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A carbohydrate with a rectangular columnar phase

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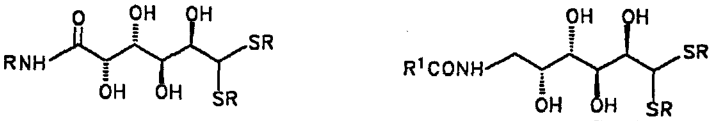
Carbohydrate dithioacetals are known to give hexagonal disordered columnar phases, but for the carbohydrate dithioacetals reported here, a new rectangular columnar phase has been found.

The thermotropic liquid crystal properties of substituted carbohydrate dithioacetals have been reported by four different groups [1–5]. Praefcke *et al.* [1] reported the occurrence of a hexagonal disordered columnar structure for these compounds. We now report a new columnar structure for some carbohydrate dithioacetals.

The substances investigated (see figure 1) have been prepared as previously described [5]. Liquid crystalline behaviour was determined visually with a Linkam THM 600 hot stage mounted on a Zeiss Ultraphot optical microscope combined with a Sharp video recorder for recording monotropic phases and metastable phase transitions. Thermal analysis has been carried out using a Perkin–Elmer DSC 7 with heating and cooling rates of $10\,\mathrm{K\,min^{-1}}$. Structural characterization has been performed using Cu–K_α radiation monochromized by a graphite crystal monochromator. The detection device was a Siemens X-1000 area detector combined with a PC for collecting, storing and processing the data or a flat film camera. The samples have been prepared in glass capillaries and oriented by permanent magnets.

Substances **1** and **2** exhibit enantiotropic hexagonal columnar disordered phases (see table 1). The phase transitions have been recorded by DSC and the phase types identified by X-ray scattering and polarization microscopy. Figure 2 shows DSC traces for **2**. The phase transition at 83°C indicates the transition to the mesophase. The clearing point, with a rather small heat of transition, occurs at 92°C. A small hysteresis for the cooling mode is detectable.



1 $R = C_8H_{17}$
2 $R = C_{12}H_{25}$

$R = C_{12}H_{25}$
$R^1 = C_{15}H_{31}$

1, N-*n*-octyl D-galacturonic acid amide di-*n*-octyl dithioacetal; **2**, N-*n*-dodecyl D-galacturonic acid amide di-*n*-dodecyl dithioacetal; **3**, N-*n*-hexadecanoyl 6-amino-6-deoxy-D-galactose di-*n*-dodecyl dithioacetal.

Figure 1. Liquid crystalline compounds investigated.

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Table 1. Phase transition temperatures for the substances investigated.

Sample	Phase transition temperatures/°C
1	C? D_{hd} 79 I
2	C 83 D_{hd} 92 I
3	C 110 (D_{rd} 84 D_{hd} 91) I

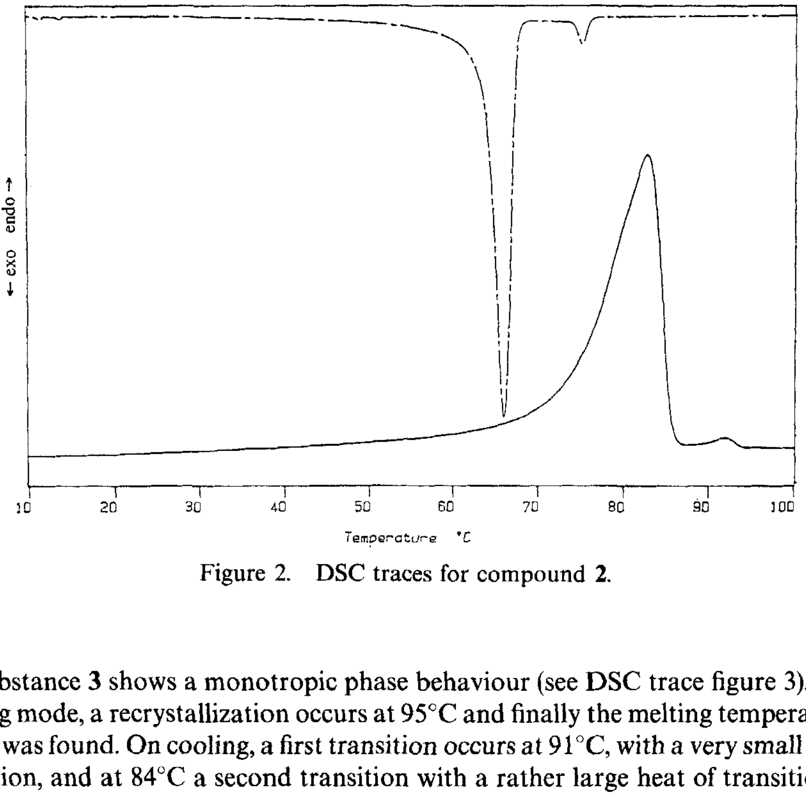

Figure 2. DSC traces for compound **2**.

