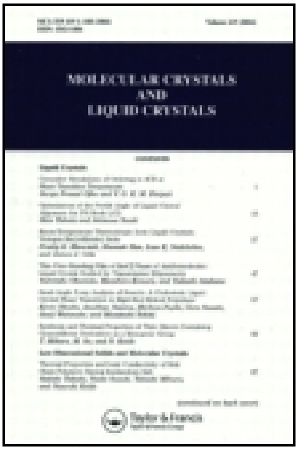

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HYDROXY GROUP CONTAINING LIQUID CRYSTALS: COLUMNAR AND CUBIC PHASES IN TWO CHAIN DIOLS

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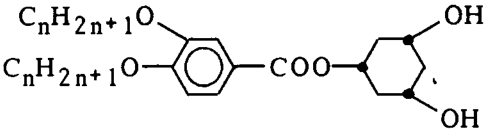
Abstract The thermal behaviour of several cis,cis-(3.5-dihydroxycyclohexyl)- 3.4-bis(alkoxy)benzoates is discussed.

INTRODUCTION

Recently the existence of associated discogens has been revealed for cis,cis-(3.5-dihydroxycyclohexyl)-3.4.5-tris(alkoxy)benzoates ("three chain diols"), whose molecular shape is not disclike itself, as in the case of conventional molecular discogens[1].

The three chain diols are capable of self organizing via hydrogen bonding. The resulting mesogenic unities consist of disclike associates or clusters of six molecules, which can arrange to hexagonal columnar D_{hd}-phases[2]. In analogy to the preparation of the three chain diols[1] we have synthesized a series of two chain diols, i.e. cis,cis-(3.5-dihydroxycyclohexyl)-3.4-bis(alkoxy)benzoates 1:



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The purity of the products was checked by thin layer chromatography (TLC), gel chromatography (GPC) and elemental analysis. The characterization was performed by means of IR, ^1H NMR and mass spectrometry. All data confirmed the structure of the thoroughly dried compounds.

THERMAL BEHAVIOUR

The thermal properties of the two chain diols in general are much more complicated than those of the three chain analogs mentioned above, or the appropriate diols possessing only one chain (cis,cis-(3.5-dihydroxycyclohexyl)-4-(alkoxy)benzoates)[3]. Furthermore there are large differences between the different members of the homologous series of the two chain diols. All compounds synthesized exhibit a broad mesophase M below the clearing point, as indicated in TABLE I.

TABLE I Transition and clearing temperatures of the highest mesophase M of 1

n		M		I
6	8.1[a]	●	68.9	●
8	63.4[b]	●	97.5	●
9	66.0[b]	●	110.0	●
10	71.9[c]	●	113.1	●
12	55.4[c]	●	123.9	●
14	60.9[c]	●	118.7	●

n = number of C-atoms
M = highest mesophase; I = isotropic phase

a) glass transition temperature; the compound shows no further phases

b) transition temperatures of an isotropic cubic phase into the mesophase M

c) Last transition of a sequence of different lower mesophases

For all compounds the mesophase M shows a focal conic texture under the polarizing microscope (FIGURE 1). Initial X-ray experiments[4] revealed a two dimensional hexagonal lattice with the lattice constant a = 35.8 Å for compound 1 with n = 10. From density measurements it can be concluded that six single molecules arrange to a disclike associate, as in the case of three chain diols.

The current investigations are expected to reveal whether the other members of the homologous series also exhibit a hexagonal columnar structure of the highest mesophase M, which is quite probable.

As can be seen by means of DSC measurements, the members of the homologous series with n = 8, 9, 10, 12 possess an unusually manifold and complicated mesomorphism below the highest mesophase M. Thus, besides a different number of metastable LC- phases, isotropic cubic phases can be observed under the polarizing microscope in the case of the compounds with n = 8, 9 (FIGURE 1). Those phases are easily achieved by annealing the compounds below the temperatures given in TABLE II, under b). For n = 8, the cubic phase is stable for several hours even at room temperature. Only after repeated shearing of the glass plates and annealing for at least 4 hours below 45 °C can a stable, very slowly growing crystalline phase K be observed under the microscope. The needle-like crystals (whiskers) show a melting point at 62.5 °C. The derivative with n = 9 exhibits a crystalline phase after annealing the sample for 3 hours at 50 °C. The melting point is 78.8 °C.

