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Liquid Crystals

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Thermotropic liquid crystalline properties of 1,2,ψ,ω-*n*-alkan-tetraols

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A homologous series of biamphiphilic 1,2,ψ,ω-alkan-tetraols has been synthesized. They form lamellar thermotropic liquid crystalline phases which have been studied by polarizing optical microscopy, as well as by X-ray investigations. Those compounds with a rather long polymethylene chain between the two diol groups exhibit a lamellar α phase and an additional low temperature mesophase, whereas short chain derivatives exhibit only the low temperature mesophase. From X-ray measurements, we conclude that this low temperature mesophase is a highly ordered phase in which the chains are rigid and tilted with respect to the hydrogen bonding networks.

1. Introduction

Hydrogen bonding plays an important role in the formation of liquid crystalline phases. The mesomorphic dimers of the 4-substituted benzoic acids [1] and the cyclohexane carboxylic acids [2], diisobutylsilandiol [3], the large family of mesomorphic carbohydrate derivatives [4–9], and related amphiphilic polyhydroxy compounds [10–12] are well-known examples. More recently, the molecular recognition directed self-assembly of supramolecular liquid crystalline phases from pyridines and carboxylic acids [13, 14] and from complementary heterocyclic components via hydrogen bonding has been described [15, 16].

Even simple *n*-alkan-1,2-diols, **1**, with a sufficiently long alkyl chain form thermotropic and, after addition of water, also lyotropic liquid crystalline phases, which consist of bilayers stabilized by hydrogen bonding networks [17, 18]. Recently we have reported that their liquid crystalline phases could be significantly stabilized by coupling of two amphiphilic diols via their hydrophobic molecular terminal groups to give biamphiphilic (bola-amphiphilic [19–21]) tetraols with extended mesomorphic ranges [22, 23].

In this paper we report details of the thermotropic liquid crystalline properties of these bola-amphiphilic tetraols. The homologous series of biamphiphilic 1,2,ψ,ω-*n*-alkan-tetraols, **2**, ranging from $n = 4$ to 18 and $n = 20$ has been synthesized.

The phase transitions were studied by polarizing optical microscopy and DSC measurements, and the molecular order within the mesophases was investigated by X-ray investigations.

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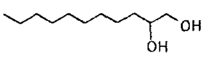
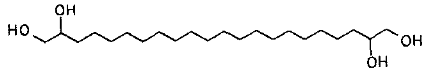
1 C 49 (L_β 42) I



