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The liquid-crystalline behaviour of amphiphilic ethane-1,2-diol derivatives incorporating a six membered ring in their principal structure

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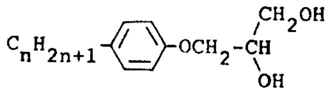
Novel 3-phenyloxy substituted propane-1,2-diol derivatives, 4-(4-*n*-hexyloxyphenyl)-butane-1,2-diol and 4-(trans-4-*n*-pyropylcyclohexyl)-butane-1,2-diol have been synthesized and their thermal behaviour has been studied. These compounds exhibit thermotropic and, after addition of water, also lyotropic liquid-crystalline behaviour. The clearing temperatures of the smectic mesophases were found to be strongly dependent on the alkyl chain length and on the structural units that link the aromatic ring to the alkyl chain and to the diol unit. The behaviour of the aromatic compounds is compared with that of the cyclohexane derivative. Thereby it has been realized that the mesophase stability of the amphiphilic diols incorporating a rigid unit is largely determined by both, the molecular geometry (molecular shape and intramolecular flexibility) and the amphiphilic structural pattern.

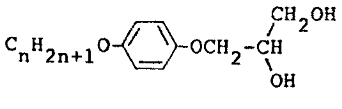
1. Introduction

Simple *n*-alkane-1,2-diols with a sufficiently long alkyl chain form thermotropic and lyotropic liquid-crystalline phases, which consist of bimolecular layers stabilized by an extended hydrogen bonding network between the diol groups [1]. Furthermore it has recently been recognized that the introduction of a single trans-1,4-disubstituted cyclohexane ring into the alkyl chain of amphiphilic propane-1,3-diol derivatives [2, 3] induces thermotropic mesophases and significantly stabilizes the lyotropic mesophases [4, 5]. Contrary to this the mesomorphic behaviour is only insignificantly influenced by the introduction of a 1,4-phenylene group (see figure 1). In order to study the nature of intermolecular forces responsible for self-organization of amphiphilic diols, some more detailed investigations are needed.

Herein we describe the synthesis and the amphotropic behaviour of novel amphiphilic ethane-1,2-diol derivatives incorporating a single benzene or cyclohexane ring as a rigid structural unit in their principal structure



(1) $n = 1$–10



(2) $n = 4$–8

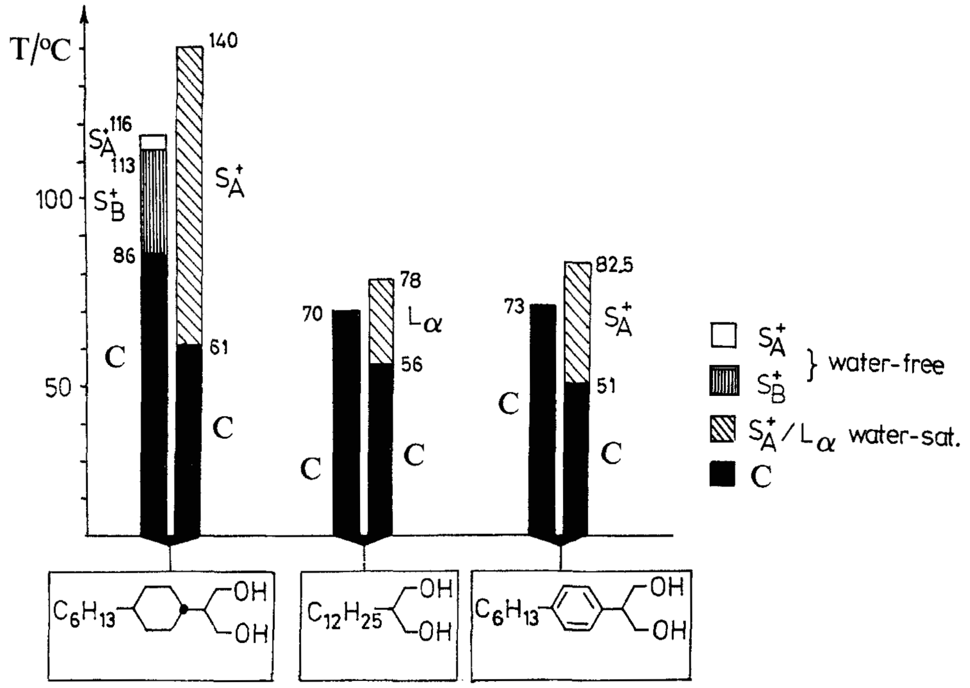
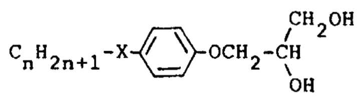
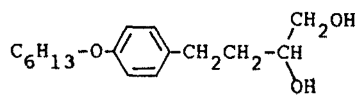


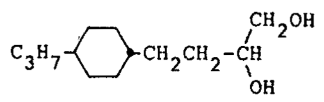
Figure 1. Comparison of the transition temperatures of different 2-substituted propane-1,3-diol derivatives in the water-free state (left hand columns) and in the water-saturated state (right hand columns).