Substance **3** shows a monotropic phase behaviour (see DSC trace figure 3). In the heating mode, a recrystallization occurs at 95°C and finally the melting temperature at 110°C was found. On cooling, a first transition occurs at 91°C, with a very small heat of transition, and at 84°C a second transition with a rather large heat of transition was detected. The two associated monotropic phase types have been identified by X-ray scattering experiments. Figures 4 and 5 (*a*) show a flat camera picture and the small angle reflection pattern of the isotropic phase of **3**. The first monotropic phase has been identified as a hexagonal columnar disordered phase, D_{hd}, (see figure 5 (*b*)). The X-ray picture was taken from a nearly monodomain sample in the columnar direction at 91°C; the small angle reflections show directly the hexagonal arrangement of the columns. The second monotropic phase has been identified as a rectangular columnar disordered phase, D_{rd}, (see figure 5 (*c*), taken at 70°C). Finally figure 5 (*d*) shows the development of polycrystalline material coming out of two monodomains of the D_{rd} phase at 96°C in the heating mode. The *d*-spacings are recorded in table 2. All the findings are supported by visual investigations using polarization microscopy (see figure 6), whereby the known textures of these columnar phases have been observed [6].

In principle, the columnar structures observed are surprising for acyclic trisubstituted compounds. Contrary to previously described disubstituted compounds, cyclic

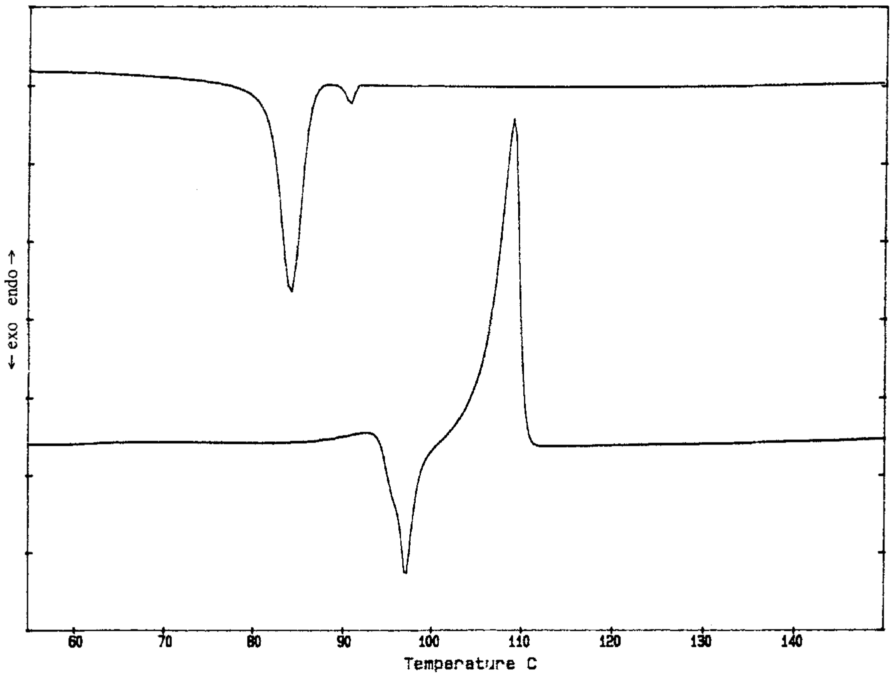

Figure 3. DSC traces for compound **3**.