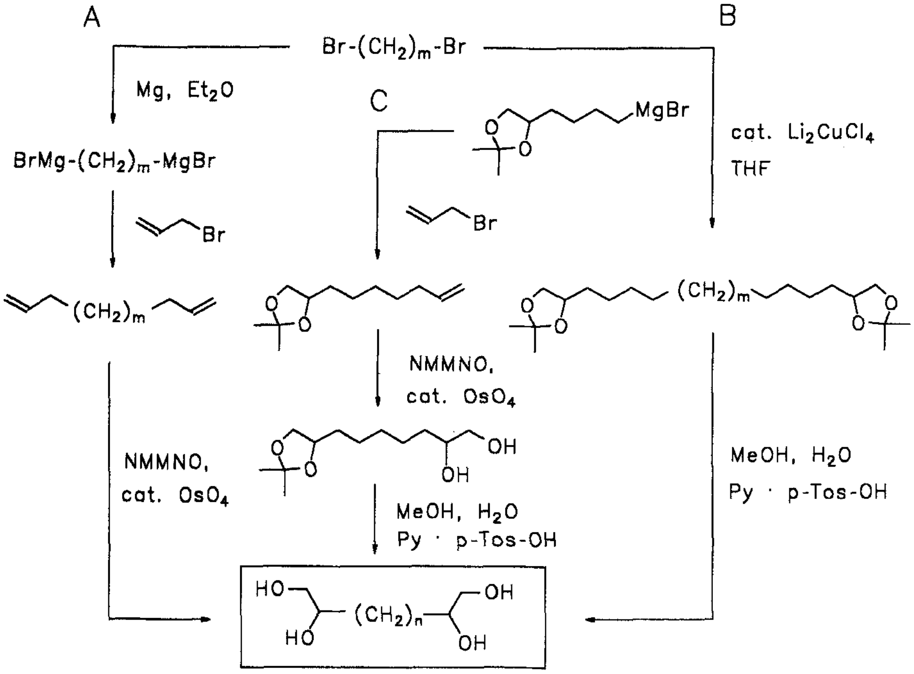
2.15 C 87 $L_{\beta'}$ 140 L_α 143 I



2. Synthesis of materials

2.1. *Routes A, B, and C.*

The synthesis of the *n*-alkan-1,2,ψ,ω-tetraols, **2**, has been carried out according to the scheme using three different approaches, *A*, *B* and *C*. Compounds **2.3**–**2.7** and **2.11** were obtained according to route *A*. Thereby, 1,ω-dihaloalkanes ($m = 4$–8, 12) were transformed into the corresponding double Grignard reagents, which were coupled with allyl bromide. The 1,ω-dialkenes obtained were twice bishydroxylated with *N*-methylmorpholine-*N*-oxide in the presence of catalytic amounts of osmium tetroxide [24]. Compounds **2.8**–**2.10**, **2.12**–**2.14** and **2.16** were synthesized by cuprate catalysed (Li_2CuCl_4) cross coupling [25] of 4-(2,2-dimethyl-1,3-dioxolan-4-yl)butyl magnesium bromide with 1,ω-dihaloalkanes ($m = 3$–10, 12), followed by deprotection of the resulting acetonides. Route *C* was used to synthesize the 1,2,8,9-tetrahydroxy-nonane (**2.2**) by cross coupling 4-(2,2-dimethyl-1,3-dioxolan-4-yl)butyl magnesium bromide with allyl bromide. Compound **2.1** was obtained from commercially available 1,7-octadiene by double bishydroxylation. The synthesis of compound **2.15** has recently



Scheme 1. Synthesis of the bola-amphiphilic 1,2,ψ,ω-*n*-alkan-tetraols, **2.1**–**2.16**.

been described [22]. The final products were purified by crystallization from chloroform.

2.2. *Experimental*

In the following section, one representative example is given for each of the synthetic routes *A* and *B*.

2.2.1. *1,20-Bis(2,2-dimethyl-1,3-dioxolan-4-yl)eicosane*

A solution of 4-(2,2-dimethyl-1,3-dioxolan-4-yl)butyl magnesium bromide was prepared by slowly adding 13 mmol (3·1 g) of 4-(2,2-dimethyl-1,3-dioxolan-4-yl)butyl bromide, dissolved in 20 ml of dry THF to 15 mmol (0·36 g) of magnesium turnings in 3 ml of THF under argon with ultrasonication at 40°C. The solution was cooled to − 30°C and a solution of Li_2CuCl_4 in dry THF (0·1 molar, 5 ml) was added, followed by slow addition of 5 mmol (1·64 g) of 1,12-dibromododecane in 5 ml of dry THF. The mixture was stirred for an additional hour at − 30°C, 12 h at − 20°C and finally 10 h at 10°C.

Afterwards, the mixture was poured into ammonium chloride solution (15 per cent, 100 ml). After addition of 50 ml of diethyl ether the organic layer was separated and the aqueous solution was twice shaken with 50 ml of diethyl ether. The unified organic layers were subsequently washed with brine (50 ml) and dried over sodium sulphate. The residue, which was obtained after evaporation of the solvents was crystallized from methanol. Yield 1·30 g (54 per cent), m.p. 74–75°C; Elemental analysis, calculated for $C_{30}H_{58}O_4$ (482·76): C, 74·63; H, 12·11 per cent. Found: C, 75·19; H, 12·50 per cent. ^{1}HNMR (ppm, $CDCl_3$): 1·22 (36 H, s, broad, CH_2), 1·33 (6 H, s, CH_3), 1·38 (6 H, s, CH_3), 1·5 (4 H, m, CH_2), 3·47 (2 H, m, CH–O), 4·02 (4 H, m, CH_2–O).

All other 1,ω-bis(2,2-dimethyl-1,3-dioxolan-4-yl)alkanes were oily or waxy compounds which were used without further purification in the next step.

2.2.2. *1,2,23,24-Tetrahydroxytetracosane* **2.16**

1,20-Bis(2,2-dimethyl-1,3-dioxolan-4-yl)eicosane (1·21 g, 2·5 mmol) was dissolved in 50 ml of methanol. After addition of water (1 ml) and pyridinium toluene sulphonate (100 mg), the solution was boiled for 2 h. The solvent was removed using a rotary evaporator and the residue was dissolved in ethyl acetate (150 ml), washed with sodium hydrogen carbonate solution (5 per cent, 50 ml) and brine (50 ml), and dried over sodium sulphate. After evaporation of the solvent the residue was repeatedly crystallized from chloroform. Yield 0·80 g (79 per cent); Transition temperatures: C 111 $L_{\beta'}$ 140 L_α 141 I. Elemental analysis, calculated for $C_{24}H_{50}O_4$ (402·64): C, 71·59; H, 12·52 per cent. Found: C, 71·29; H, 12·56 per cent. ^{1}HNMR (ppm, DMSO-*d*6): 1·23 (36 H, s, broad, CH_2), 1·36 (4 H, m, CH_2), 3·22 (4 H, t, CH_2–O), 3·34 (2 H, m, CH–O), 4·29 (2 H, d, CH–O$\underline{H}$), 4·38 (2H, t, CH_2–O$\underline{H}$).

