Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Staufer, Günter , Schellhorn, Matthias and Lattermann, Günter(1995) '*Cis, cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkoxy)benzoates Thermal behaviour and water absorption', Liquid Crystals, 18: 4, 519 — 527

To link to this Article: DOI: 10.1080/02678299508036654

URL: http://dx.doi.org/10.1080/02678299508036654

LIQUID CRYSTALS, 1995, VOL. 18, NO. 4, 519–527

Cis, *cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkoxy)benzoates
Thermal behaviour and water absorption

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(*Received 20 June 1994; accepted 5 August 1994*)

A homologous series of liquid crystalline *cis,cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkoxy)-benzoates ('two chain' diols) is described. The formation of different mesophase structures by these compounds is influenced by the length of the alkoxy side chains; changes from smectic via cubic to hexagonal columnar mesophases have been established in a certain chain length range. The aggregation to 'supramolecular' structures via hydrogen bonding seems to be necessary for the different mesophases. Not only the behaviour of the freeze dried products, but also that of samples which had absorbed water, either from a saturated atmosphere or from direct contact, is described.

1. Introduction

First results of investigations of *cis,cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkoxy)benzoates ('two chain' diols) have been reported in a previous publication [1]. As supposed there, and has been demonstrated for polycatenar compounds [2], 3,4-substitution causes a rich polymorphism in these compounds. Whereas the *cis,cis*-(3,5-dihydroxycyclohexyl) 4-alkoxybenzoates ('one chain' diols) [3, 4], like other 'one chain' diols [5, 8], exhibit only a smectic mesophase, the *cis,cis*-(3,5-dihydroxycyclohexyl) 3,4,5-tris(alkoxy)benzoates ('three chain' diols) [3, 9–12] form a hexagonal columnar mesophase. However, in the case of the 'two chain' diols, several, partly metastable mesophases of both types and also a cubic mesophase can be observed [1]. Other thermotropic cubic phases are known for a few examples of different, non-chiral mesogens, for example, several strontium soaps [13], biphenyl carboxylic acid derivatives [14–20], bis-4-(alkoxy)benzoic acid hydrazides [21–24], polycatenar compounds [25–29], *scyllo*-inositol hexaesters [30], ellagic acid derivatives [31, 32] and recently a liquid crystalline silver complex [33].

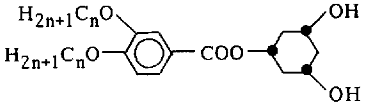
Besides lyotropic systems, full transitions from smectic via cubic to hexagonal columnar mesophases have until now been observed only with polycatenar compounds and the 'two chain' diols. Apparently, the amphiphilic character of diol mesogens [11] and their association behaviour via hydrogen bonding [10] place this class of compounds just between thermotropic and lyotropic systems.

Additional to the previous paper [1], we wish to give a detailed description of the thermal behaviour of the freeze dried and of the water saturated samples. Furthermore, the water absorption from a saturated atmosphere as well as from direct contact will be discussed.

2. Synthesis

The synthesis of the *cis,cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkoxy)benzoates with the general formula given in figure 1 is described elsewhere [9, 11]. In contrast to the mesomorphic 4-alkoxybenzoic acids [34], 3,4-bis(alkoxy)benzoic acids synthesized with *n* C-atoms per alkoxy chain are only crystalline compounds for $n = 3$–16 and 18. Their melting points lie in the range 115 to 156°C.

The 'two chain' diols were characterized by means of ^{1}H NMR, IR and mass spectrometry (MS); their purity was checked by size exclusion chromatography (SEC), thin layer chromatography (TLC) and elemental analysis. The data confirm the structure in each case [35] and are summarized in the experimental part. The thermal behaviour was investigated by means of DSC and polarizing microscopy. The analysis of the water absorption was performed in the manner described elsewhere [11].



$n = 5$-12, 14

Figure 1. General formula of the 'two chain' diols.

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* Author for correspondence.

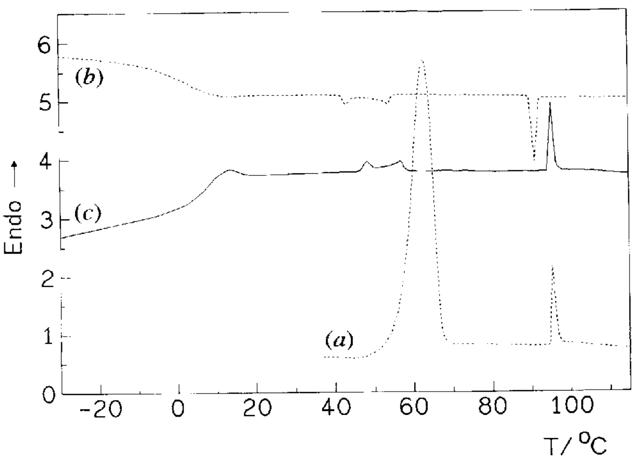


Figure 2. DSC thermogram of the freeze dried 'two chain' diol with $n = 8$. (*a*) First heating curve, (*b*) cooling curve, (*c*) second heating curve.

