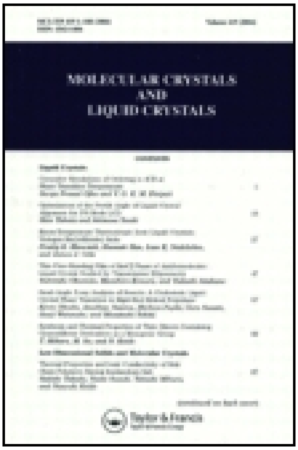

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Liquid Crystalline Structures of the 2-(trans-4-n-alkylcyclohexyl)propan-1,3-diols

S. Diele [a] , A. Mädicke [a] , E. Geißler [a] , K. Meinel [a] , D. Demus [a] & H. Sackmann [a]
[a] Martin-Luther-Universität Halle-Wittenberg, Sektion Chemie, Mühlpforte 1, 4020, Halle/S., GDR

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Liquid Crystalline Structures of the 2-(*trans*-4-*n*-alkylcyclohexyl)propan-1,3-diols

S. DIELE, A. MÄDICKE, E. GEIßLER, K. MEINEL, D. DEMUS and H. SACKMANN
Martin-Luther-Universität Halle-Wittenberg, Sektion Chemie, Mühlpforte 1, 4020 Halle/S., GDR

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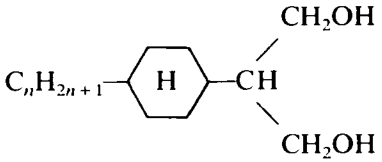
X-ray, miscibility and calorimetric studies of four homologous 2-(*trans*-4-*n*-alkylcyclohexyl)-propan-1,3-diols are reported. The specific intermolecular interactions lead to novel variants of smectic structures of types A and B, designated with A^+ and B^+. They are explained by a bi-molecular layer with intercalated alkyl chains. The hydrogen bonded molecular arrangement causes a well defined layer periodicity even in the A^+ phases. Both phases A^+ and B^+ do not show a complete miscibility with conventional liquid crystals.

INTRODUCTION

In a recent paper[1] some results obtained for the hexyl homologue of substances with the general formula



have been reported briefly.

Now the measurements have been completed by additional X-ray, miscibility and calorimetric studies, including examination of further homologues of the series.

The work aims at elucidating the mesogenic structures of substances which can give rise to specific intermolecular interactions. Because of their chemical structure, the substances under discussion may be assumed to provide a link between non-amphiphilic and amphiphilic compounds, *e.g.*, soaps, tensides and phospholipids, all of which form liquid crystal phases.

EXPERIMENTAL

The texture observations involving the pure and mixed phases were performed using a polarizing microscope.

The calorimetric studies were done by means of a DSC 2 (Perkin Elmer, Conn., USA). X-ray patterns of powder-like samples were taken using Guinier equipment. Oriented samples were obtained by applying a magnetic field of about 1.8 tesla and cooling down the sample from the isotropic state into the mesomorphic phase. Generally it was very difficult to achieve oriented samples of good quality.

The *d*-values (layer thicknesses) were measured by means of small angle X-ray equipment.

RESULTS

Transition heats

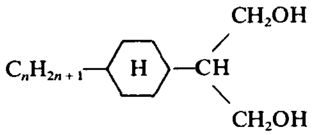
Table I displays the transition temperatures (°C) and enthalpies (kJ mol^{-1}) for the substances investigated. The first transition (Figure 1) always has the highest value of enthalpy, indicating that it marks the melting process.

Textures and miscibility

A preliminary designation of the liquid crystalline phases was made on the basis of texture observations. All textures correspond to the known textures of conventional liquid crystals, *e.g.*, the A$^+$ phases exhibit a fan shaped texture (Figure 2), and the B$^+$ phases mosaic textures with bâtonnets and pseudo-isotropic regions (Figure 3). Cooling down the sample from the A$^+$ phase usually generates paramorphotic fan-shaped texture for the B$^+$ phase.