2.2.3. *1,11-Dodecadiene*

1,6-Dibromohexane (6·07 g, 25 mmol), dissolved in 40 ml of diethyl ether, was added to 60 mmol (1·46 g) of magnesium turnings in 5 ml of THF under an argon atmosphere at 40°C. The resulting Grignard solution was filtered under argon and 0·15 mol (18·1 g) of allyl bromide was added dropwise at reflux temperature. Boiling was continued for 10 h. After cooling to room temperature, ammonium chloride solution (15 per cent, 150 ml) was added carefully with stirring. The organic layer was separated and the aqueous phase shaken twice with diethyl ether (2 × 50 ml).

The combined organic layers were washed with ammonium chloride solution (15 per cent, 50 ml) and brine, and dried over sodium sulphate. After careful evaporation of the solvent, the residue was distilled *in vacuo* to yield 2·62 g (63 per cent) of 1,11-dodecadiene, b.p. 88–90°C at 15 torr; ^{1}HNMR (ppm, $CDCl_3$): 1·26 (12 H, s, broad, CH_2), 2·01 (4 H, q, $-C\underline{H}_2-CH=$), 4·90 (2 H, dd, *cis* $\underline{H}_2C=CH-$), 4·96 (2 H, dd, *trans* $\underline{H}_2C=CH-$), 5·68–5·85 (2H, $H_2C=C\underline{H}-$).

2.2.4. *1,2,11,12-Tetrahydroxydodecane* **2.5**

1,11-Dodecadiene (2·5 g, 15 mmol) was added to a solution of 42 mmol (4·9 g) of *N*-methylmorpholine-*N*-oxide in 75 ml of acetone. To this solution, 0·5 ml of water and 0·2 ml of osmium tetroxide solution (1 per cent in toluene) were added. The resulting mixture was stirred for 24 h at room temperature. After this time, starting materials could no longer be detected and the mixture was worked up. Sodium bisulphite (saturated aqueous solution, 5 ml) was added and the resulting slurry was vigorously stirred for half an hour at room temperature. Afterwards, the solids were filtered off through a pad of Celite, the residue was washed twice with hot ethyl acetate (2 × 150 ml) and the solvents were distilled off using a rotary evaporator. The residue was dissolved again in hot ethyl acetate (250 ml) and the warm solution was washed with sulphuric acid (10 per cent, 50 ml), sodium bicarbonate solution (5 per cent, 50 ml) and brine, and finally dried over sodium sulphate. After evaporation of the solvent, the residue was repeatedly crystallized from chloroform. Yield: 1·62 g (69 per cent); Transition temperatures: C 114 ($L_{\beta'}$ 100) I; Elemental analysis, calculated for $C_{12}H_{26}O_4$ (234·34): C, 61·51; H, 11·18 per cent. Found: C, 60·97; H, 11·10 per cent. ^{1}HNMR (ppm, DMSO-*d*6): 1·23 (12 H, s, broad, CH_2), 1·36 (4 H, m, CH_2), 3·22 (4 H, t, CH_2-O), 3·34 (2 H, m, CH–O), 4·29 (2 H, d, CH–O$\underline{H}$), 4·38 (2 H, t, CH_2-OH); IR (cm^{-1}, KBr): 3300, 2900, 1460, 1370, 1100, 1060, 1020, 970, 870 cm^{-1}.

3. Thermotropic properties of 1,2,ψ,ω-*n*-alkan-tetraols

The results of calorimetric measurements and investigations of the compounds on a heating stage using polarizing microscopy are collected in table 1. With respect to their mesomorphic phase sequences, the compounds may be divided into two groups. Firstly, the compounds **2.8–2.16** with a rather long polymethylene chain between the diol groups ($n = 11$–20), and secondly those with a short chain (compounds **2.1–2.7**; $n = 4$–10). The behaviour of compound **2.13** ($n = 16$) is typical for the first-group: by cooling from the isotropic melt, a fan-like texture, which is characteristic for the smectic A phase and the lamellar α phase (L_α) appears (see figure 1 (*a*)). Slightly shearing the sample very easily gives rise to a homeotropic orientation. On further cooling, at 138°C, a transition to a mosaic-like texture (see figure 1 (*b*), (*c*)) is observed. On cooling from the homeotropically oriented L_α phase, this transition could also be observed by the appearance of grey mosaic-like regions. Both transitions are accompanied by rather large transition enthalpies.

Compounds **2.2–2.7** with short polymethylene chains ($n = 5$–10) do not exhibit the high temperature mesophase. On cooling from the isotropic melt, the formation of doubly refracting lancets and regions with low birefringence are observed. Typical textures of this low temperature phase, are given in figure 2. The observed textures have some similarities to the texture of the smectic B phase and the high temperature phase ('plastic phase') of paraffins. Figure 2 (*b*) displays a part of the sample which consists mainly of the low doubly refracting regions. On further cooling stripes become clearly visible (see figure 2 (*c*)). Their appearance takes place over a broad temperature range

Table 1. Temperatures (°C) and associated enthalpy values (kJ mol^{-1}, lower lines in brackets) of transitions determined for the 1,2,ψ,ω-n-alkane-tetraols **2·1–2·16**.