3. Results and discussion of the thermal behaviour

3.1. *Freeze dried products*

3.1.1. *DSC measurements*

All DSC measurements on the 'two chain' diols (freeze dried and water saturated) were carried out generally with a heating and cooling rate of $10\,\mathrm{K\,min^{-1}}$. Different rates used are specified in each case. Representatively, the DSC thermogram of the 'two chain' diol with $n = 8$ is given in figure 2. The small peaks between 40 and 60°C are a consequence of the complicated polymorphism, which is described in detail in § 3.1.2.

The temperatures and enthalpies of the crystal transitions and of the clearing points of the highest temperature mesophase of all the *cis*,*cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkoxy)benzoates are summarized in table 1. The crystal transitions (C_{1-3}) were clearly established by their enthalpies, by polarizing microscopy and by X-ray measurements [36].

The different crystalline phases C_1–C_3 have been assigned according to their temperature ranges. It is obvious that phase C_3 is a virgin phase, which is present only on the first heating and occurs later on only after several months, with the exception of the compound with $n = 9$, which needs only hours for recrystallization of C_3.

After the first heating, the 'two chain' diol with $n = 5$ shows only one mesophase, indicated as monotropic with respect to the virgin phase, at all temperatures. The dry 'two chain' diols with $n = 6$ and 7 exhibit no crystalline phase, neither as prepared nor after annealing several days at higher temperatures (40 and 60°C).

On cooling below the glass transition, the mesophase is frozen in. The same phenomenon was observed for the compounds with $n = 8$ and 9. The glass transitions and the corresponding ΔC_p values for the compounds with $n = 5$–9 are summarized in table 2. No glass transitions could be detected for compounds with $n > 9$; these show one or two stable crystalline phases (C_1, C_2), additional to the 'virgin' phase C_3.

For the higher homologues ($n \geqslant 10$), additional to their mesophase, one or more crystalline phases could be detected on the second and further measuring cycles.

The dependence of the transition temperatures of the freeze dried 'two chain' diols on the length of the alkoxy side chains is given in figure 3.

3.1.2. *Polarizing microscopy*

With respect to the mesophases formed, the *cis*,*cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkoxy)benzoates can be divided into three different groups (cf. figure 3).

Table 1. Transition temperatures (°C) and, in brackets, transition enthalpies ($\mathrm{kJ\,mol^{-1}}$) of the freeze dried 'two chain' diols. *n*: number of C-atoms in the side chain; C_1, C_2, C_3: crystalline phases; M: mesophase; I: isotropic phase.

n	C_1		C_2		C_3		M†		I
5	–		–		●	73·0 (23·2)‡	●	[66·5 (0·8)]	●
6	–		–		–		●	69·0 (0·6)	●
7	–		–		–		●	74·0 (0·5)	●
8	–		–		●	63·0 (16·6)‡	●	95·5 (0·9)	●
9	–		–		●	79·0 (10·9)‡§	●	109·5 (0·9)	●
10	–		●	29·0 (11·2)‖	●	72·0 (12·0)‡	●	113·5 (1·1)	●
11	●	26·5‖	●	38·5 (18·6)‖¶	●	82·0 (44·7)‡	●	123·0 (1·2)	●
12	●	37·5‖	●	47·5 (25·0)‖¶	●	79·5 (21·6)‡	●	124·0 (1·4)	●
14	●	59·5 (36·7)‖	●	66·0‡	●	78·5 (50·9)‡††	●	119·5 (1·2)	●

† Clearing temperature of the highest temperature mesophase.
‡ Only on first heating.
§ Only on second and further heating after annealing for several hours at 50°C.
‖ Only on second and further heating.
¶ Transition enthalpy for C_1 and C_2.
†† Transition enthalpy for all crystalline phases on the first heating.
[ ] Monotropic liquid crystalline phase.

Table 2. Temperatures for the glass transition T_g (°C) and for the cubic/hexagonal columnar transition T_{cub} (°C) with related ΔC_p values ($J K^{-1} mol^{-1}$) and transition enthalpies ΔH ($kJ mol^{-1}$) of the freeze fried 'two chain' diols.

n	T_g	ΔC_p	T_{cub}	ΔH
5	7	225		
6	7·5	190		
7	6	220		
8	5	215	63	0·64
9	8	210	66	0·82

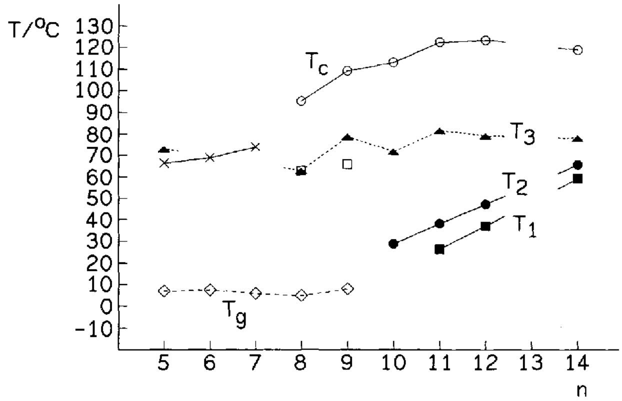


Figure 3. Transition temperatures (°C) of the freeze dried 'two chain' diols as a function of the length of the alkoxy chains n. T_c: clearing temperature. Mesophases, ×, smectic; □, cubic; ○, hexagonal columnar. Melting temperature, T_3: first heating, T_2: second and further heatings. T_1: crystal–crystal transition. T_g: glass transition temperature.