X = CO, COO, OOC
(3) (4) (5)



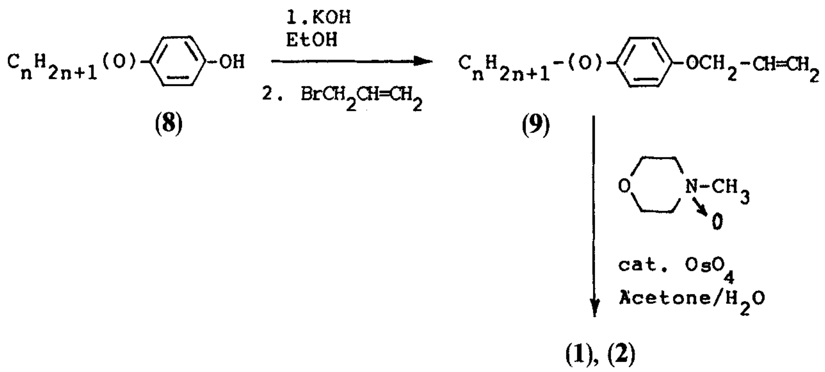
(6)



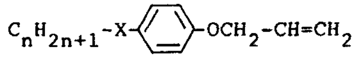
(7)

2. Synthesis

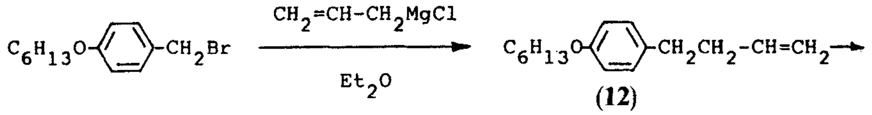
The two homologous series of racemic propane-1,2-diol derivatives (**1**) and (**2**) were synthesized in two steps. Treatment of 4-substituted phenols (**8**) with potassium hydroxide in ethanol followed by addition of allyl bromide gave the allyl ethers (**9**) which were hydroxylated with *N*-methylmorpholine-*N*-oxide in the presence of catalytic amounts of osmium tetroxide [6]



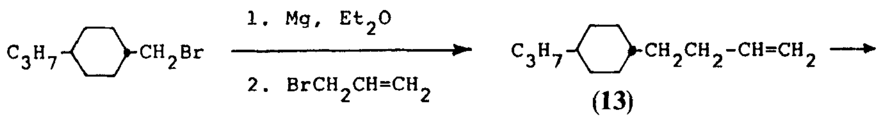
Compounds (**3**) were obtained in the same way starting with 4-acylphenols. The allyl ethers (**10**) and (**11**) were prepared by esterification reactions and the ethylenic hydrocarbon derivative (**12**) was synthesized by coupling allyl magnesium chloride with 4-*n*-hexyloxybenzyl bromide. Compound (**13**) was obtained by treatment of trans-4-propylcyclohexylmethylmagnesium bromide with allyl bromide.



(**10**) X = COO
(**11**) X = OOC



(**6**)



(**7**)

Hydroxylation using the procedure previously described gave the amphiphilic diols (**3**)–(**7**) in 80–85 per cent yields. All diol compounds were purified by flash chromatography (eluent: chloroform + 5 per cent methanol) and/or by recrystallization from *n*-hexane.

3. Results

The thermal behaviour of all compounds was monitored by thermomicroscopy. The transition temperatures observed for the two homologous series (**1**) and (**2**) are given in figures 2 and 3. The compounds (**1.3**)–(**1.10**) and (**2.2**)–(**2.5**) exhibit enantiotropic mesophases whereas compound (**1.2**) was monotropic. No thermotropic mesophase could be observed for the short chain compounds (**1.1**) ($n = 1$) and (**2.1**) ($n = 4$) due to the rapid crystallization of the supercooled samples. The transition from the isotropic phase could be seen by the formation of bâtonnets which coalesce to form a focal-conic, fan-like texture with large homeotropic areas, which is typical for smectic A phases of non-amphiphilic mesogens [7]. The texture is also identical with that observed for the S_A phases of single chain carbohydrate liquid crystals [8–10] and the