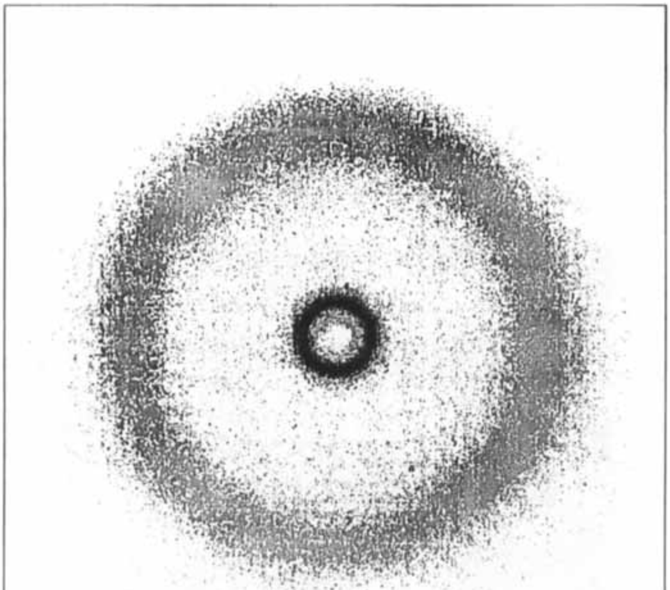

Figure 4. Flat camera picture of compound **3**; isotropic phase.

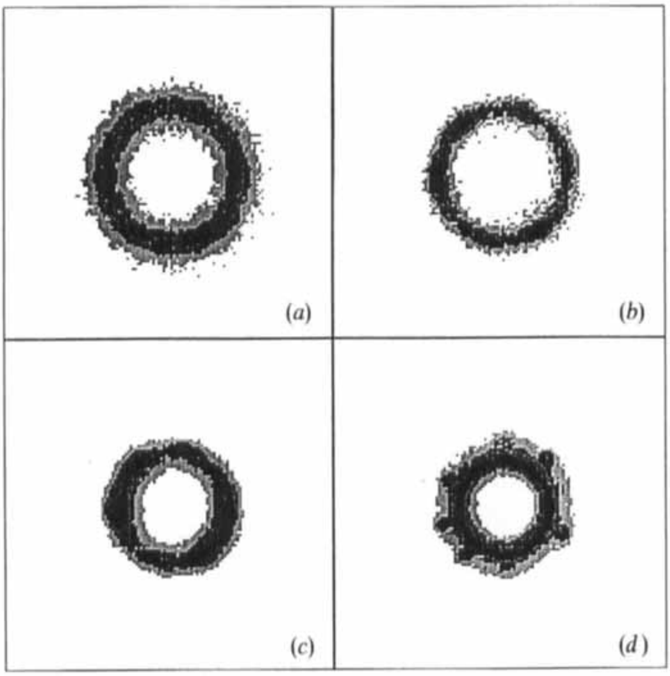

Figure 5. Flat camera pictures for compound 3. (*a*) Isotropic phase. (*b*) D_{hd} phase, 91°C. (*c*) D_{rd} phase, 70°C. (*d*) crystalline phase.

Table 2. Lattice parameters of the mesophases of the substances investigated.

Sample	Unit cell parameters *a*/Å	*b*/Å	Length of molecule/Å	Lateral distance/Å	Phase type
1			28		D_{hd}
2	28·2		37		D_{hd}
3	34		44	4·72	D_{hd}
4	36·2	50	44	4·53	D_{rd}

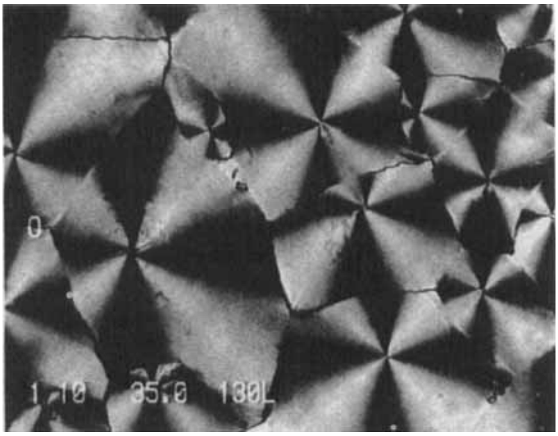

Figure 6. Texture of the D_{rd} phase of **3** at 35°C.

and acyclic, our substances [1, 3, 6, 7] are not able to form the PPM (Pie–Piece–Mesophase)-structure [3]. We suggest rather that the columns are constructed from single molecules which are arranged one above the other without a preferred orientation. The construction of the columns is supported by the strong H-bond interactions due to the hydroxyl-groups in the middle of the molecules and by a separation into hydrophilic and hydrophobic molecular parts. The differences between the theoretical values of the molecular length and the measured columnar dimensions are an indication of intercalation of the alkyl chains and favour the idea of hydrophobic van der Waals interactions of the side chains.

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