The compounds with short alkoxy side chains (n = 5–7) possess exclusively a smectic mesophase of the bilayered S_{A_d} type [36], similarly to the 'one chain' diols [3,4]. The typical texture, mostly homeotropic areas with birefringent domains around air bubbles can be observed on cooling from the isotropic melt. This orientation can be frozen in on further cooling below T_g.

After cooling from the isotropic melt, the higher homologues with $n \geq 10$, possessing only a hexagonal columnar D_{hd} phase [36], show a pseudo-focal-conic (spherulithic) texture, which is similar to that of the 'three chain' diols described earlier [9–12, 35]. On further cooling a crystallization process could be observed.

In the third group, the 'two chain' diols with $n = 8$ and 9, the situation is much more complicated, as demonstrated by the transition scheme for the compound with $n = 8$ (see figure 4). In addition to different metastable liquid crystal phases, an optically isotropic cubic mesophase appears slowly after annealing for several hours just below the temperature T_{cub}, given in table 2.

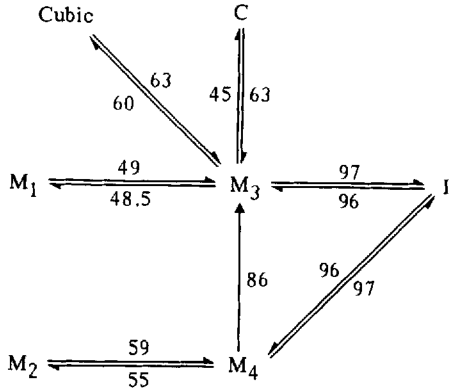
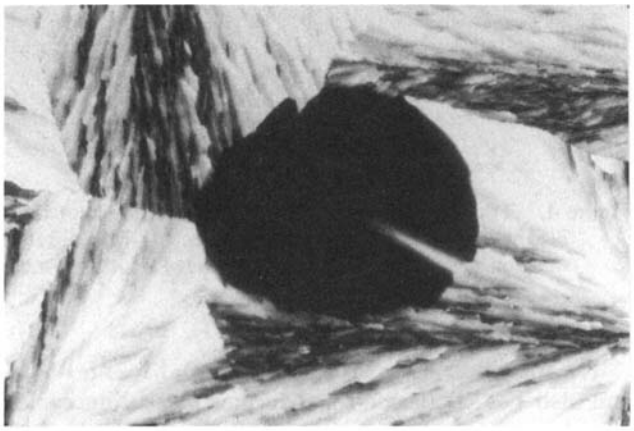


Figure 4. Transition scheme for the freeze dried 'two chain' diol with $n = 8$. C: crystalline phase; M_1–M_4: different mesophases; Cubic: cubic mesophase; I: isotropic melt.

The transitions $C \rightarrow M_3$ (first heating), $M_3 \rightarrow I$, $I \rightarrow M_3$ and also $I \rightarrow M_4$ (second and further measuring cycles) are detectable by polarizing microscopy and DSC measurements (cf. figure 2), but $M_3 \rightarrow M_1$ and $M_4 \rightarrow M_2$ only by polarizing microscopy.

In order to explain the transition scheme (see figure 4), we give a detailed description of the polarizing microscopic investigations. On cooling the 'C–8 two chain' diol below the clearing temperature, two coexisting textures are observed; pseudo-focal-conic domains (M_3), as well as 'high temperature' homeotropic domains (M_4) (see figure 5 (*a*)). From its texture, M_3 can be judged to be the D_{hd} phase, known from the compounds with $n \geq 10$. On further cooling, the transition $M_4 \rightarrow M_2$ occurs at 55°C (see figure 5 (*b*)), the columnar mesophase M_3 is unchanged. At 48°C, the pseudo-focal-conic texture of M_3 is transformed into the 'low temperature' homeotropic oriented mesophase M_1 (see figure 5 (*c*)), while the mesophase M_2 remains unchanged. During the cooling cycle, around 60°C, the slow growth of the cubic mesophase into the textures of the mesophases M_3 and M_4 can be observed as optically isotropic domains (see figure 5 (*b*) and (*c*)). Another photographic section of the sample shows the growth in progress of the cubic phase into M_3 after annealing for one hour at 60°C (see figure 5 (*d*)). After 5 h, the conversion into the cubic mesophase is nearly complete. A slight shearing at 45°C causes the very slow growth of the crystalline phase C into the cubic phase and the 'low temperature' homeotropic phase M_1 (see figure 5 (*e*)). Without shearing, the compound recrystallizes only over a period of several months. Furthermore, the cubic and the 'low temperature' homeotropic mesophase (M_1) can be observed at the same time.