TABLE I

Transition Values



n	Substance code		cr		B$^+$		A$^+$		is
2	**2**	*a*	·	55.9	·	86.2	—	—	·
		b	·	16.0	·	6.3	—	—	·
5	**5**	*a*	·	73.1	·	113.8	—	—	·
		b	·	21.1	·	7.4	—	—	·
6	**6**	*a*	·	85.9	·	113.3	·	116.0	·
		b	·	27.2	·	2.1	·	6.4	·
10	**10**	*a*	·	99.0	—	—	·	111.2	·
		b	·	38.7	—	—	·	7.0	·

[a] Transition temperatures (°C)
[b] Transition enthalpies (kJ/mol^{-1})

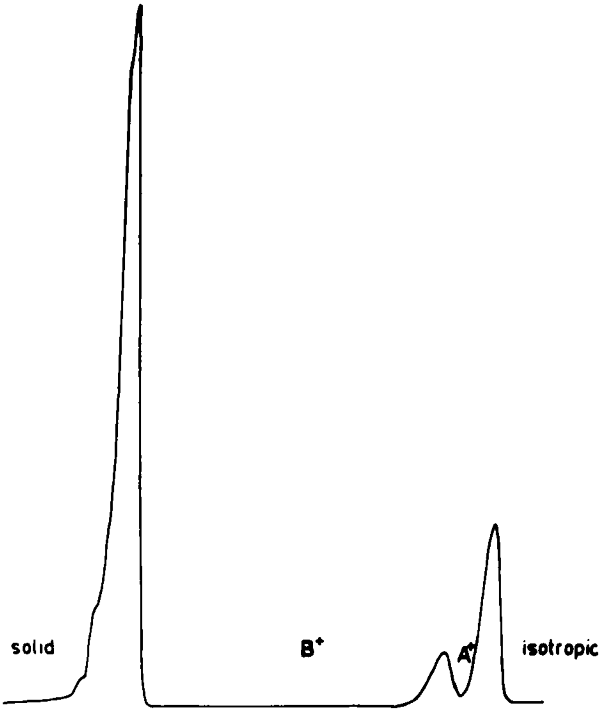


FIGURE 1 DSC trace for substance **6**.

A designation A or B, respectively, for the phases under discussion could not be obtained by miscibility studies. In binary systems with conventional thermotropic liquid crystals of defined phase type (A and/or B), complete miscibility was not observed in any case. In Table II, the reference substances used as components in these binary systems are listed.

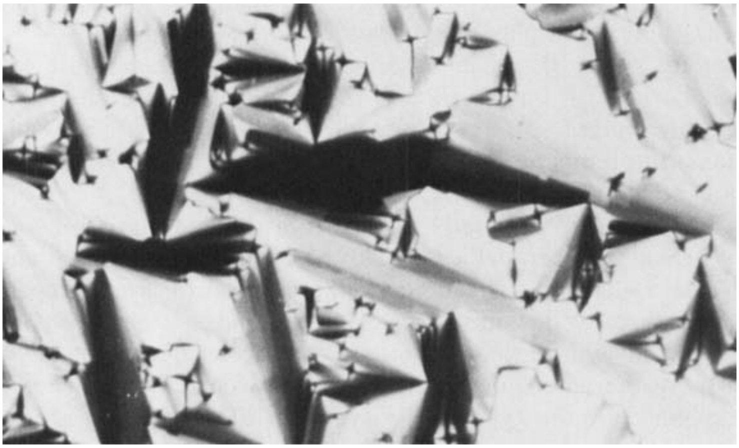


FIGURE 2 Texture of the A^+ phase of substance **6**.

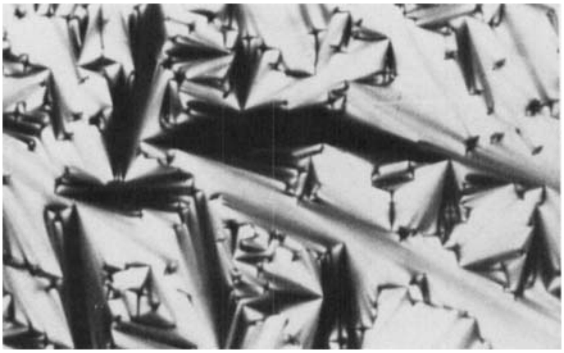


FIGURE 3 Texture of the B^+ phase of substance **6**.

The phase diagrams of two of the investigated systems are given in Figures 4 and 5. In the system shown in Figure 4, a broad miscibility gap between the two smectic phases was observed. In the system shown in Figure 5, the two phases A^+ and A, B^+ and B, respectively, of the two components do not show a complete miscibility. At intermediate concentrations, mesomorphic phases disappear, a quite unusual observation for binary A- and B-phase systems.

