdot}5$ Å	$\theta_2 = 1{\cdot}44°$	$d_2 = 30{\cdot}7$ Å
$\theta_3 = 2{\cdot}05°$	$d_3 = 21{\cdot}6$ Å	$\theta_3 = 1{\cdot}89°$	$d_3 = 23{\cdot}4$ Å
		$\theta_4 = 2{\cdot}025°$	$d_4 = 21{\cdot}8$ Å
		$\theta_5 = 2{\cdot}26°$	$d_5 = 19{\cdot}5$ Å
		$\theta_6 = 2{\cdot}36°$	$d_6 = 18{\cdot}7$ Å
$\theta_W = 9{\cdot}50°$	$d_W = 4{\cdot}70$ Å	$\theta_W = 9{\cdot}20°$	$d_W = 4{\cdot}80$ Å



(*a*) (*b*)

Figure 4. (*a*) Flat-film camera picture of the small-angle reflections of substance **1** at 155°C. (*b*) Scheme of the reflections.

(*a*) (*b*)

Figure 5. (*a*) Area detector picture of the cubic mesophase of substance **2** at 160°C. (*b*) Small-angle reflections of figure 5 (*a*).

be isotropic and therefore cubic. Using the Lorentz–Lorenz equation, the densities of both substances could be evaluated on the basis of the observed values of the refractive index and values of the polarizability estimated by an incremental method [21]. The density of both substances is approximately $1{\cdot}15\,\mathrm{g\,cm^{-3}}$.

In order to obtain preliminary structural information, X-ray experiments were performed using the Guinier technique. A typical pattern consisting of two sharp and intense small-angle reflections and one diffuse wide-angle reflection was obtained. Using longer exposure times, it was possible to obtain additionally several weak small-angle reflections (see the table). The small-angle reflections did not match a layered or a hexagonal structure, and hence the structure present must be different.

More information about the phase structure of the substances could be expected by investigation of oriented samples and obtaining 2-dimensional pictures using a flat-film camera. Therefore the following techniques were used to grow large monodomains in the samples. The most successful method proved to be the use of several heating and cooling cycles around the clearing point:

(1) Heating into the isotropic phase about 5 K above the phase transition temperature;
(2) application of a magnetic field for orientation (*c.* 0·8 T);
(3) cooling down into the mesophase (rate approximately $0{\cdot}5\,\mathrm{K\,h^{-1}}$) to 5 K below the phase transition temperature.

In contrast to the technique described by Leadbetter *et al.* [13], the orientation disappeared after two days of annealing. Finally, the X-ray pattern shown in figure 4 (*a*) for substance **1** was obtained by exposing only one monodomain. The pattern displays

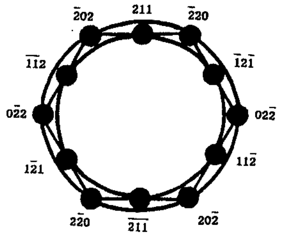


Figure 6. Indexing scheme for the small angle reflections of figures 4 (*a*) and 5 (*b*).

6 spot-like reflections matching a regular hexagon. On the middle of each side of the hexagon there is an additional spotlike reflection. These 12 reflections (see figure 4 (*b*)) are located on two rings corresponding to the diffraction angles $\theta_1 = 1\cdot34^\circ$ and $\theta_2 = 1\cdot53^\circ$, values which are in good agreement with the intense small-angle reflections observed with the Guinier technique (see the table).

Substance **2** showed a similar diffraction pattern, recorded by an area detector system (see figure 5). The θ values for the reflections observed were $\theta_1 = 1\cdot24^\circ$ and $\theta_2 = 1\cdot44^\circ$. The intensities of the reflections measured in arbitrary units match the relation $I_{\theta 1}:I_{\theta 2} = 100:34$.

In order to exclude the existence of reflections at smaller θ values, experiments with a Rigaku Denki small-angle camera (sample–film distance 300 mm, beam diameter 0·3 mm) were performed. No additional reflections could be recorded.

The observed reflections were indexed using the equation for a cubic elementary cell

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2).$$

The $\sin\theta$ values of the small-angle reflections of substance **1** match the proportions $\sqrt{3}:\sqrt{4}:\sqrt{7}$, and of substance **2**, the proportions $\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{8}:\sqrt{10}:\sqrt{11}$. However, it is impossible to obtain *hkl* values for a proportion 7. Therefore it was necessary to multiply the values of the *hkl* indices by the factor two. Then the spacing ratios obtained are:

Substance **1** $\sqrt{6}:\sqrt{8}:\sqrt{14}$

and

Substance **2** $\sqrt{6}:\sqrt{8}:\sqrt{14}:\sqrt{16}:\sqrt{20}:\sqrt{22}$

These values lead to the following indices and lattice parameter a of the unit cell:

Substance **1** (211), (220), (321), $a = 80\cdot5$ Å

and

Substance **2** (211), (220), (321), (400), (420), (322), $a = 87\cdot4$ Å.