The polymorphism described for the dry 'C–8 two chain' diol leads to the question as to whether M_1–M_4 are really partially coexisting mesophases with different transition temperatures? For 4′-*n*-hexadecyloxy- and 4′-*n*-octadecyloxy-3′-nitrobiphenyl-4-carboxylic acid, Demus described a similar complicated polymorphism with the formation of a metastable mesophase during an inhibited nucleation of the cubic (S_D) phase [18, 37]. So, it seems to be obvious, depending on the conditions of supercooling and superheating, that we could observe really different mesophases as shown in figure 4.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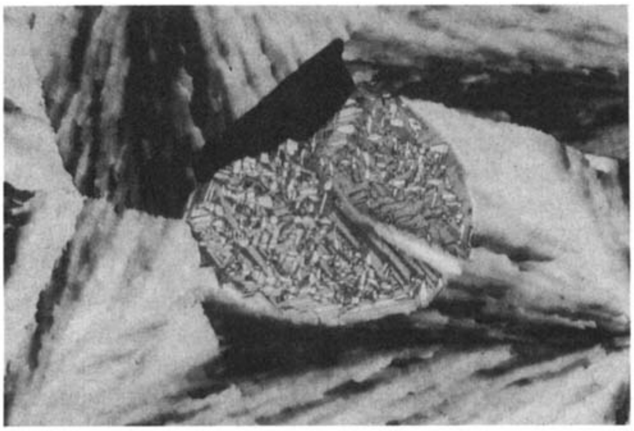
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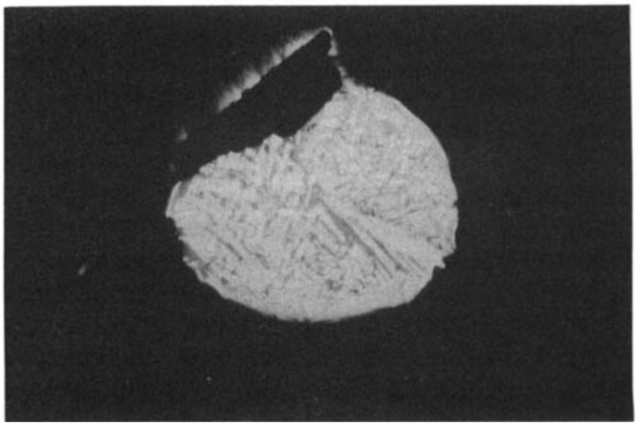
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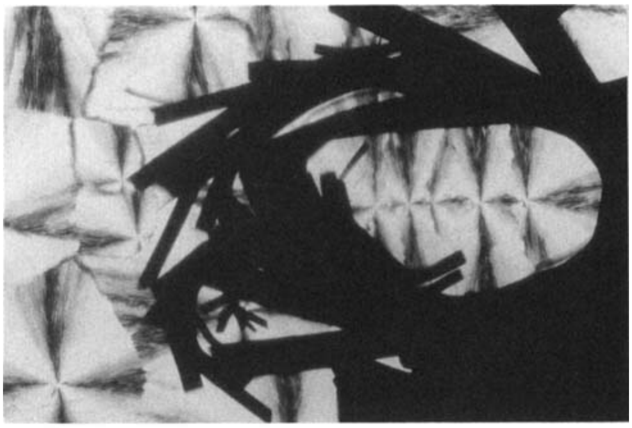
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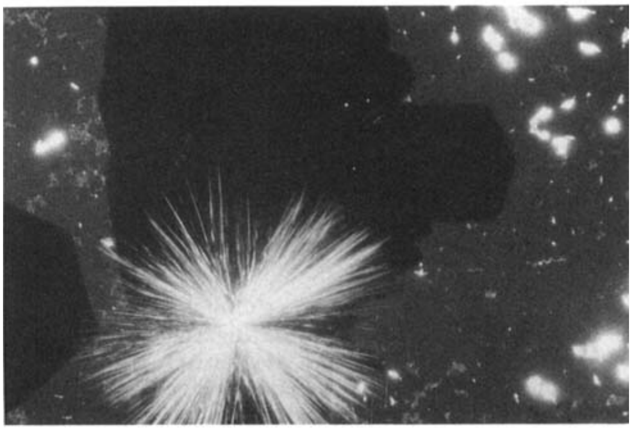

(*e*)

Figure 5. Optical textures (crossed polarizers) of the freeze dried ‘two chain’ diol with $n = 8$. (*a*) Cooling from the isotropic melt to 85°C; (*b*) cooling to 55°C; (*c*) cooling to 48°C; (*d*) annealing one hour at 60°C; (*e*) after shearing at 45°C.

3.2. *Water saturated products*

3.2.1. *DSC measurements*

As known from other hydroxy group-containing liquid crystals [11], the phase behaviour of the *cis,cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkoxy)benzoates is strongly influenced by water absorption, due to the amphiphilic nature of these compounds. The mesophase behaviour of the ‘two chain’ diols that have absorbed water from a saturated atmosphere (cf. § 4.1), is quite different from that of the freeze dried samples. In general, the transition temperatures are higher.

In order to elucidate the results of the DSC measurements, a plot of the transition temperatures versus the number of C-atoms in the alkoxy chains is given in figure 6.

The results of the DSC measurements of all water saturated 'two chain' diols are summarized in table 3.

The absorption of a stoichiometric amount of one mol of water per mol of two chain diol (cf. § 4.1) influences above all the crystallinity. On the one hand, this is obvious by the appearance of new crystalline phases for the compounds with $n = 6$, 7 and 9, and on the other hand by the disappearance of one of three crystalline phases for the 'two chain' diol with $n = 14$, and also the total disappearance of crystallinity for the compound with $n = 5$. The 'C–5 two chain' diol exhibits only a liquid crystalline phase which can be frozen in at − 13°C. In analogy to the freeze dried samples, a strong hindrance of crystallization is observed for the compounds with $n = 6$–8. Their crystalline phases, detectable on the first heating, reappear only after several months. Therefore, on second and further DSC cycles, a glass transition can be observed. The glass transition temperatures, which are drastically decreased compared with those in the freeze dried state, and the corresponding ΔC_p values are summarized in table 4.