X-ray studies

The Guinier patterns of the A^+ and B^+ phases exhibit an inner reflection and its higher orders indicate a layer packing. In the patterns of the A^+ phases, a diffuse outer scattering at Bragg angles between 10 and 11 degrees proves the statistical distribution of the lateral distances, which is well known for smectic A phases. In the patterns of the B^+ phases, several outer interferences have been detected (Figure 6) which seemed to be a contradiction of the patterns of conventional B phases. However, in connection with the patterns obtained from the oriented samples described below, these interferences could be indexed assuming a hexagonal cell. Table III displays the calculated lattice constants.

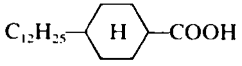
The patterns of the B^+ phases are independent of temperature in the case of substances **2** and **6**. A qualification is required in the case of substance **5**. The positions of the outer interferences are altered slightly. Therefore only those patterns obtained at temperatures between 70°C and 80°C are comparable with the patterns of the homologues.

From the patterns of oriented samples it was proved that the long axes of the molecules are aligned perpendicularly to the magnetic field (see Figure 2 of Reference 1). This alignment is caused by the absence of aromatic parts from the chemical structures of the substances. This is found in other substances too, and comparative studies have been reported.[2] As a consequence of this orientation, the intensity of the outer interferences is usually located on a nearly closed ring. This is explained by the cylindrically symmetrical distribution around the short molecular axis, according to which different parts of the sample—with different orientations of the layer normal—are irradiated.