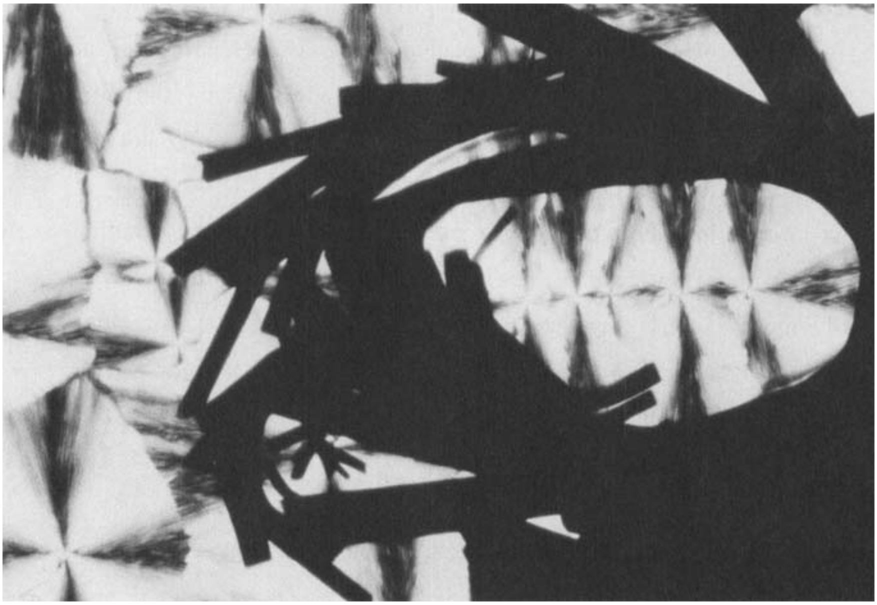

FIGURE 1 Optical texture of 1 with n = 8 at 60 °C; between crossed polarizers.

DISCUSSION

So far only few examples of thermotropic liquid crystals exhibiting cubic phases are known in the literature. Apart from several strontium soaps[5], four biphenyl carbonic acid derivatives with lateral nitro or cyano groups[6], bishydrazides of 4-(alkoxy)benzoic acids[7] and recently several biforked mesogens[8,9] have been described. With respect to the structure of cubic phases two molecular models were originally proposed: either a cubic arrangement of two interpenetrating, infinite, three-dimensional networks of interconnected rods[10] or an aggregation of molecules in spherical micelles[11]. Both models are still a matter of discussion[12-14].

With respect to the two chain diols presented here, some remarks can be made even now:

a) if we assume, as is highly probable, the same structure for the highest mesophase M of compound **1** with n = 8,9 as for n = 10 (6 molecules per disc; as in the case of three chain diols[2]), the argument against the aggregation in micelles (" inconveniences of space filling by aliphatic chains in the central part"[12]) could not be applied to the two chain diols.

b) the formation of dimers of the two chain diols is sterically not possible, as can be concluded from CPK molecular models. Thus, the dimeric or "double" structure of the mesogenic molecule[6] is apparently not necessary for the formation of cubic phases in general.

c) strong interactions between single molecules e.g. hydrogen bonding, seem to play an important role in view of the structure of cubic phases. An outboard dipole[13] (-CN or NO_2-) should not be necessary for cubic phase formation in general, as is still shown with biforked mesogens.

To sum up, it may be said that further detailed investigations of two chain diols of the type presented here should reveal interesting information with respect to the following points:

1) the explanation of the structure of the various metastable mesophases observed by DSC and polarizing microscopy

2) the possibility of achieving further information on cubic phases of a new class of compounds at relatively low temperatures

3) the question about the structural position of the two chain diols between the related one chain diols, exhibiting smectic double layers[3], and three chain diols with simple hexagonal columnar phases[1,2]. This intermediate position seems to be the key to the complicated mesomorphism of this class of LC compounds.

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