The strong increase in the clearing temperatures, with respect to the freeze dried samples, is more pronounced for the compounds with short alkoxy side chains ($n = 5$–9; cf. table 2 and table 3). A further consequence of the water absorption is the disappearance of different mesophases, especially in the case of the compound with $n = 8$, for which the DSC thermogram (cf. figure 2) is given in figure 7. Here, only the cubic and the hexagonal columnar mesophase can be detected. After water absorption, the formation of the cubic mesophase is much faster than in the freeze dried state (cf. § 3.2.2). Therefore, it is not necessary to anneal the samples to get complete formation of the cubic phase. In the compound with $n = 9$, having absorbed water, the cubic phase is no longer present, and only the hexagonal columnar mesophase remains.

The division into three types established for the mesophase behaviour of the freeze dried *cis,cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkoxy)benzoates is also applicable to the samples that had absorbed water from a saturated atmosphere, but with another distribution. The homologues with short alkoxy chains ($n = 5$–7) exhibit a smectic mesophase of the S_{A_d} type as in the dry state. The number of 'two chain' diols possessing a hexagonal columnar mesophase is increased, i.e. $n = 9$–12 and 14 (cf. § 3.1.1). The middle group with more than one mesophase now consists of only the 'two chain' diol with $n = 8$ (cf. figure 8).

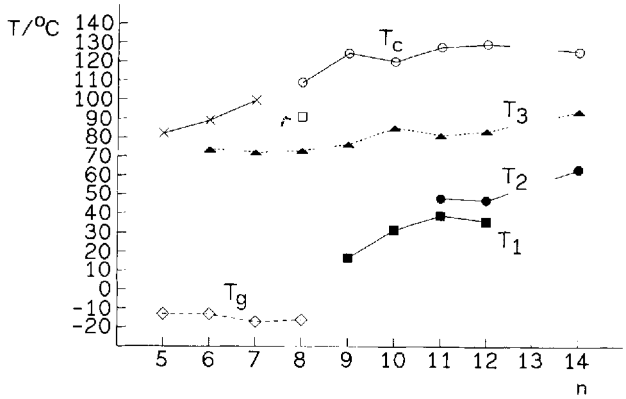


Figure 6. Dependence of the transition temperatures (°C) of 'two chain' diols that have absorbed water from a saturated atmosphere on the length of the alkoxy chains *n*. T_c: clearing temperature. Mesophases, ×, smectic; □, cubic; ○, hexagonal columnar. Melting temperature, T_3: first heating, T_2: second and further heatings. T_1: crystal–crystal transition. T_g: glass transition temperature.

3.2.2. *Polarizing microscopy*

The observed textures are the same as for the freeze dried state. The 'two chain' diols with the smectic mesophase show a mostly homeotropic texture, while the compounds with the hexagonal columnar mesophase exhibit the well-known pseudo-focal-conic texture.

Because of the very fast formation of the cubic phase (within several seconds), in contrast to the freeze dried samples, its growth in regular geometric domains cannot be observed.

4. Results and discussion of the water absorption

4.1. *Water absorption from a saturated atmosphere*

The method of investigating the water absorption from a saturated atmosphere has been described elsewhere [11]. In general, one mol of water per mol of *cis,cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkoxy)benzoate is absorbed, as shown in figure 9 for $n = 10$ and 12. The absorption time strongly depends on the length of the alkoxy chains and also on the nature of the mesophase formed. So, the 'two chain' diols possessing only a hexagonal columnar mesophase ($n = 10$–12, 14) reach the maximum limit within 24 h. The rate of water absorption becomes smaller with increasing length of alkoxy chains (cf. figure 9).

The situation is completely different in the case of the 'two chain' diols with short alkoxy side chains ($n = 5$–7), forming a smectic mesophase. Though the hydrophoby of these compounds should be lower compared with the homologues with longer alkoxy chains, the water absorption is much slower as can be seen from figure 10 for the 'two chain' diol with $n = 5$. The limiting value of one mol of water is only reached after weeks. Apparently, in the

Table 3. Transition temperatures (°C) and, in brackets, transition enthalpies (kJ mol^{-1}) of the 'two chain' diols that have absorbed water from a saturated atmosphere. *n*: number of C-atoms in the chain; C_1, C_2, C_3: crystalline phases; M: mesophase; I: isotropic phase.

n	C_1		C_2		C_3		M†		I
5	–		–		–		●	82·5 (1·0)	●
6	–		–		●	74·0 (39·4)‡	●	89·5 (0·8)	●
7	–		–		●	72·5 (49·3)	●	100·0 (0·5)	●
8	–		–		●	73·5 (50·6)‡	●	109·5 (0·5)	●
9	●	17·0 (7·1)§	–		●	77·0 (48·6)	●	125·0 (1·0)	●
10	●	32·0 (10·0)§	–		●	86·0 (42·8)	●	121·0 (1·3)	●
11	●	39·5§	●	48·5 (31·1)§‖	●	82·0 (61·5)	●	128·5 (1·4)	●
12	●	36·5§	●	47·5 (30·2)§‖	●	84·5 (65·0)	●	130·5 (1·5)	●
14	–		●	64·0 (41·4)§	●	95·0 (50·9)	●	126·5 (1·5)	●

† Clearing temperature of the highest temperature mesophase.
‡ Only on first heating.
§ Only on second and further heating.
‖ Transition enthalpy for C_1 and C_2.

smectic phase water absorption is much slower than in the hexagonal columnar phase. Furthermore, it can be noticed that the different nature of the absorbing phase in the same compound is important. Being in the mesophase after the first heating, the sample absorbs water more quickly than the crystalline phase, despite its large surface area due to freeze drying.

