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Hydroxy group containing liquid crystals

I. Synthesis and characterization of *cis, cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(decyloxy)benzoate and derivatives

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The first example of a new class of diol mesogens is described. *Cis, cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(decyloxy)benzoate was synthesized starting from *cis, cis*-phloroglucitol, which had been protected by phenylboronic acid. Polarizing microscopy and calorimetric measurements provide evidence for a broad mesophase range, including room temperature. The existence of a hexagonal columnar structure is probable. Furthermore several derivatives are described.

1. Introduction

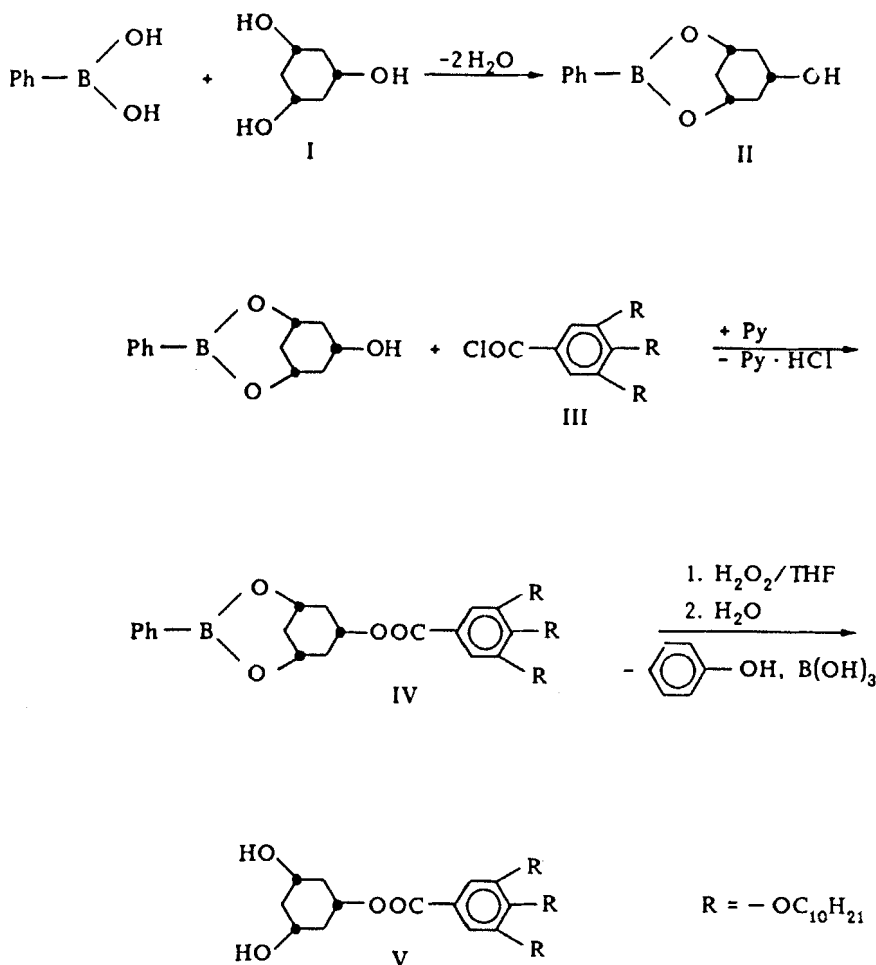
Until recently only a relative small number of mesogens have been known to possess hydroxy groups. So, less than 1 percent of calamitic compounds with one OH-group per molecule have been listed in related compendia [1, 2], mesogens with two or more OH-groups are far rarer. A few years ago the existence of both thermotropic and lyotropic mesophases was demonstrated not only for cellulose and cellulose derivatives [3] and for a large number of cyclic carbohydrates and related derivatives [4-6], but also for compounds with only two terminal hydroxy groups [7]. All species possess one aliphatic chain substituent [4-6]. This finally put paid to the apparently widespread opinion, that 'molecules exhibiting hydrogen bonded structures do not form liquid crystals' [6]. Indeed, this meaning could never have been correct, since on the other hand, the existence of liquid-crystallinity of several classes of compounds exhibiting hydrogen bonding had already been well-known for a long time. So, among others, alkylsubstituted benzoic acids belong to a group of liquid crystals, where a rod-like central core is formed by dimerization of carboxyl groups due to hydrogen bonding [8]. Beside this formation of dimeric rigid units, hydrogen bonding has been known to play a role as an anisotropic, cohesive force between a large number of suitable single molecules, causing liquid crystallinity. So, 20 years ago, short 2-monoglycerides had been shown to form thermotropic mesophases corresponding to a bilayered lamellar structure [9]. Also, to our knowledge, all monoalkyl carbohydrate liquid crystals, including open chain derivatives [10], form bilayer mesophases of the interdigitated S_{A_d} type, being first described with terminal polar liquid crystal compounds, with cyano or nitro groups [11].