Compound	n	C		$L_{\beta'}$		L_α		I	Reference
2.1	4	●	79 (36·7)	—	—	—	—	●	[23]
2.2	5	●	77 (37·8)	(●	36·0) (7·2)	—	—	●	[23]
2.3	6	●	90/101 (45·6)	(●	75·0) (10·4)	—	—	●	
2.4	7	●	118 (46·3)	(●	90·0) (12·6)	—	—	●	
2.5	8	●	88/114 (45·7)	(●	110) (15·3)	—	—	●	
2.6	9	●	110 (42·4)	●	115 (17·2)	—	—	●	[23]
2.7	10	●	85 (30·0)	●	124 (18·9)	—	—	●	
2.8	11	●	52/57/95/101 (41·5)	●	127 (20·0)†	●	128	●	
2.9	12	●	77/87 (31·7)	●	132 (9·6)	●	134 (12·7)	●	
2.10	13	●	56/78/90 (38·7)	●	131 (10·6)	●	136 (13·3)	●	
2.11	14	●	79 (21·5)	●	134 (11·0)	●	137 (14·6)	●	
2.12	15	●	89 (45·4)	●	135 (12·4)	●	139 (15·0)	●	
2.13	16	●	84 (24·0)	●	138 (14·0)	●	142 (15·5)	●	
2.14	17	●	61 (41·4)	●	139 (15·1)	●	143 (15·6)	●	
2.15	18	●	87 (20·3)	●	140 (17·0)	●	143 (15·2)	●	[22]
2.16	20	●	94/104/111 (40·1)	●	140 (39·0)†	●	141	●	

† Enthalpy corresponds to the total area under both peaks.

and is not connected with an endotherm in the DSC traces (see figure 3). Compound **2.1** with a tetramethylene chain ($n = 4$) is a crystalline substance and no mesomorphic properties could be observed, even in the supercooled state.

Some of the tetraols exhibit an extensive crystalline polymorphism. Several transitions between crystalline phases, as well as different melting points dependent upon the thermal history of the samples could be detected. The dependence of the thermotropic properties of the biamphiphilic n-alkan-1,2,ψ,ω-tetraols on the length of the polymethylene chain between the diol groups in graphically displayed in the diagram given in figure 4. Here only the highest melting points of the crystalline phases are considered. It is obvious that the mesophase stability continuously increases with growing polymethylene chain length without a significant odd–even effect.

Also the enthalpies of the phase transitions between the mesophases and from the mesophases to the isotropic liquid continuously grow with increasing spacer length. However, the melting enthalpies remain of the same order of magnitude, but in the case of the long chain homologues, a significant odd–even effect could be observed, with