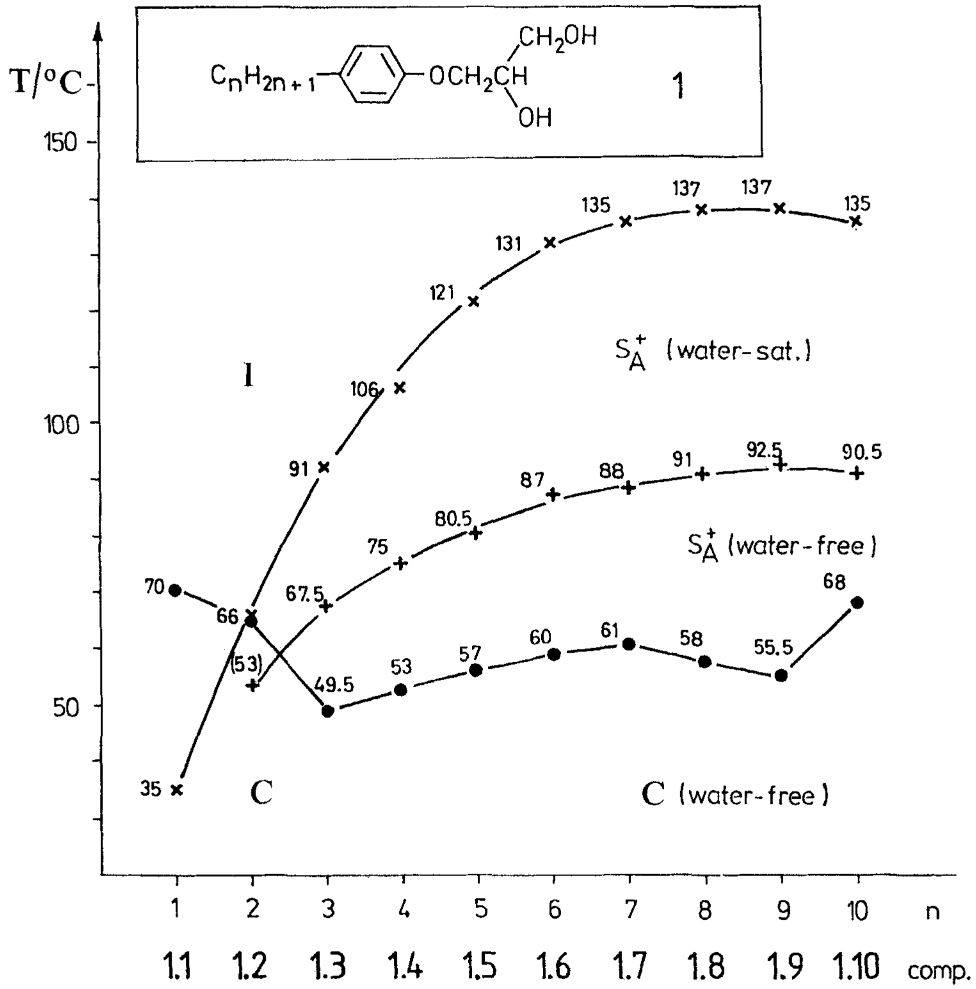


Figure 2. Plot of the transition temperatures against the number of carbon atoms in the alkyl chain of the 3-(4-alkyl-phenyloxy)-propane-1,2-diols (1) (●, crystal→thermotropic mesophase (liquid); +, thermotropic mesophase→liquid; ×, lyotropic mesophase→liquid).

high temperature mesophase (L_α) of medium chain *n*-alkane-1,2-diols [1]. The precise nature of this mesophase is presently under investigation and the results of the X-ray measurements will be presented in a forthcoming paper. The thermotropic mesophase stability of the 3-(4-*n*-alkylphenyloxy)-propane-1,2-diols (**1**) increases continuously with growing chain length until a maximum ($T_{cl} = 92°C$) is reached for the 3-(4-*n*-nonylphenyloxy)-propane-1,2-diol (**1.9**). Afterwards the clearing temperature slowly decreases again. This behaviour is well known for the homologous series of other diol compounds [1, 3] and also for amphiphilic single tailed and double tailed carbohydrate based mesogens [11, 12].

The ability of many amphiphilic mesogens to form lyotropic mesophases is well known. We found the influence of small amounts of water on the liquid-crystalline behaviour of amphiphilic diols to be huge [1–3, 13]. The 3-phenyloxy-propane-1,2-diol

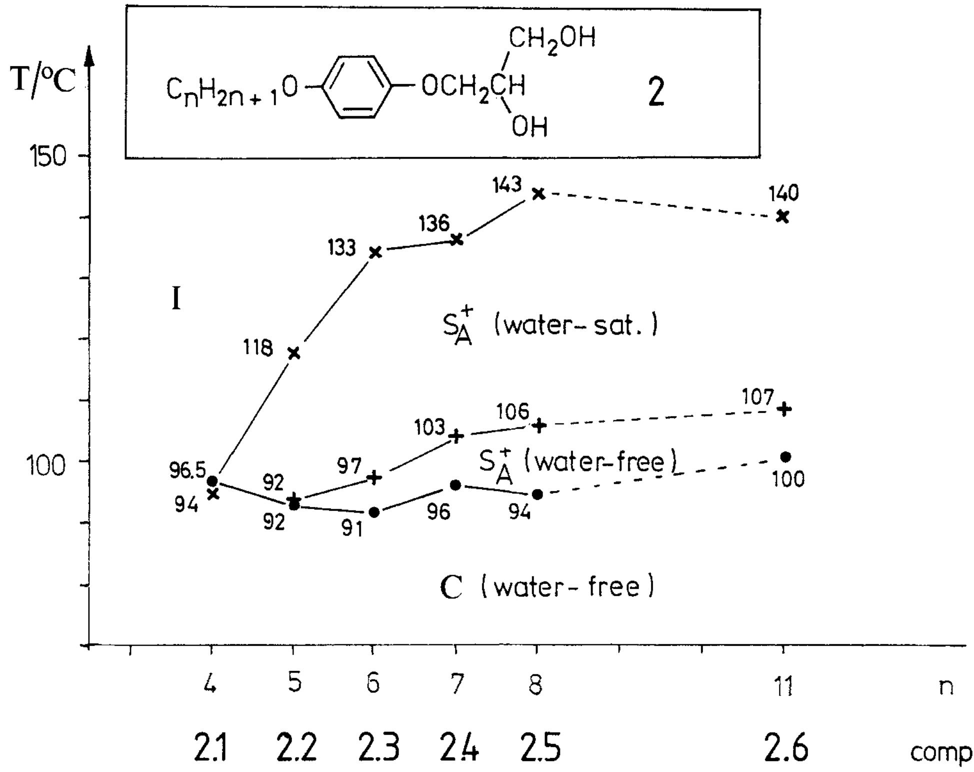
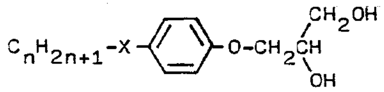