TABLE II

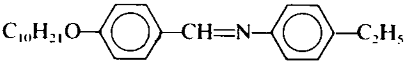
Reference Substances

Trans-4-*n*-dodecylcyclohexane-1-carboxylic acid



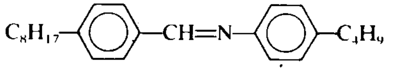
Cr 51 B 95 is

4-Ethyl-*N*-[4-*n*-decyloxybenzylidene]aniline



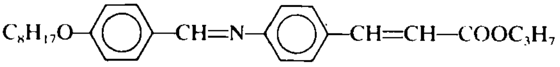
Cr 61.5 B 66.2 A 77.0 is

4-*n*-Butyl-*N*-[4-*n*-octyloxybenzylidene]aniline



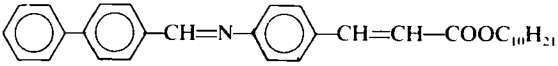
Cr 39.5 G 62.5 B 66.5 A 80.5 is

n-Propyl 4-[4-*n*-octyloxybenzylideneamino]cinnamate



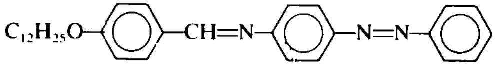
Cr 66.4 B 105.4 A 154.0 is

n-Decyl 4-[4-phenylbenzylideneamino]cinnamate



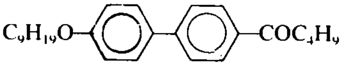
Cr 72.5 E 89.0 B 153.3 A 184.5–186.3 is

4-[4-*n*-Dodecyloxybenzylideneamino]azobenzene



Cr 105.0 B 125.0 A 160.0 is

4-*n*-Nonyloxy-4′-pentanoylbiphenyl



Cr 102.0 E 105.9 B 115.1 A 143.4 is

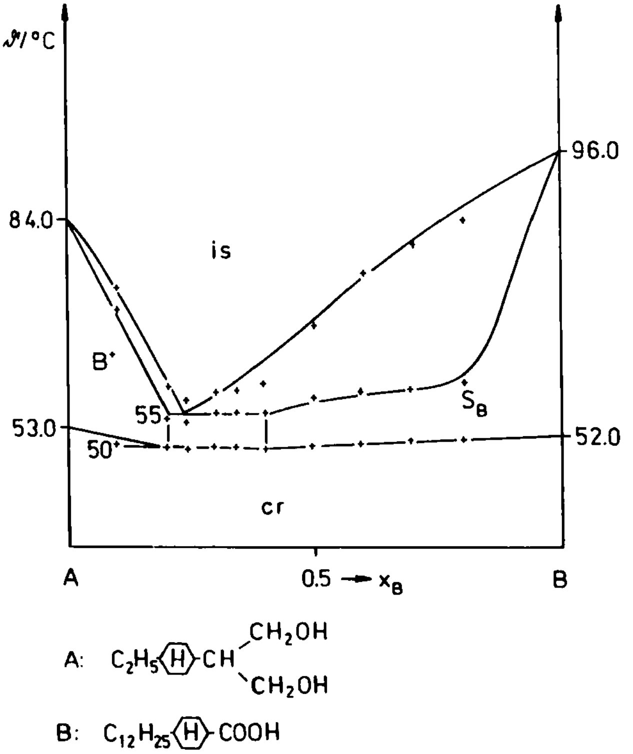


FIGURE 4 Phase diagram of a binary system.

A high number of orders of the inner spot-like reflection have been observed on the meridian of the patterns (direction perpendicular to the field direction). This high number of orders (up to 6 in the B^+ phases and up to 4 orders in the A^+ phases) points to an unusually pronounced layer periodicity.

The outer rings of diffuse scattering in the A^+ phases and the interferences of the B^+ phases exhibit intensity maxima on the equator of the patterns. In connection with the layer-reflections, this proves the perpendicularly aligned building units within the smectic layers.

In each case only one reflection has been observed on the equator of the pattern. In all patterns of oriented B^+ phases, more than one outer reflection could be detected only in directions outside the equator (Figure 7). This is a proof that the additional reflections must be indexed as (hkl) with $l \neq 0$, as was done in the evaluation of the Guinier patterns.

In one case, a pattern of the B^+ phase of substance 6 exhibited outer Bragg spots at the position 1, 0, ± 1/2, whereas the intensity of the (100) spot was drastically reduced. This indicates an ABAB packing of the layers in well oriented samples and explains why the intensity of the 101 interference of the Guinier pattern is higher than the intensity of the 100 interference.

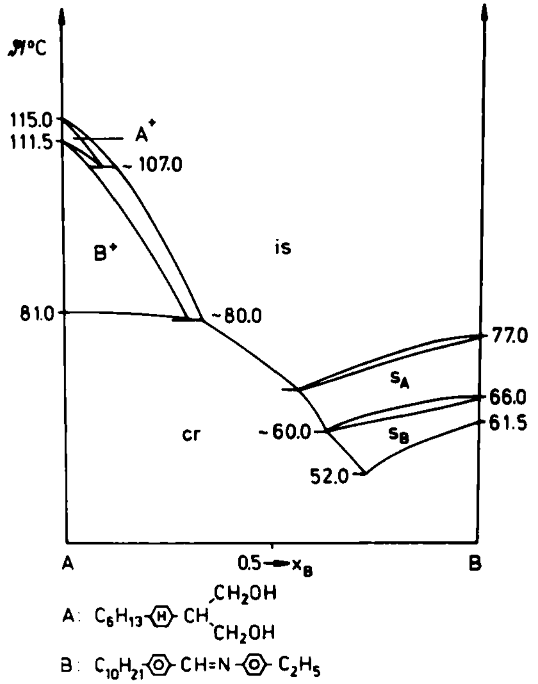


FIGURE 5 Phase diagram of a binary system.

DISCUSSION

The enthalpies of the transition into the B^+ phase, as well as the textures and the plastic behavior of the phases under discussion indicate liquid crystalline properties. On the other hand, the miscibility studies of the A^+ and B^+ phases respectively, point to peculiarities of these phases.

Comparing the *d*-values with the lengths of the molecules, a ratio $d/L \cong 1.6$ is found. This points to bi-molecular smectic layers. In Figure 8, the *d*-values for the A^+ and B^+ phases are plotted as a function of the number *n* of carbon atoms in the alkyl chains. An extrapolation to $n = 0$, corresponding to a chain length of zero, yields a value of about twice that of the core of the molecule, consisting only of the propandiol group and the cyclohexane ring. This leads to a model which is schematically shown in Figure 9. Two layers of molecules are arranged anti-parallel and are linked by hydrogen bonds. As spectroscopic measurements[3] exclude free O—H-bands, hydrogen bonds between neighboring molecules of the same layer must also be assumed. Therefore a network of hydrogen bonds in a plane perpendicular to the long axes of the molecules exists within the bi-molecular layer.