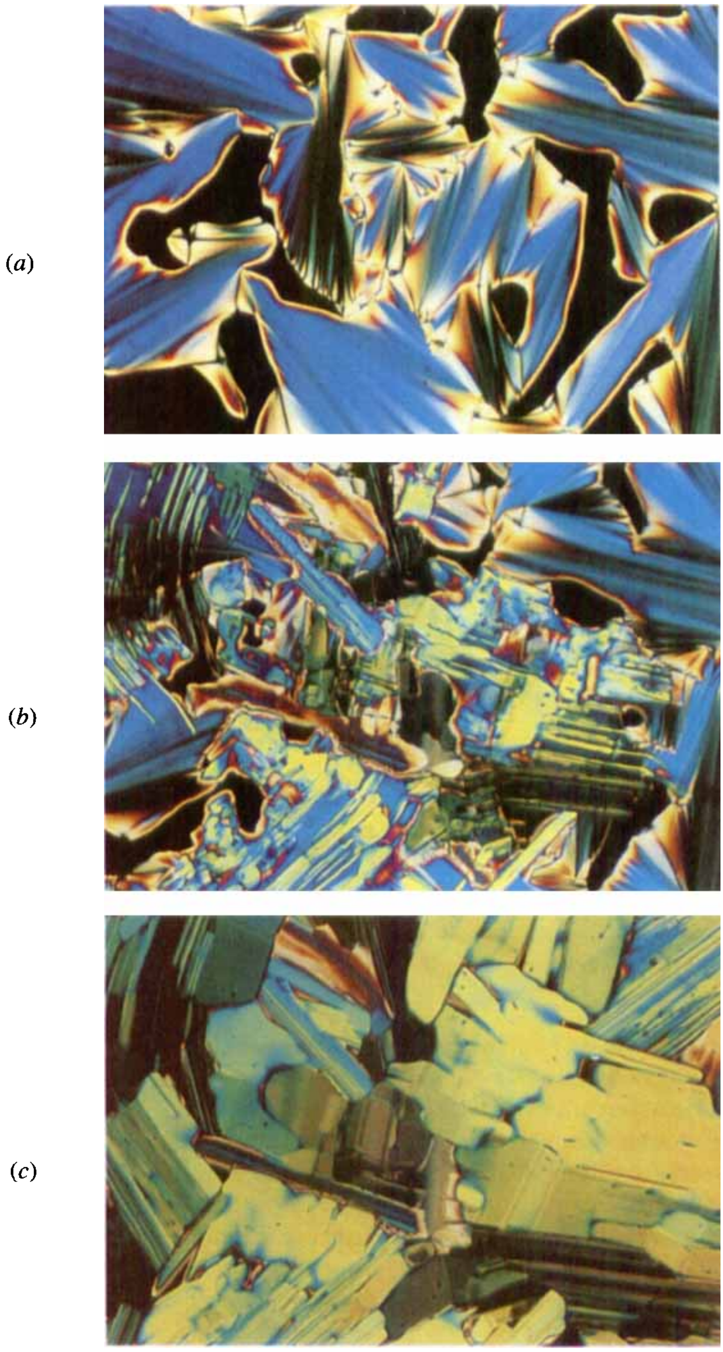


Figure 1. Polarized optical microscopic textures of **2.13** (*a*) L_α phase at 141°C, (*b*) transition from the L_α phase to the low temperature mesophase ($L_{\beta'}$) at 138°C, (*c*) low temperature mesophase ($L_{\beta'}$) at 129°C (× 200).

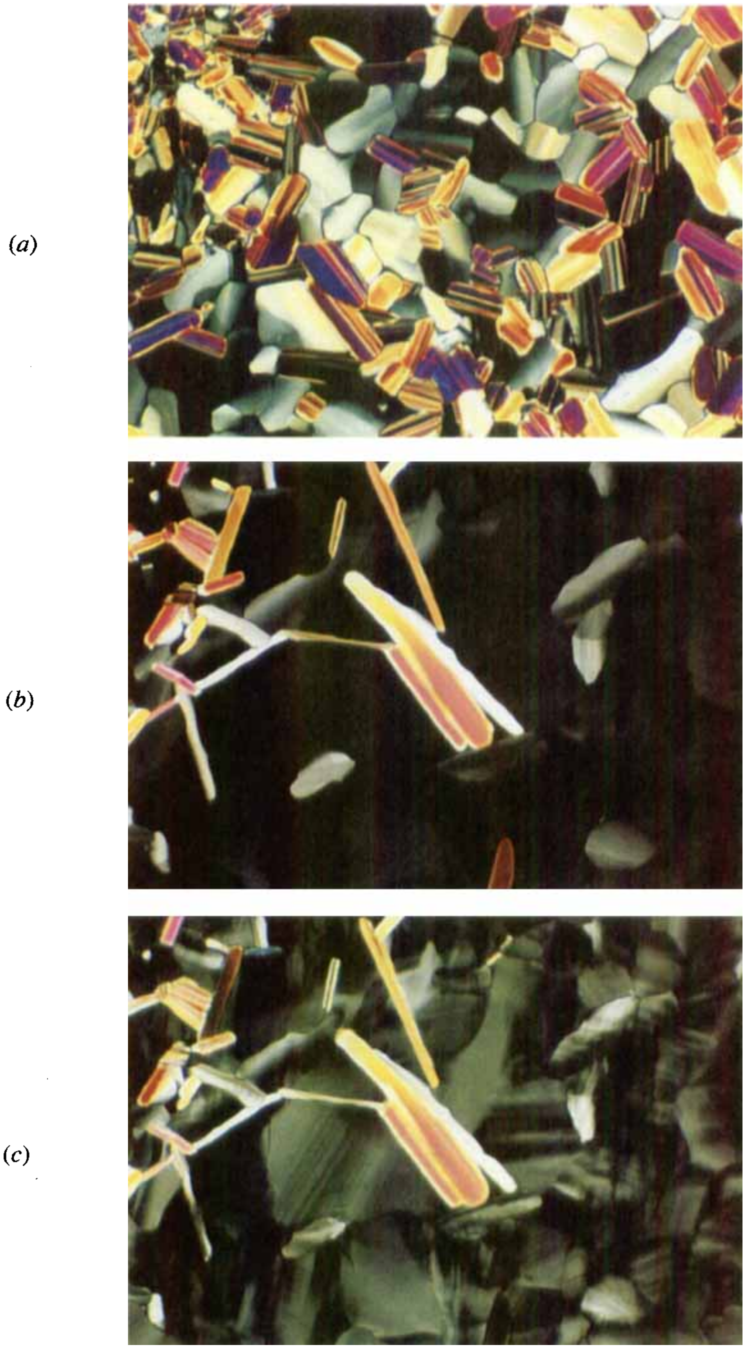


Figure 2. Polarized optical microscopic textures of the mesophase ($L_{\beta'}$) of compound **2·7** as obtained by cooling from the isotropic melt (*a*) at 113°C, (*b*) another area of the same sample at 120°C, (*c*) same area as (*b*) at 90°C (×200).