Taking all of these examples into consideration, it seems to be no longer quite correct, that terminal hydroxyl groups should lead to polymeric hydrogen bonding, favouring a non parallel arrangement and thus preventing liquid-crystallinity [8]. With one exception, the mesogenic carbohydrates, carbohydrate derivatives and monoglycerides examined so far have no more than one alkyl chain per molecule.

Only one group of double-tailed carbohydrate-based mesogens have been described till now [27, 28]. Here we wish to describe the first example of a new series of diol mesogens, possessing three alkoxy chains per molecule.

2. Synthesis

According to the scheme 1 we protected two hydroxy groups of *cis*, *cis*-1,3,5-cyclohexanetriol (*cis*, *cis*-phloroglucitol) I, which had been synthesized from 1,3,5-trihydroxybenzene by catalytic hydrogenation [12], by reaction with benzenboronic acid [13]. The resulting product II was esterified with the acid chloride III, which was obtained as described in literature [14]. The deprotection reaction of IV was carried out by varying known conditions [15]. The products were characterized by means of I.R., ^1H N.M.R., ^{13}C N.M.R. and mass spectrometry, their purity was checked by G.P.C. and elemental analysis. The data confirmed the structure. Special attention should be paid to the dry state of the resulting diol compound V. In the following the thermal behaviour of the absolutely dry product is described. The situation after water absorption will be discussed in a subsequent paper.



Scheme 1

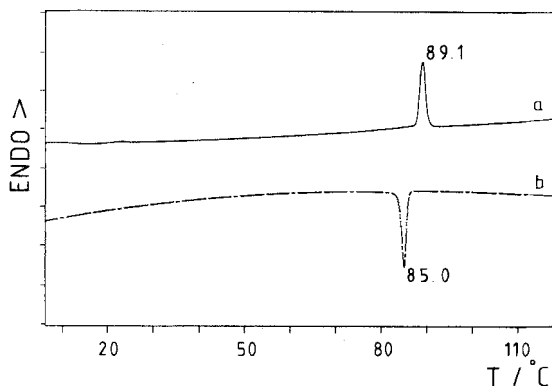


Figure 1. D.S.C. thermogram of V. (a) heating curve, (b) cooling curve; heating and cooling rate $10^{\circ}\text{C}/\text{min}$.

3. Phase behaviour

3.1. D.S.C. measurements

On heating and cooling down to -50°C with $10^{\circ}\text{C}/\text{min}$ the absolutely dry product shows only one peak at 89.1°C , and 85.0°C , respectively (cf. figure 1). The small enthalpy value of $\Delta H = 1.5 \text{ kJ mol}^{-1}$ (-1.6 kJ mol^{-1}) indicates the presence of a mesophase.

3.2. Polarizing microscopy

On cooling the isotropic melt, homeotropic regions and a variant of the focal conic texture with spherulitic domains can be observed (cf. figure 2). On further cooling to room temperature a slight continuous change in the colour of the texture can be observed (cf. figures 2 and 3). Only on heating, do streak-like defects appear on the mesomorphic domains (cf. figure 4). The formation of these defects is reversible, depending on the heating and cooling cycles.