The hydrocarbon chains of adjacent bi-molecular layers are nearly completely interdigitated. In this way the bi-molecular layers constitute a smectic layer with $d \cong 1.6\ L$. Because of the molecular arrangement within the smectic layers caused

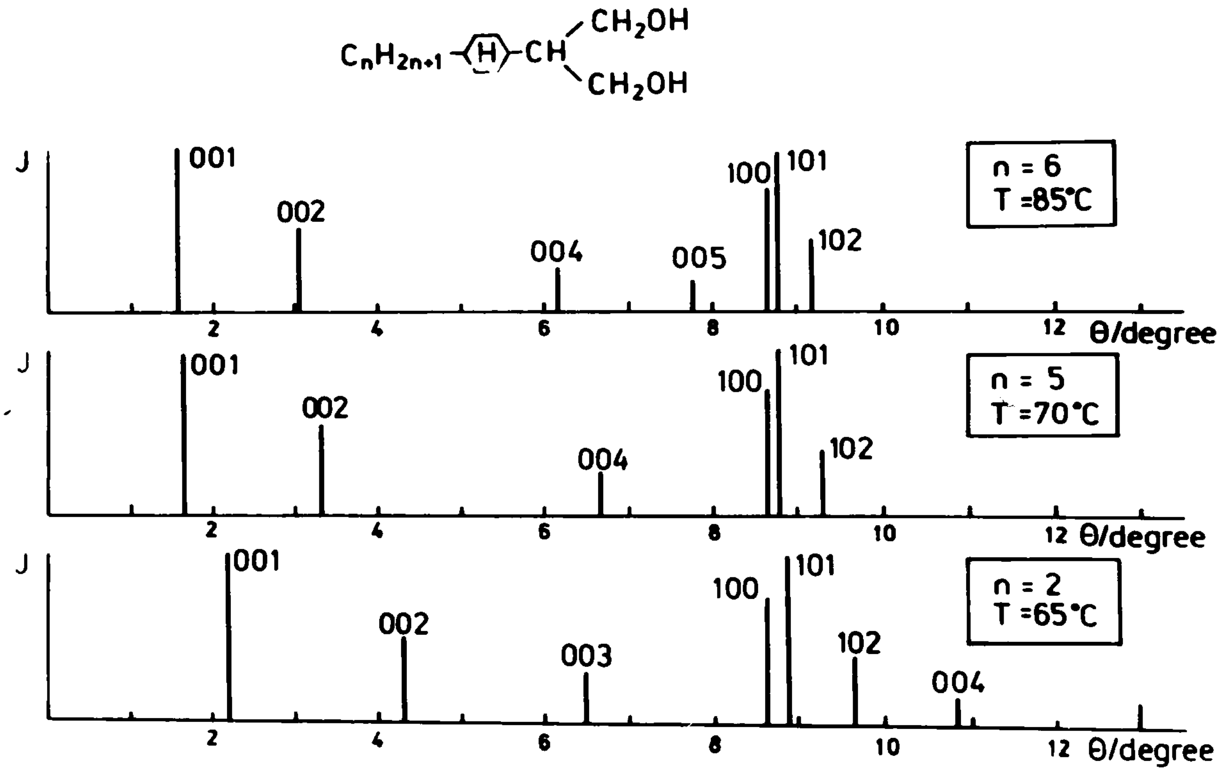


FIGURE 6 Schematic plot of the observed interferences in the B^+ phases of substances **2**, **5** and **6**.

TABLE III

Structural Parameters

	a (nm)	*d* (nm)	*L* (nm)	*d*/*L*
2	0.593	2.040	1.26	1.62
5 70°C	0.589	2.644	1.60	1.65
6	0.596	2.828	1.76	1.61

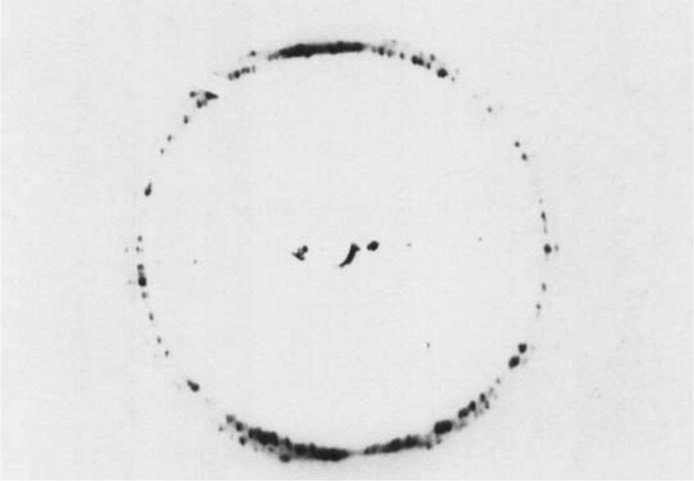


FIGURE 7 Diffraction pattern of the oriented B$^+$ phase of substance **6**.