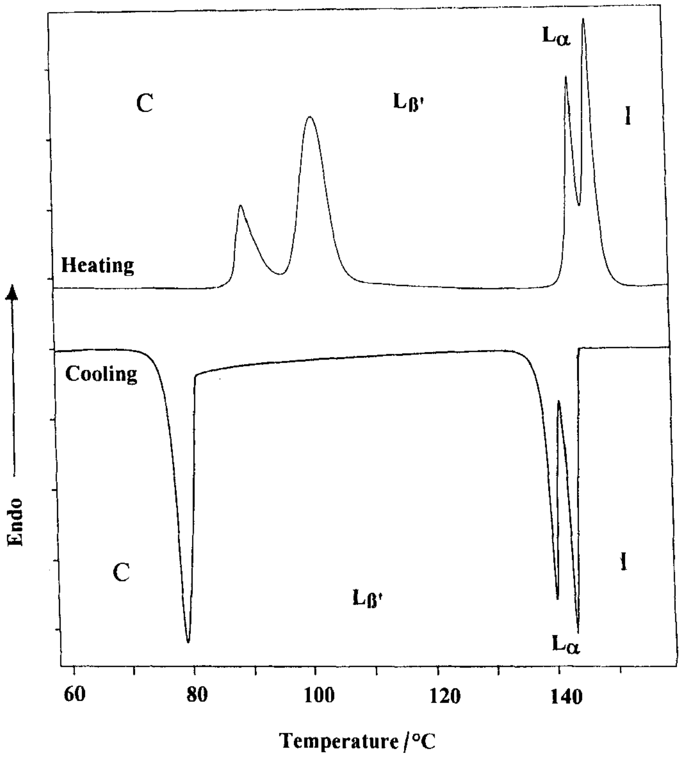


Figure 3. DSC traces for compound **2·9** (Perkin–Elmer DSC 7, rates of heating and cooling: 5 K min^{-1}).

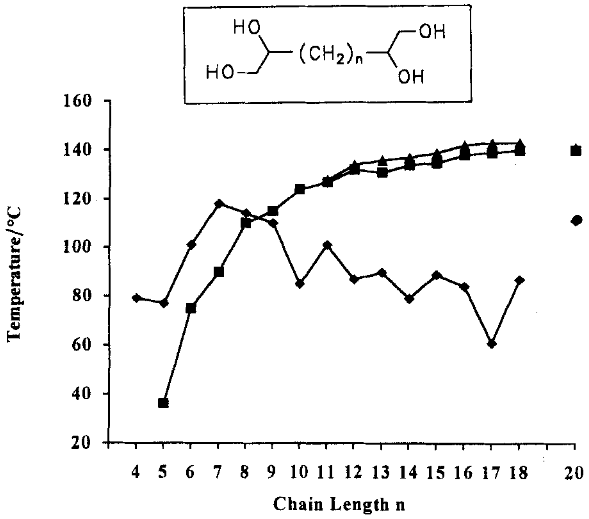


Figure 4. Transition temperatures as a function of the number of methylene groups (C–I or C–L$_{\beta'}$ (◆); L$_{\beta'}$–I or L$_{\beta'}$–L$_{\alpha}$ (■); L$_{\alpha}$–I (▲)).

the even numbered members displaying the lower values. Probably the stability of the crystal lattice differs or the most stable crystalline state is not obtained even after prolonged storage due to kinetic inhibition. Further investigation of the mesophases was made by X-ray investigations.

4. X-ray studies

The X-ray studies have been performed as a function of temperature on the homologues with $n = 8$ to $n = 20$. The Guinier goniometer, and in some cases also a

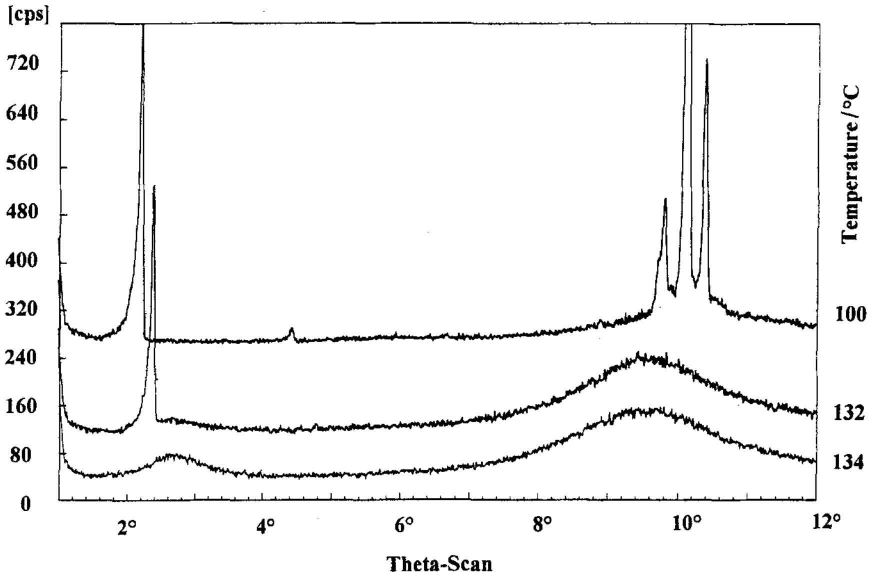


Figure 5. X-ray scattering of compound **2·9** in the $L_{\beta'}$, L_α and isotropic liquid phases.