The 'two chain' diols with $n = 8$ and 9 (smectic, cubic and hexagonal columnar mesophases) exhibit the same behaviour as the compounds with $n = 10$–12 and 14, showing only the hexagonal columnar mesophase, and give absorption of one mol of water within 24 h.

4.2. *Water absorption in direct contact*

The method of water absorption through direct contact was described in a previous paper [11]. Because of the differences in the water absorption from a saturated atmosphere, we investigated with particular care a 'two chain' diol from the smectic type ($n = 5$) and one from the hexagonal columnar type ($n = 12$) (cf. § 3.1.1 and 3.2.1).

Compared to the freeze dried state and to that having absorbed water from a saturated atmosphere, the phase behaviours of both diols ($n = 5$ and 12) change drastically in direct contact with water.

In the case of the smectic 'C-5 two chain' diol, a crystalline phase with a melting point at 71°C ($\Delta H = 43{\cdot}8$ kJ mol^{-1}) is observed on the first as well as on subsequent heatings. Because of the strong increase in the clearing temperature of the smectic phase up to 100·5°C ($\Delta H = 1{\cdot}0$ kJ mol^{-1}), enantiotropic mesomorphism is now observed.

In the case of the 'C-12 two chain' diol, possessing a hexagonal columnar mesophase, in direct contact with water, only two different crystalline phases at 43·5°C ($\Delta H = 10{\cdot}9$ kJ mol^{-1}) and 81·5°C ($\Delta H = 57{\cdot}9$ kJ mol^{-1}) are detectable. Up to a temperature of 150°C, no clearing point is found. Around this temperature, the pressure caused by the excess of water opens the DSC pans, so that reproducible measurements are no longer possible.

In contrast to the *cis,cis*-(3,5-dihydroxycyclohexyl) 3,4,5-tris(dodecyloxy)benzoate, which incorporate stoichiometric amounts of water with the formation of a mono- and dihydrate showing thermotropic behaviour

Table 4. Glass transition temperatures T_g (°C) and ΔC_p values (J K^{-1} mol^{-1}) of the 'two chain' diols that have absorbed water from a saturated atmosphere.

n	T_g	ΔC_p
5	− 13	180
6	− 13	215
7	− 17	310
8	− 16	230

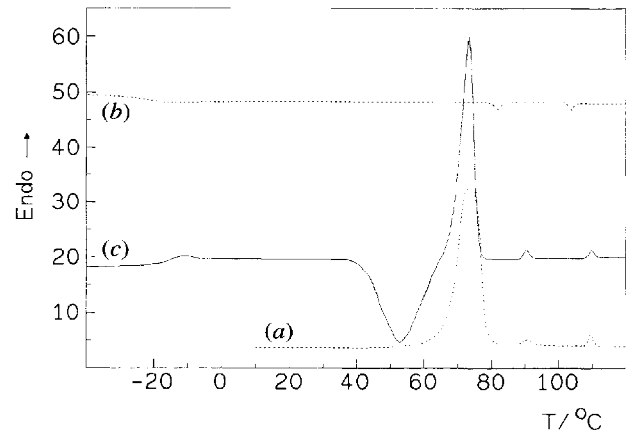
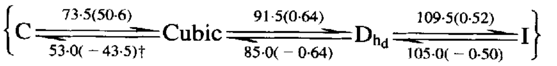


Figure 7. DSC thermogram of the 'two chain' diol with $n = 8$ after absorbing water from a saturated atmosphere. (*a*) First heating curve, (*b*) cooling curve, (*c*) second heating curve.



$$\left\{\mathrm{C}\underset{53\cdot0(-43\cdot5)\dagger}{\overset{73\cdot5(50\cdot6)}{\rightleftharpoons}}\mathrm{Cubic}\underset{85\cdot0(-0\cdot64)}{\overset{91\cdot5(0\cdot64)}{\rightleftharpoons}}\mathrm{D_{h_d}}\underset{105\cdot0(-0\cdot50)}{\overset{109\cdot5(0\cdot52)}{\rightleftharpoons}}\mathrm{I}\right\}$$

† The cubic mesophase can be frozen in at −16°C; recrystallization occurs on heating the sample at the indicated temperature.

Figure 8. Transition scheme of the 'two chain' diol with $n = 8$ after absorbing water from a saturated atmosphere. C: crystalline phase; Cubic: cubic mesophase; D_{h_d}: hexagonal columnar mesophase; I: isotropic melt.