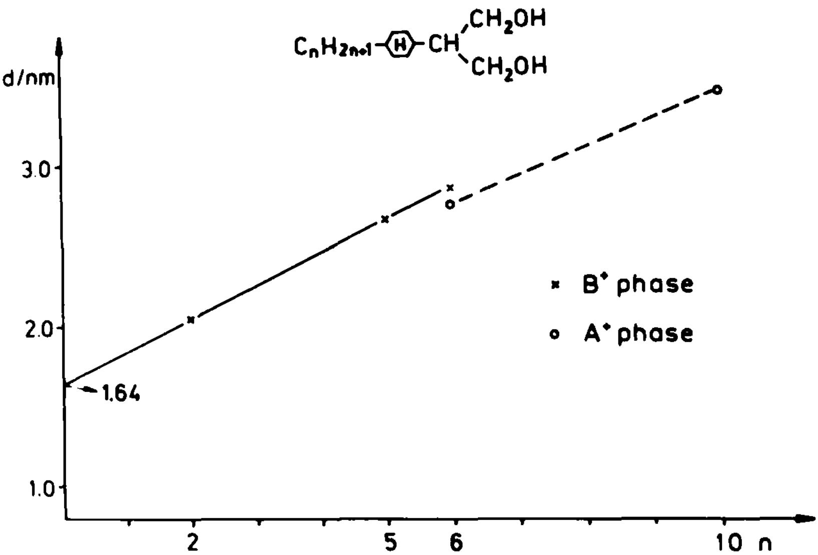


FIGURE 8 Layer spacings as a function of the number of carbon atoms in the alkyl chains (*n*).

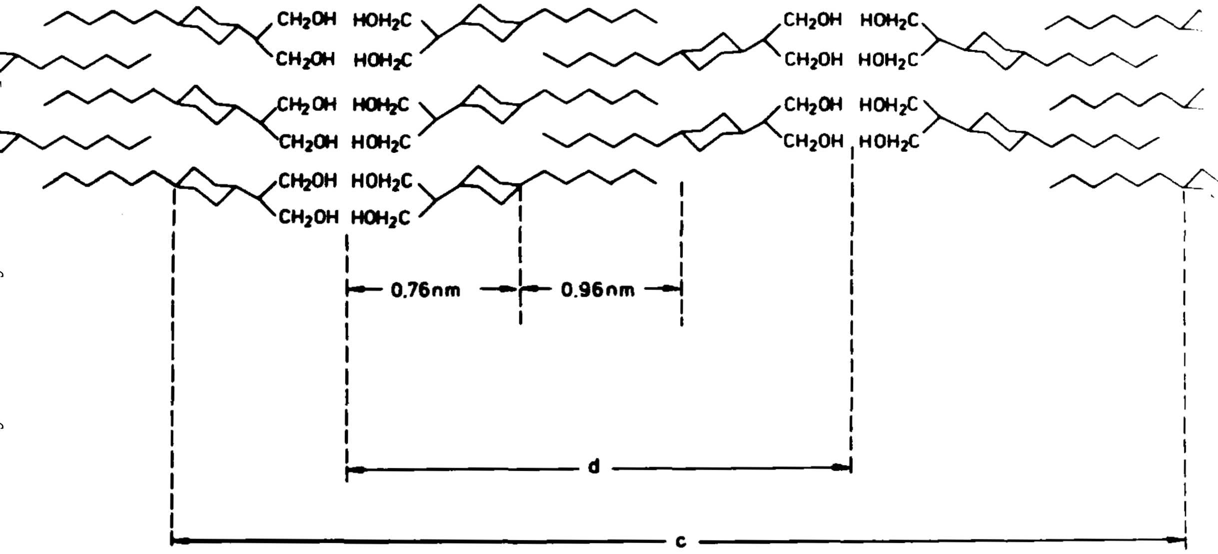


FIGURE 9 Schematic plot of the proposed structure (a stereographic drawing is given in Reference 1).

by this special kind of interaction, the translational movement of the molecules perpendicular to the layers is strongly restricted. Well defined layers are formed, which explains the high periodicity of the layers found even in the patterns of the A^+ phases.