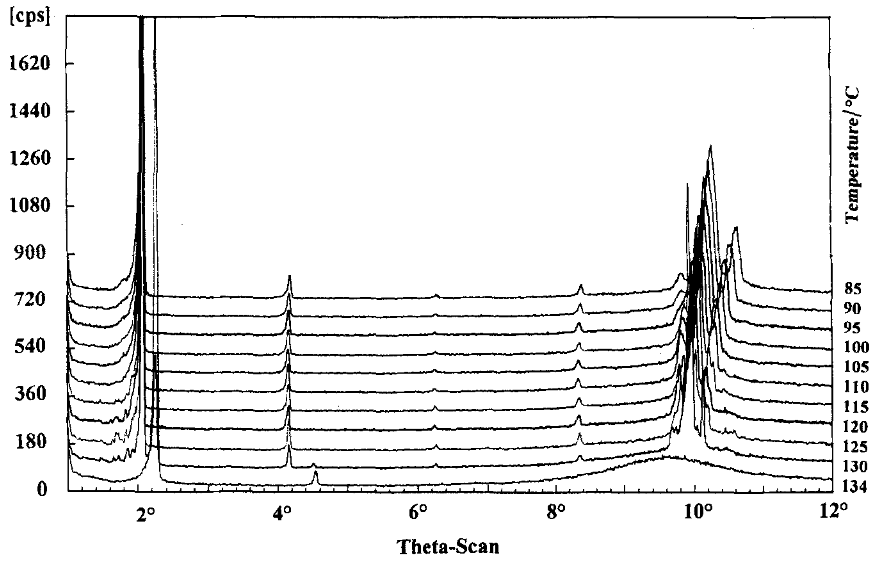


Figure 6. Temperature dependence of the X-ray reflections of compound **2.10**.

Guinier film camera have been used to investigate non-oriented samples of the compounds. Figures 5 and 6 show representative goniometer traces for the low and high temperature phases. The pattern of the low temperature phase is characterized by several reflections around a Bragg angle of 10 degrees, as well as by several orders of a layer reflection at small angles. At the transition into the high temperature phase, the position of the layer reflection is changed discontinuously (see figure 6, trace at $T = 130°C$, in which two spacings can be seen due to a small temperature gradient). The outer reflections disappear, and only a diffuse scattering is detected in this scattering region. Figure 6 displays the temperature dependence in more detail. The outer reflections are continuously shifted to smaller angle and they approach each other more and more with increasing temperature, whereas the position of the layer reflection is nearly independent of temperature over the range of the phase. These X-ray studies point to a transition from a layer structure with order in the layers to a layer structure without order (L_α).

Figure 7 shows the *d*-values as a function of the number of methylene groups. The linear dependence of the *d*-values up to high numbers of *n*, in relation to the sharp reflections in the wide angle region, supports the assumption of rigid chains in the low temperature phase.

The increase in the values per methylene group of about 0·11 nm points to a tilted alignment of the chains with respect to the hydrogen bonding networks formed by the diol groups at both ends of the molecules. Therefore we propose to designate this low

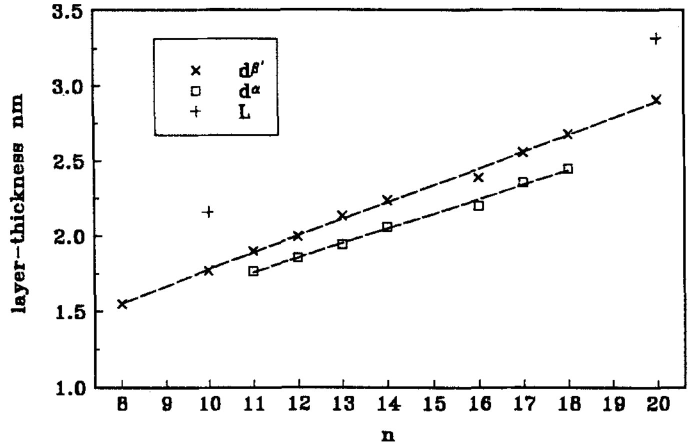


Figure 7. Dependence of the *d*-values on the number of methylene groups.