Figure 3. Plot of the transition temperatures against the number of carbon atoms in the alkyl chain of the 3-(4-alkyloxyphenyloxy)-propane-1,2-diols (**2**) (●, crystal→thermotropic mesophase (liquid); +, thermotropic mesophase→liquid; ×, lyotropic mesophase→liquid).

derivatives (**1**) and (**2**) are no exception. The melting temperatures decrease and the clearing temperatures increase with increasing water content until a maximal water content is reached. The transition temperatures of the water saturated samples are also given in figures 1–6 and in table 1. They were determined using contact preparations in sealed capillaries. The thermotropic clearing temperatures of the 4-alkoxy substituted 3-phenyloxy-propane-1,2-diols (**1**) are slightly above those of the analogous 4-alkyl derivatives (**2**). Such behaviour is well known for all non-amphiphilic mesogens with aromatic rigid cores like phenylbenzoates and biphenyls [14].

In contrast to this, the clearing temperatures of the lyomesophases of short chain 4-alkoxyphenyl derivatives (**2**) are significantly lower than those of the 4-alkylphenyl derivatives (**1**) with the same total chain length. Furthermore, we found this difference to vanish with increasing chain length and finally to be reversed at a certain chain length (figure 4). This indicates, that the mesophase stability of these amphiphilic diols is mainly influenced by essentially the same factors which govern the mesophase stability of non-amphiphilic calamitic mesogens such as the molecular shape and the flexibility of the linking unit between the rigid core and side chains (RCH_2–ar > RO–ar) [15]. However for short chain derivatives there seems to be an additional mesophase destabilizing effect of the ether oxygen influencing especially the lyotropic mesophases.

Table 1. Transition temperatures (°C) of different 4-substituted 3-phenyloxypropane-1,2-diols (**1**)–(**5**).



		$n=5$															$n=8$–11												
			Water-free					Water-saturated									Water-free					Water-saturated				
X	I_{HX}	Compound	C		S_A^+		I	C		S_A^+		I	Compound	n	C		S_A^+		I	C		S_A^+		I
$-CH_2CH_2-$	0	**1.7**	●	61	●	88	●	●	<20	●	135	●	**1.10**	8	●	68	●	90·5	●	●	42	●	135	●
$-CH_2O-$	0·11	**2.3**	●	91	●	97	●	●	50	●	133	●	**2.6**	10	●	100	●	107	●	●	77	●	140	●
$-CH_2\overset{O}{\overset{\|}{C}}-$	0·31	**3.1**	●	77	—	—	●	●	52	●	83	●	**3.2**	10	●	100	●	107	●	●	69	●	141	●
$-O-\overset{O}{\overset{\|}{C}}-$	0·44	**4.1**	●	46	(●	−2)	●	●	<0	●	37	●	**4.2**	11	●	45	●	58	●	●	20	●	112	●
$-\overset{O}{\overset{\|}{C}}-O-$	0·44	**5.1**	●	79	—	—	●	●	35	●	68	●	**5.2**	11	●	98	(●	91)	●	●	68	●	133	●

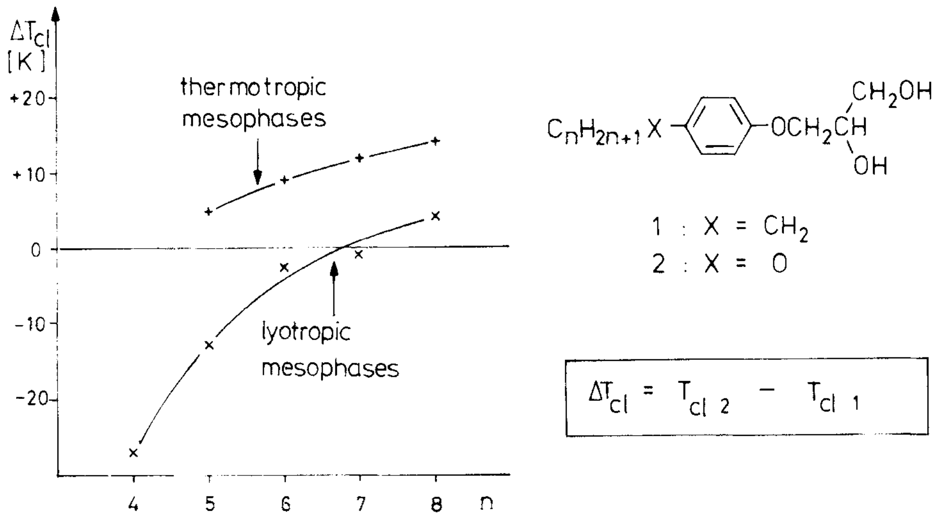
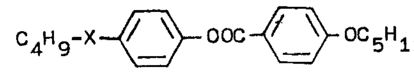


Figure 4. Plot of the amounts of mesophase (de)stabilization observed in line with the replacement of the methylene group, which connects the alkyl chain with the benzene ring, by an ether oxygen (×, lyotropic mesophase; +, thermotropic mesophase).