The lateral distances are subject to a statistical distribution in the A^+ phase, whereas the packing of the molecules within the layers of the B^+ phase can be considered as hexagonal.

In this sense, the B^+ and A^+ phases exhibit structural features common to conventional B and A phases.

An intercalation of molecules into the adjacent layer demands free space especially in the more ordered phase B^+. As is shown (Figure 10) by space-filling models, the bulky diol group offers the possibility for such free space. On the basis of the X-ray data, the area of the hexagon was calculated as $f_{\text{hex}} = 93$ Å^2. Six alkyl chains (three of the upper and three of the lower layer) occupy an area $f = 108$ Å^2. The difference is believed to be within the limits of error.

By an intercalation of molecules of adjacent layers with a hexagonal structure, an ABAB packing of the layers is favoured. This was proved in one case by the X-ray studies. According to this, the translation period *c* is twice the smectic layer thickness *d* (Figure 9). Small distortions, *e.g.*, alterations of the positions of the hydrogen bonds in the area of the head groups, may destroy this type of packing on a long range scale and give rise to an AAA packing in the average bulk of the sample.

The phases under discussion belong to the class of associated smectic liquid crystals with molecular double layers. Concerning the structures at the molecular level, the A^+ phases of the diol derivatives are in between the neat phases of soaps and the A phases of substances with terminal polar substituents.

The layers of neat phases are composed of ionic head groups and molten alkyl chains. The layers of the A_2 phases of terminally polar substances are formed by a head-to-head arrangement of the terminal polar substituents.

With respect to the head-to-head arrangement, it may be expedient to designate the A^+ phases of the diol-derivatives as A_2, but with intercalated alkyl chains. First investigations of the liquid crystalline phases of derivatives of glycopyranosides have been reported by Barrall *et al.*[4] Recently the crystal structures[5] as well as a

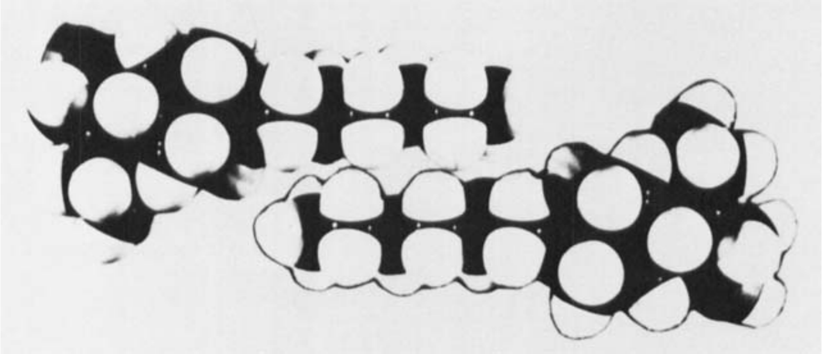


FIGURE 10 Intercalation of the alkyl chains shown on the basis of space-filling models.

smectic phase[6] of type A have been described for certain sugars. They probably exhibit similar A phase structures with interacting hydrogen bridges and overlapping alkyl chains. Therefore the derivatives of diols may be considered as compounds with very simple molecular structures falling in the class of associated smectics found in thermotropic as well as lyotropic systems.

Acknowledgments

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References

1. S. Diele, E. Geissler, H.-M. Vorbrodt and H. Zaschke, *Mol. Cryst. Liq. Cryst. Lett.*, **102**, 181 (1984).
2. S. Diele, H. Kresse and D. Demus, *Z. Phys. Chem. (Leipzig)*, **261**, 759 (1980).
3. A. Kolbe, private communication.
4. E. Barrall, B. Grant, M. Oxsen, E. T. Samulski, P. C. Moewa, J. R. Knox, R. R. Gaskill and J. L. Haberfeld, *Org. Coat. Plast. Chem.*, **110**, 67 (1979).
5. G. A. Jeffrey, *Mol. Cryst. Liq. Cryst.*, **110**, 221 (1984).
6. J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, **110**, 208 (1984).