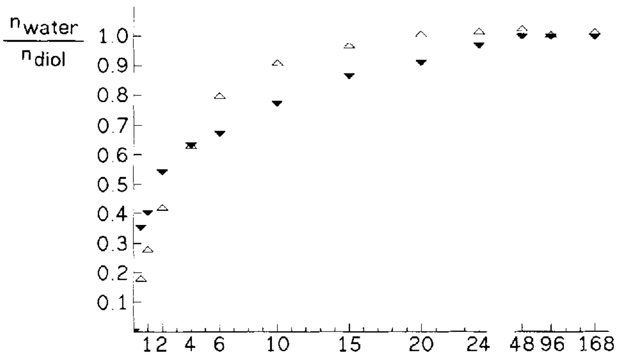


Figure 9. Rate of water absorption (mol of water per mol of 'two chain' diol) from a saturated atmosphere for the compounds with $n = 10$ (△) and $n = 12$ (▼).

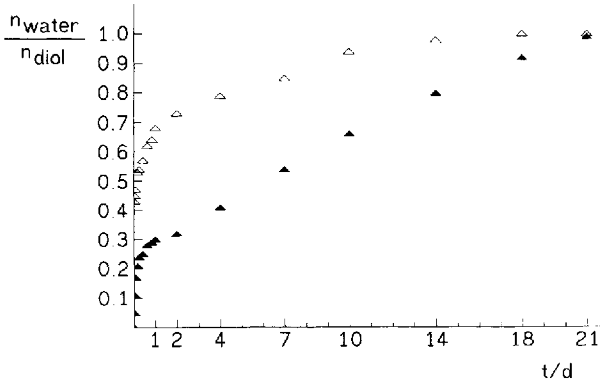


Figure 10 Rate of water absorption (mol of water per mol of 'two chain' diol with $n = 5$) from a saturated atmosphere, in the crystalline phase (▲) and in the mesophase (△).

(liquid crystal water) [11], for both 'two chain' diols no stoichiometric water incorporation was found. The determined amount was influenced by the molar excess of water in each DSC pan. Thus, in the case of the diol with $n = 12$, values from 2 up to 8·5 mol of water per mol of diol have been found.

5. Conclusions

The *cis,cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkoxy)benzoates, aggregating via hydrogen bonding, form smectic, cubic and hexagonal columnar mesophases, dependent on the length of the alkoxy chains.

In this behaviour, the 'two chain' diols can be compared with tetracatenar compounds, which play in intermediate role in polycatenar compounds [2]. Whereas tricatenar mesogens, i.e. rod-like molecules with a 'two chain' and a 'one chain' end, exhibit mostly lamellar phases, penta- and hexacatenar mesogens preferably form columnar phases. In between, with tetracatenar compounds, a competition occurs between lamellar and columnar mesomorphism, dependent on the position and length of the alkyl chains. The mesomorphism of polycatenar compounds seems to be governed by the delicate balance between discoid and rod-like structural elements. However, the mesomorphism of the diol mesogens is caused by aggregation via hydrogen bonding. In all these families of mesogens, the kind of polymesomorphism seems to depend on the degree of the curvature of the interface either between the aromatic core and aliphatic chains in polycatenar compounds or between the hydrophilic central region and the hydrophobic outer chain area of the diol mesogens. Here, with long alkoxy side chains ($n \geqslant 10$), a strong curvature of the interface occurs, leading to sufficient space filling in the peripheral alkyl chain region and hence to columnar mesomorphism. With short alkoxy side chains ($n = 5$–7), the curvature is so reduced that only the lamellar bilayer mesophase S_{A_d} appears. The compounds with $n = 8$ and 9 are on the borderline between the two cases and therefore they form lamellar as well as columnar mesophases with an intermediate cubic phase. The X-ray investigations of the cubic phase will be reported in the future [36].

As compared to polycatenar compounds and with respect to the hydrogen bonding and also the pronounced influence of the absorbed water on the thermal behaviour, the observed thermotropic polymorphism is still more similar to that of lyotropic systems [38, 39].

6. Experimental

6.1. *Instruments*

IR: Bio Rad/Digilab FTS 40. ^{1}H NMR: Bruker AC 250 (250 MHz). MS: Varian MAT 312. Elemental analysis: Mikroanalytisches Labor Ilse Beetz, Kronach. Polarizing microscopy: Leitz Labolux 12 Pol, Mettler hot stage FP 82, photoautomat Wild MPS 45/51 S. DSC: Perkin–Elmer DSC 7 (temperatures were taken from peak maxima). MPLC—see § 6.2 below: Kronwald Separationstechnik, pump Sepapress HPP 100/50, Sepacon GCU 311 control, detection by Sepachrom UV/VIS 400, Sepachron HPP column (length 539 mm) filled with HD-SIL 30–60 (20–45 μm). SEC: Waters model 510, RI detector Waters 410, UV detector 254 nm Waters 440, eluent: THF, columns: PL-gel 600 × 7·5, pore width 100, 500 Å.

6.2. *Purification and characterization*

The purification of all 'two chain' diols was carried out by middle pressure chromatography (MPLC) with ethyl acetate as eluent. In some cases a further recrystallization was necessary to yield the pure compound. The solvents used are given below. At least one freeze drying procedure from a benzene solution was performed to yield the lyophilized diols.

All 'two chain' diols show nearly identical IR and ^{1}H NMR spectra; therefore, as a typical example, only the data for the 'two chain' diol with $n = 10$ are given below. In all other cases, the spectra are similar and confirm the structure.