Table 2. Transition temperatures (°C) of different substituted phenyl benzoates [14].



X	C		N		I
$-CH_2CH_2-$	●	39	●	55	●
$-CH_2O-$	●	62	●	80	●
$-CH_2-\overset{O}{\overset{\|}{C}}-$	●	73	S_A	108	●
$-O-\overset{O}{\overset{\|}{C}}-$	●	70	●	(61)	●
$-\overset{O}{\overset{\|}{C}}-O-$	●	76	●	113	●

In order to test the generality of any trends observed, compounds (**3**)–(**5**) with different linking units between alkyl chain and rigid core were investigated. The values given in table 1 indicate that the mesophase stability of the short chain amphiphilic diols is mainly determined by the hydrophility of these linking units. Thereby Seiler's increments [16] were used as a scale for their ability to be involved in hydrogen bonds. However there are some deviations from this general trend ((**1**) versus (**2**) and (**4**) versus (**5**)) which reflect the order of mesophase stability usually observed for calamitic

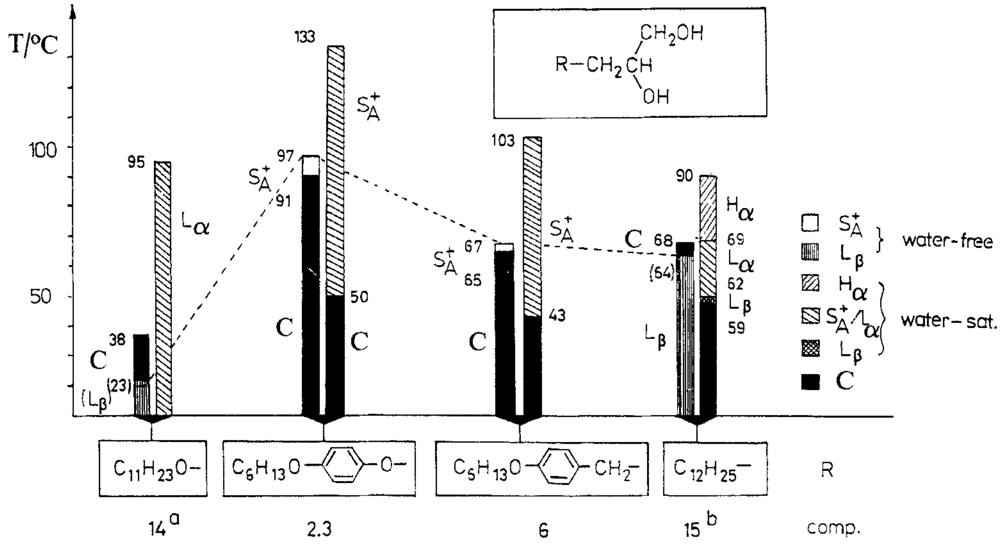


Figure 5. The influence of the linking unit between the diol group and the hydrophobic chain on the thermotropic (left hand columns) and lyotropic transition temperatures (right hand columns) of amphiphilic diols. a, DSC measurements indicate the presence of a phase transition at 86°C, therefore the existence of an additional mesophase, presumably a H_α phase above 86°C must be assumed [26]. b, Determined by DSC measurements [27].