Table 2. Lattice parameters of the low temperature mesophase of compound **2·9** at $T = 100°C$. ($a = 1·00$ nm, $b = 0·514$ nm, $c = L = 2·38$ nm, $\beta = 122·8°$.)

Θ_{obs}	*hkl*
2·21	001
4·41	002
9·80	$11\bar{1}$
10·12	110
10·57	200

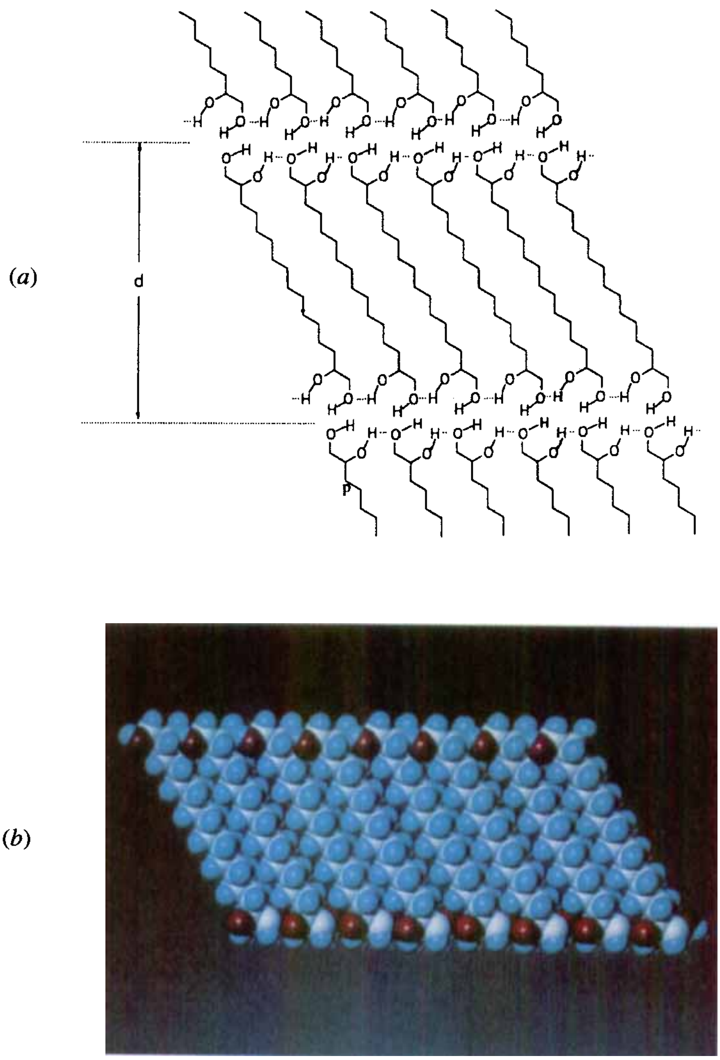


Figure 8. Structural sketch (*a*) and space filled molecular model (*b*) (SYBYL, version 6·03, Tripos Associates, Inc., St. Louis [27]) of the assumed supramolecular structure of the hydrogen bonding networks between the diol groups in the low temperature mesophase ($L_{\beta'}$) of the bola-amphiphilic tetraols **2** (this example is for compound **2.9**; hydrogen bonds between the layers are not drawn).

temperature phase as $L_{\beta'}$, according to the Luzzati nomenclature [26]. With respect to the value of 0·125 nm per methylene group found for paraffin chains, an average tilt angle of 28 degrees can be estimated. The evaluation of the diffraction pattern on the basis of a monoclinic cell (see table 2), with $c = L$, yields in the case of compound **2.9**, a monoclinic angle $\beta = 122{\cdot}8$ degrees ($\beta = 90 + \alpha$), which is in a good agreement with the estimation.

On the basis of the experimental values, a model of the packing is proposed as sketched in figure 8. It is assumed that the primary OH-groups interact via hydrogen bonding with the secondary OH-groups of the corresponding neighbouring molecule. In this way the tilt angle α of about 30 degrees could be explained.

The layer thickness decreases discontinuously at the transition into the high temperature phase. This transition has a high transition enthalpy which is of the same order of magnitude as the transition to the isotropic phase. It can be assumed that in the high temperature phase, the methylene chains are liquid-like, as in the case of the L_α phase of lyotropic systems. The melting of the polymethylene chains must be accompanied by a reorganization of the hydrogen bondings which must also contribute to the transition enthalpy. With respect to the high transition enthalpy between the two mesophases and the high viscosity, the low temperature phase should be considered as more solid like, although the X-ray-patterns are very similar to those of the low temperature mesophases of amphiphilic diol compounds [12, 17, 18]. Furthermore, the transition to the $L_{\beta'}$ phase could not be supercooled and the melting enthalpies are larger. However, in contradiction to the diols, the compounds under discussion are fixed via hydrogen bonding at both ends of the molecule. Therefore the intermolecular interactions would be expected to be much stronger compared with those of the diol derivatives.

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