4. Discussion

The texture of the mesophase of product V, resembles the textures of S_A phases [16, 17]. Therefore, and given the knowledge of the infrared absorption band at 3378 cm^{-1} , characteristic of hydrogen bonding [18], we could assume, at first glance, a smectic bilayer phase as for example carbohydrate mesogens. However, initial X-ray measurements [19] clearly show a two dimensional hexagonal lattice, with the lattice constant a of 40.8 \AA . This intercolumnar distance corresponds to nearly 1.5 times the length of one diol molecule V with extended alkyl chains. Density measurements [19] reveal that about five or six molecules form one slice in a column. In consequence we must count on the formation of disc-like associates of the diol mesogen caused by hydrogen bonds. They should be in a dynamic state, as mentioned for carbohydrate mesogens [10]. This could be responsible for the slight, continuous change in colour with temperature of the texture (cf. figures 2 and 3), when the dry product is observed between crossed polarizers. The fact that the new diol mesogen does not crystallize and exists only as mesophase is known only from amphiphilic anion salts in which the lipophilic groups are of a non-compact type [20]. So, among others, the pure sodium di(2-ethylhexyl)acetate exhibits an inverse hexagonal or inverse middle phase, M_2 , where the hydrophilic groups form the cores and the alkyl chains the outer sphere.

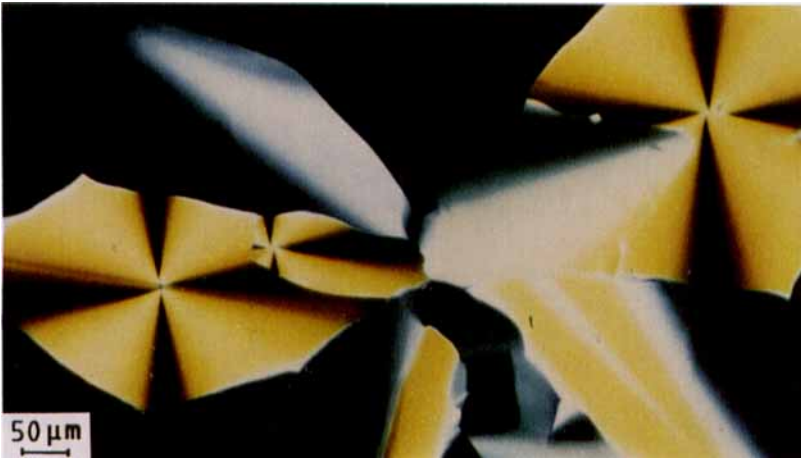


Figure 2. Optical texture of V after cooling from the isotropic melt to 80°C; between crossed polarizers.

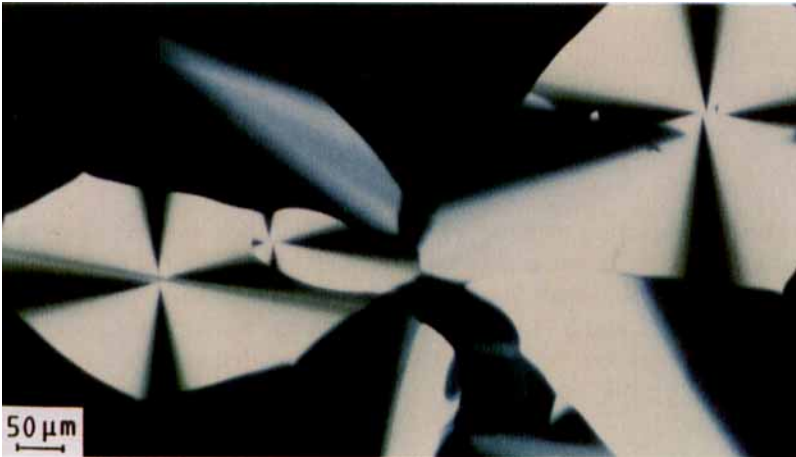


Figure 3. Optical texture of V after cooling from the isotropic melt to room temperature; between crossed polarizers.