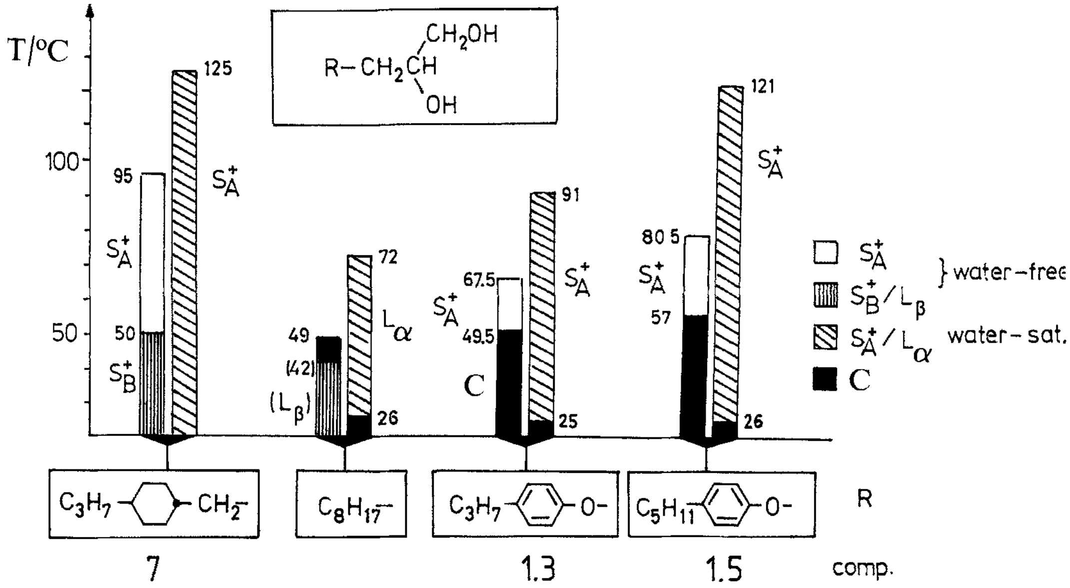


Figure 6. Comparison of the mesophase behaviour of undecane-1,2-diol with that one of the substituted ethane-1,2-diol derivatives incorporating a trans-1,4-cyclohexylene (**7**) or a 1,4-phenylene unit (**1.3**) and (**1.5**) (left hand columns: water-free samples; right hand columns: water-saturated state).

mesogens [14]. The influence of the hydrophility of the connecting unit upon the clearing temperatures decreases with elongation of the alkyl chain. Finally the order of mesophase stability of the long chain compounds (table 1) resembles that which is usually observed for non-amphiphilic calamitic mesogens (see table 2).

Obviously, the mesophase stabilization observed in line with the insertion of a 1,4-phenylen unit depends largely on its substituent pattern. This is especially true for the link between the core and diol unit. If the benzene ring is linked with the diol unit via an ethylene bridge (compound (**6**)) the mesophase stabilizing effect is insignificant. However it could be largely increased if the highly flexible RCH_2–ar-linkage of compound (**6**) is replaced by the oxymethylene linkage (compound (**2.3**)) (see figure 5). The conjugation of the lone pairs at the ether oxygen with the aromatic π-system decreases the flexibility and in this way gives rise to largely increased clearing temperatures. This is especially evident when comparing 3-(4-hexyloxyphenyloxy)-propane-1,2-diol (**2.3**) with 3-undecyloxypropane-1,2-diol (**14**) as given in figure 5. In contrast to this, a large mesophase stabilization is observed if a cyclohexane ring is linked with the diol unit via an ethylene bridge (compound (**7**)) since the rotational barrier of the alkyl-cyclohexyl unit is much larger than the rotational barrier of the highly flexible alkyl-aryl unit [17] (see figure 6). When comparing compounds (**7**) and (**1.3**) it must be taken into account that the chain of compound (**7**) is much more hydrophobic than the 4-propylphenyloxymethylene chain of (**1.3**). Therefore the comparison with one of the long chain derivatives (**1**) (e.g. (**1.5**)) should be more realistic and indicates that the clearing temperatures of both compounds are of the same order of magnitude. In this way the intramolecular flexibility plays an important role for the thermotropic and lyotropic liquid-crystallinity of amphiphilic diols and presumably also for the mesophases of all other amphiphilic compounds.

The same arguments could be used to explain the absence of thermotropic properties and the low lyotropic mesophase stability of the 2-arylsubstituted propane-1,3-diol derivatives (see figure 1). Finally we would like to comment on the fact that the kind of rigid core also determines the nature of the mesophases observed. The aromatic derivatives exhibit only a smectic A phase whereas a smectic B phase is found for the cyclohexane derivative.

4. Discussion

The formation of mesophases is caused by certain interactions between the molecules. In classical non-amphiphilic liquid crystals such interactions are mainly steric ones depending on the geometry of the single molecule. However there is another group of liquid-crystalline compounds in which the mesogenic unit is represented by an aggregation of single molecules. For example 4-*n*-alkyl(oxy)benzoic acids [18, 19] and substituted cinnamic acids [20] form mesogenic dimers associated by intermolecular hydrogen bonding. In contrast to these carboxylic acid derivatives the amphiphilic diols form large aggregates associated by an extended hydrogen bonding network. This is caused by the cooperative nature of the hydrogen bonding in alcohols which favours the formation of large aggregates. These aggregates consist of parallel and equidistant layers separated by the hydrophobic chains. The addition of water largely influences the mesomorphic properties of the amphiphilic diols. Though the hydration of the diol group is strongly restricted (two to three molecules of water per molecule diol) these water molecules lead to a remarkable stabilization of the liquid-crystalline phases due to an increased hydrogen bonding density between the head groups. The mesophases formed in the presence of water may be designated as lyotropic mesophases but there is

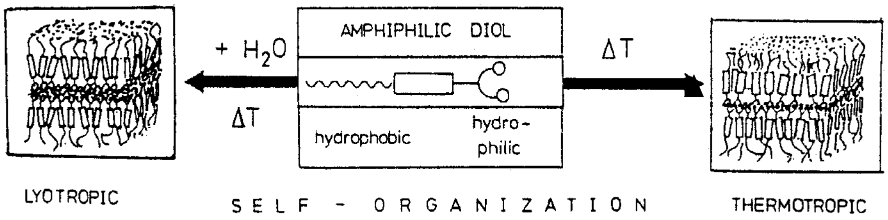


Figure 7. The molecular self-organization of amphiphilic diols.

no sharp frontier line between the thermotropic and lyotropic phases. In this way these compounds may be looked upon as amphotropic materials.