6.2.1. cis,cis-*(3,5-Dihydroxycyclohexyl) 3,4-bis(pentyloxy)benzoate:* n = *5*

Recrystallization from benzene. White powder. Yield: 48 per cent. MS (*m/e*): 408 (100 per cent). $C_{23}H_{36}O_6$ (408·53) Calculated (per cent): C 67·62, H 8·88, O 23·50; Found (per cent): C 67·69, H 8·94, O 23·37.

6.2.2. cis,cis-*(3,5-Dihydroxycyclohexyl) 3,4-bis(hexyloxy)benzoate;* n = *6*

Recrystallization from toluene. Colourless wax. Yield: 51 per cent. MS (*m/e*): 436 (100 per cent). $C_{25}H_{40}O_6$ (436·59) Calculated (per cent): C 68·78, H 9·23, O 21·99; Found (per cent): C 68·80, H 9·16, O 22·04.

6.2.3. cis,cis-*(3,5-Dihydroxycyclohexyl) 3,4-bis(heptyloxy)benzoate;* n = *7*

Colourless wax. Yield: 55 per cent. MS (*m/e*): 464 (100 per cent). $C_{27}H_{44}O_6$ (464·64) Calculated (per cent): C 69·80, H 9·54, O 20·66; Found (per cent): C 69·85, H 9·52, O 20·63.

6.2.4. cis,cis-*(3,5-Dihydroxycyclohexyl) 3,4-bis(octyloxy)benzoate;* n = *8*

White powder. Yield: 62 per cent. MS (*m/e*): 492 (100 per cent). $C_{29}H_{48}O_6$ (492·69) Calculated (per cent): C 70·70, H 9·82, O 19·48; Found (per cent): C 70·79, H 9·78, O 19·43.

6.2.5. cis,cis-*(3,5-Dihydroxycyclohexyl) 3,4-bis(nonyloxy)benzoate;* n = *9*

White powder. Yield: 59 per cent. MS (*m/e*): 520 (100 per cent). $C_{31}H_{52}O_6$ (520·75) Calculated (per cent): C 71·50, H 10·06, O 18·43; Found (per cent): C 71·43, H 10·01, O 18·56.

6.2.6. cis,cis-*(3,5-Dihydroxycyclohexyl) 3,4-bis(decyloxy)benzoate;* n = *10*

White powder. Yield; 69 per cent. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0·86 (2 × t; 6 H, $-C\underline{H}_3$), 1·15–1·65 (br; 14 H, $-C\underline{H}_2-$), 1·58 (br; 3 H, $-HC\underline{H}_{ax}-$), 1·80 (m; 4 H, $OCH_2C\underline{H}_2-$), 2·11 (s; 2 H, $-O\underline{H}$), 2·29 (m; 3 H, $-HC\underline{H}_{eq}-$), 3·82 (m; 2 H, $-C\underline{H}-OH$), 4·01 (2 × t; 4 H, $OC\underline{H}_2-$), 4·98 (m; 1 H, $-C\underline{H}-OOC$), 6·82 (d; 1 H, aromatic, 5-position, $J = 8·6$ Hz), 7·50 (d; 1 H, aromatic, 2-position, $J = 1·9$ Hz), 7·59 (dd; 1 H, aromatic, 6-position, $J = 8·6$ Hz + 1·9 Hz). IR (KBr, cm^{-1}): 3382, 2922, 2851, 1703, 1599, 1516, 1468, 1431, 1292, 1273, 1225, 1141, 1111, 1032, 995, 760. MS (*m/e*): 548 (100 per cent). $C_{33}H_{56}O_6$ (548·80) Calculated (per cent): C 72·22, H 10·28, O 17·49; Found (per cent): C 72·13, H 10·26, O 17·61.

6.2.7. cis,cis-*(3,5-Dihydroxycyclohexyl) 3,4-bis(undecyloxy)benzoate;* n = *11*

White powder. Yield: 60 per cent. MS (*m/e*): 576 (100 per cent). $C_{35}H_{60}O_6$ (576·85) Calculated (per cent): C 72·88, H 10·48, O 16·64: Found (per cent): C 72·82, H 10·42, O 16·75.

6.2.8. cis,cis-*(3,5-Dihydroxycyclohexyl) 3,4-bis(dodecyloxy)benzoate;* n = *12*

White powder, Yield: 54 per cent. MS (*m/e*): 604 (100 per cent). $C_{37}H_{64}O_6$ (604·91) Calculated (per cent): C 73·47, H 10·66, O 15·87; Found (per cent); C 73·57, H 10·70, O 15·73.

6.2.9. cis,cis-*(3,5-Dihydroxycyclohexyl) 3,4-bis(tetradecyloxy)benzoate;* n = *14*

White powder. Yield: 71 per cent. MS (*m/e*): 660 (100 per cent). $C_{41}H_{72}O_6$ (661·01) Calculated (per cent): C 74·50, H 10·98, O 14·52; Found (per cent): C 74·42, H 10·93, O 14·65.

We wish to acknowledge gratefully the financial support of the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich SFB 213, Projekt C 14). Furthermore, we want to thank Professor O. Nuyken, München, for his helpful encouragement of this work.

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