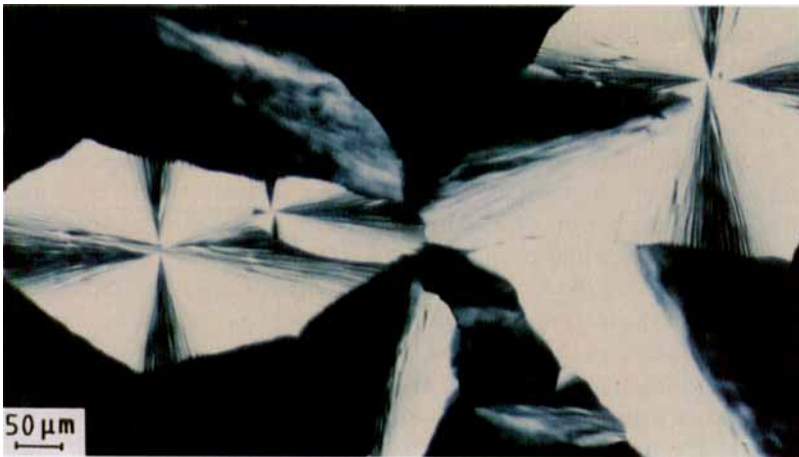


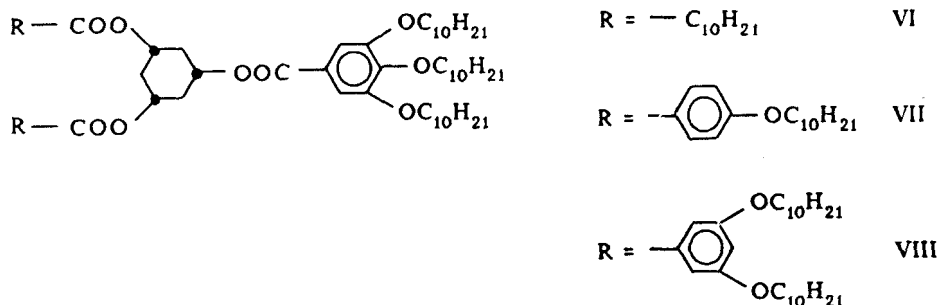
Figure 4. Optical texture of V. Streak-like defects on heating from room temperature to 40°C; between crossed polarizers.

The branched character of the hydrocarbon groups prevents both crystallization of the latter and of the polar groups. In our case the non-compact type of the lipophilic area will be caused by the three alkyl chains in the 3,4,5-positions of the benzene ring in the molecule. Besides this, amphiphilic anion salts exhibit some other characteristics which differ from those of diol mesogens. Firstly, they frequently undergo decomposition without a previous transition to an isotropic liquid, secondly, their hydrophilic cores are linked together by ionic forces. Nevertheless, the similarities between both groups of mesogens are obvious.

The associates forming a hexagonal columnar mesophase are quite different in structure from those of phasmids [21], which fill the gap between rod-like and disc-like liquid crystals [22]. Besides some similarity with the formation of the discotic mesophase of di-isobutylsilane diol [24], in our case, the diol mesogen seems rather to be a missing link between the carbohydrate or polar mesogens and the anhydrous mesophase forming amphiphilic anion salts in general [23]. Furthermore, the new hydroxy group containing liquid-crystalline compound can be classified as non-ionic, three arm amphotrope [25]. Its lyophilic character will be described in part II and subsequent papers of this series.

5. Derivatives

In order to further demonstrate the role of hydrogen bonding in the formation of the mesophase and also to consider, how unsymmetrical substitution will change the thermal behaviour of tristar-discogens [26], we synthesized the compounds VI, VII and VIII. As may be seen from D.S.C. measurements, compound VI shows on the first heating the endotherm of a crystalline modification K_1 , as can be seen under the microscope at 40.7°C with $\Delta H = 107.45 \text{ kJ mol}^{-1}$ (cf. figure 5, curve a). Cooling shows a small exotherm at -42.6°C which appears with an enthalpy of $\Delta H = -21.5 \text{ kJ mol}^{-1}$. Further heating shows three endo- and one exotherm (cf. figure 5, curve c). The first small endotherm at -32°C exhibits a transition enthalpy of $\Delta H = -14.57 \text{ kJ mol}^{-1}$. Following recrystallization at -10.7°C leads to a second crystalline modification K_2 , appearing as thin needles under the polarizing microscope. After a solid transition the third modification, K_3 , melts at 20.8°C ($\Delta H = 57.33 \text{ kJ mol}^{-1}$). Cooling the isotropic melt always leads to the small exotherm at -42.7°C with an enthalpy value of $\Delta H = -21.5 \text{ kJ mol}^{-1}$ (cf. figure 5, curve b, d). The ΔH value of the exotherm on cooling ($-21.5 \text{ kJ mol}^{-1}$) seems to be too small for a recrystallization process. The first endotherm of the second and subsequent heatings can be attributed to the exotherm. The difference in their enthalpy values may be explained by the uncertainty of measurement in this temperature range (e.g. different slope of the baselines).