The mesophases of amphiphilic *n*-alkane-1,2-diols could be significantly stabilized by the introduction of rigid structural units into the hydrophobic chain. In this way the molecular self-organization is additionally favoured by interactions between the hydrophobic chains. Due to this dual nature of the amphiphilic diols incorporating a rigid unit, their mesophase stability is largely determined by both, the molecular geometry (molecular shape and intramolecular flexibility) and the amphiphilic structural pattern which sometimes may be contradictory.

We would also like to comment on the possibility to change from smectic/lamellar to columnar order by changing the number and position of side chains, as recently demonstrated for some aldose dithioacetales [12, 21], inositol and inosose derivatives [22, 23], and at benzoyloxycyclohexane-3,5-diol derivatives [24, 25]. Further investigations in the field of amphiphilic diols which include the combination of diol structure and calamitic liquid crystal structures are on the way.

5. Experimental

5.1. *4-*n*-Butylphenyl allyl ether*

0·07 mol allyl bromide (8·47 g) was added to a solution of 0·07 mol potassium hydroxide (3·9 g) and 0·05 mol of the appropriate 4-substituted phenol in 100 ml ethanol. This mixture was refluxed for 1 hour, allowed to cool, diluted with 500 ml water and extracted twice with ethyl ether (2 × 100 ml). The combined organic solutions were washed twice with water and dried over sodium sulphate. Finally the solvent was evaporated and the residue was used without further purification for the next step.

5.2. *4-(4-*n*-hexyloxyphenyl)-but-1-ene* (**12**)

0·02 mol 4-*n*-hexyloxybenzyl bromide (5·4 g) was added to a stirred solution of 0·15 mol allylmagnesium chloride (15·12 g) in 50 ml tetrahydrofuran during 15 min at 25°C under an argon atmosphere. The mixture was refluxed for 12 hours, allowed to cool and then hydrolyzed by carefully adding a saturated ammonium chloride solution. Organic materials were extracted with ethyl ether and the combined extracts were washed with saturated aqueous sodium bicarbonate and brine. After drying over sodium sulphate the solvent was evaporated to give an oily residue, which was used for the hydroxylation without further purification. ^1H NMR (80 MHz, $CDCl_3$, ppm): 7·14 (d, $J = 8{\cdot}7$ Hz, 2 H, H–ar); 6·84 (d, $J = 8{\cdot}7$ Hz, 2 H, H–ar); 6·15–5·66 (m, 1 H, $-CH{=}CH_2$); 5·19–4·92 (m, 2 H, $-CH{=}CH_2$); 3·97 (t, $J = 6{\cdot}3$ Hz, 2 H, $-CH_2\text{–}O-$); 2·80–2·22 (m, 4 H, $-CH_2-$); 1·87–1·18 (m, 8 H, $-CH_2-$); 1·00 (t, $J = 5{\cdot}4$ Hz, 3 H, $-CH_3$).

5.3. *4-(trans-4-*n*-propylcyclohexyl)-but-1-ene* (**13**)

A Grignard compound was prepared by adding a solution of 0·02 mol trans-4-*n*-propylcyclohexylmethyl bromide (4·38 g) in 15 ml ethyl ether to 0·021 mol (0·51 g) magnesium turnings under ultrasonic irradiation. 0·03 mol allyl bromide (3·6 g) was added and the mixture was refluxed for 48 hours. Afterwards, 50 ml saturated ammonium chloride solution was added carefully. The organic layer was separated and the aqueous layer was extracted twice with ethyl ether (2 x 50 ml). The combined extracts were washed with 5 per cent aqueous sodium bicarbonate and brine. After drying over sodium sulphate the solvent was evaporated and the residue was distilled under reduced pressure (b.p.: 70°C at 0·2 mm Hg) to yield 2·2 g (**13**) (69 per cent).

5.4. *Hydroxylation procedure*

Into a 50 ml flask with a magnetic stirrer was placed a solution of 0·011 mol of *N*-methylmorpholine-*N*-oxide monohydrate in a mixture of water (1 ml) and acetone (20 ml). 0·01 mol of the appropriate olefin was added to the solution, followed by 0·1 ml of a 5 per cent toluene solution of osmium tetroxide. The resulting mixture was stirred overnight at room temperature. Then 6 ml of saturated aqueous sodium bisulphite was added and stirring was continued for 10 min. The mixture obtained was filtered through a Celite pad and the latter was washed with ethyl acetate (3 x 50 ml). The combined solutions were concentrated under reduced pressure to afford a residue which was distributed in a mixture of 100 ml ethyl acetate and 50 ml water. The organic phase was separated and washed with 2 M sulphuric acid, saturated aqueous sodium bicarbonate and brine and then dried over sodium sulphate. After evaporation of the solvent the crude diol was purified by flash chromatography (silicagel, eluent: $CHCl_3$/methanol, 9 : 1) and/or recrystallization from *n*-hexane. Yields 70–95 per cent. Selected spectroscopic data are given below:

(**1.6**): IR ($CHCl_3$, cm^{-1}): 1520, 1620 (C=C–arom); 2875, 2945 (C–H–aliphat.); 3020 (C–H–ar); 3460 (borad), 3590 (O–H).