An indexing similar to the one described here was earlier proposed by Tardieu and Billard [9] for the reflections obtained from investigation of the cubic phase of 4′-*n*-hexadecyloxy-3′-nitrobiphenyl-4-carboxylic acid.

The flat-plate camera reflections can now be indexed as shown in figure 6. There are only two space groups that match the proposed indexing: space group No. 220, I-4-3 d and space group No. 230, Ia-3d; both relate to body centred cubic cells. Only these two space groups have the conditions [22] which explain the absence of reflections with lower indices (100), (110), (111), (200) and (210) which could never be observed in our case.

$$hkl\colon h+k+l=2n,\quad h00\colon h=4n,\quad hhl\colon 2h+l=4n,\quad hk0\colon h,k=2n,$$

$$h,k,l,\ \text{permutable}$$

A distinction between the space groups is not possible on the basis of our measurements.

Space group No. 230 is frequently described in the literature for lyotropic cubic phases. A general picture of the structure of the space group Ia-3d for the cubic mesophase of a lipid–water system was earlier established by Luzzati [4]. There, the structure is described by a network of cylinders which are mutually interwoven, but not connected. This complex structure exhibits an X-ray pattern similar to that of our observations, and this points to similarities of the structures. Using the estimated densities and the lattice parameters, the unit cells of these cubic structures contain about 700 molecules. Therefore, the reflections obtained come from a superstructure built up by aggregates of molecules. In contrast, the diffuse wide-angle diffraction implies an almost amorphous arrangement of molecules or molecular parts, like the alkyl chains.

In the literature, two in principle different structures of the cubic phase have been discussed. As a most simple step for molecular assembly in a cubic structure, we have assumed globular arrangements (micelles) of molecules as the constituent units, as proposed in [4, 11]. Later Leadbetter *et al.* [13, 14], published arguments which support the existence of micelles. In contradiction to this model, Tardieu and Billard [9], Guillon and Skoulios [12] and Lydon [10] explain the structure in analogy to lyotropic systems [5] by a network of cylinders. Similarly, Fang and Levelut [15, 16] discuss the cubic structure of certain phasmidic compounds on the basis of a Schwarz minimal surface formed by two 'Labyrinths' of layers.

As also in the other cases, the information from our X-ray studies is not sufficient to prove one of these models. Some arguments, however, point rather to the network model:

(1) Considering the chemical structures of compounds **1** and **2**, the sugar moieties may play the role of the hydrophilic head groups and the alkyl chains of the hydrophobic parts of a lyotropic system. The different characters of both

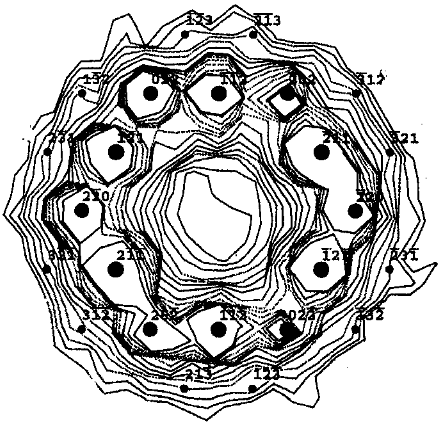


Figure 7. Overlay of a simulated diffraction pattern (points) on the experimentally obtained diffraction pattern of substance **2** (surface plot).

molecular parts may force a separation between them and hence generate a structural formation similar to the surfactant–water systems. The interpretation given by Luzzati and Spegt can then be applied.

(2) Attempts have been made to model the structure and to simulate the X-ray diffraction pattern by the CERIUS 3.1 program. Because of the complex structure, the calculation requires necessarily a severe limitation or simplification of the molecular structures. On the assumption that the hydrogen bond plays an important role in the structure formation, in a molecular model, all atoms have been rejected with the exception of the oxygen atoms. With these atoms, the structure of the space group Ia-3d has been built up and its X-ray diffraction patterns have been simulated. In more than 50 attempts, only such structures in which a network has been formed yielded sufficient agreement between the simulated and measured intensities of the reflections (see figure 7). The simulated patterns of micellar structures were quite different to those obtained.

Therefore we prefer to explain the structure of the cubic phase in the substances under discussion by a network formed by cylinders. In order to form such complex structures, the molecules must have special structural elements, and this would explain why only a few substances show such thermotropic cubic phases. Further investigations in this area are in progress [23].

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