(**1.8**): ^1H NMR (80 MHz, $CDCl_3$, ppm): 7·21 (d, J = 8·7 Hz, 2 H, H–ar); 6·81 (d, J = 8·7 Hz, 2 H, H–ar); 3·6–4·2 (m, 5 H, $-CH_2O-$, $=C\mathit{H}OH$); 2·96 (t, J = 7·5 Hz, $-C\mathit{H}_2$–ar); 1·8–2·7 (broad, 2 H, $-O\mathit{H}$); 1·05–1·8 (m, 12 H, $-CH_2-$); 0·86 (t, J = 5·4 Hz, 3 H, $-CH_3$).

(**2.4**): ^1H NMR (80 MHz, $CDCl_3$, cm^{-1}): 6·82 (s, 4 H, H–ar); 3·7–4·1 (m, 7 H, $-C\mathit{H}_2O\mathit{H}$, $-C\mathit{H}_2-O-$, $=C\mathit{H}O\mathit{H}$); 1·1–1·9 (m, 10 H, $-CH_2-$); 0·89 (t, J = 5·4 Hz, 3 H, $-CH_3$).

(**3.2**): ^1H NMR (80 MHz, $CDCl_3$, ppm): 7·84 (d, J = 8·7 Hz, 2 H, H–ar); 6·93 (d, J = 8·7 Hz, 2 H, H–ar); 3·7–4·2 (m, 5 H, $-C\mathit{H}_2O-$, $=C\mathit{H}OH$); 2·90 (t, J = 7·6 Hz, 3 H, $-C\mathit{H}_2-CO-$); 2·17 (broad, 2 H, $O\mathit{H}$); 1·1–1·9 (m, 18 H, $-CH_2-$); 0·87 (t, J = 5·4 Hz, 3 H, $-CH_3$).

(**4.1**): ^1H NMR (200 MHz, $CDCl_3$, ppm): 6·92 (dd, 4 H, CH–ar); 3·7–4·1 (m, 5 H, $-C\mathit{H}_2-O-$, $=C\mathit{H}-OH$); 2·74 (broad, 1 H, OH); 2·51 (t, J = 7·5 Hz, 2 H, $-C\mathit{H}_2-CO-$); 2·20 (broad, 1 H, OH); 1·69 (m, 2 H, $-C\mathit{H}_2-CH_2-CO-$); 1·3–1·4 (m, 6 H, $-CH_2-$); 0·90 (t, 3 H, $-CH_3$).

(**4.2**): IR ($CHCl_3$, cm^{-1}): 1500, 1600 (C=C–ar); 1750 (C=O); 2855, 2925 (C–H–aliphat.); 3000 (C–H–ar); 3460 (broad), 3590 (O–H).

(**5.1**): ^1H NMR (80 MHz, $CDCl_3$, ppm); 7·98 (d, J = 8·7 Hz, H–ar); 6·90 (m, J = 8·7 Hz, 2 H, H–ar); 4·27 (t, J = 7·5 Hz, 2 H, $-C\mathit{H}_2-O-$); 3·8–4·1 (m, 5 H, $-CH_2-O-$, $=C\mathit{H}OH$); 2·37 (broad, 2 H, $-OH$); 1·2–1·8 (m, 6 H, $-CH_2-$); 0·87 (t, J = 5·4 Hz, 3 H, $-CH_3$).

(5.2): IR ($CHCl_3$, cm^{-1}): 1510, 1605 (C=C–ar); 1705 (C=O); 2855, 2920 (C–H–aliphat.); 3005 (C–H–ar); 3465 (broad), 3590 (O–H).

(6): ^1H NMR (80 MHz, $CDCl_3$, ppm): 7·09 (d, $J=8{\cdot}7$ Hz, 2 H, H–ar); 6·81 (d, $J=8{\cdot}7$ Hz, 2 H, H–ar); 3·93 (t, $J=6{\cdot}3$ Hz, 2 H, $-CH_2$–O–ar); 3·74–3·45 (m, 3 H, =C*H*OH, –C*H*$_2$OH); 2·80–2·57 (m, 2 H, $-CH_2$–ar); 2·50 (s, broad, 2 H, –OH); 1·85–1·34 (m, 10 H, $-CH_2-$); 0·91 (t, $J=5{\cdot}4$ Hz, 3 H, $-CH_3$).

(7): ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 72·70 (=CHOH); 66·62 (CH_2OH); 39·73 ($-CH_2-$); 37·94 (=CH–); 37·49 (=CH–); 33·29 ($-CH_2-$); 33·21 (4C, $-CH_2-$); 30·57 ($-CH_2-$); 19·96 ($-CH_2-$); 14·32 ($-CH_3$).

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