Scheme 2

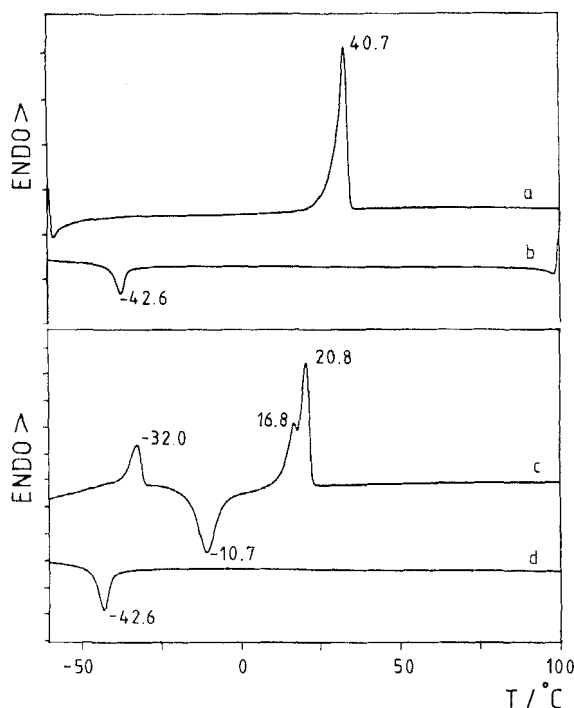


Figure 5. D.S.C. thermogram of VI. (a) first heating; (b) (d) cooling; (c) second heating; heating and cooling rate $10^{\circ}\text{C}/\text{min}$.

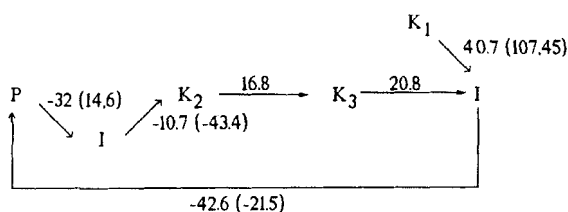


Figure 6. Transition scheme of VI. Temperatures in $^{\circ}\text{C}$; in brackets: enthalpies in kJ/mol .

Therefore, we establish the transition scheme (cf. figure 6); phase P can presumably be regarded as monotropic mesophase.

The next product, compound VII, exhibits only a melting point to the isotropic liquid at $T_m = 46^{\circ}\text{C}$ without further transitions down to -50°C . Compound VIII exists only as an oil, even down to -60°C . The drastic destabilization concerning the disappearance of the mesophase after esterification of the two hydroxyl groups of V shows the importance of the hydrogen bonding for the formation of liquid-crystallinity with respect to this compound. Furthermore, the necessity of complete covering of the peripheric area of discotics with alkyl side chains is clearly demonstrated. Slight reduction of the number of lateral chains from nine in tristar discotics [26] to seven in compound VIII, where four of the chains are in the 3,5 positions, completely destroys the mesophase.

6. Experimental

Chemicals: 1,3,5-trihydroxybenzene (Fluka), Ni-Al-alloy (Merck), Celite (Aldrich), phenylboronic acid (Janssen), 3,4,5-trihydroxybenzoic acid methyl ester (Fluka), undecanoic acid (Aldrich), 4-hydroxybenzoic acid methyl ester (Fluka), 3,5-dihydroxybenzoic acid methyl ester (Aldrich), 1-bromo decan (Aldrich), powdered sodium carbonate (Riedel de Häen), were purchased commercially

3,4,5-tris(decyloxy)benzoic acid chloride (III) [14] and 3-phenyl-2,4-dioxa-3-bora-bicyclo [3.3.1]-nonan-7-ol (II) [13] were synthesized according to the literature.

IV

In a 100 ml round bottom flask 4.3 g II were dissolved in 70 ml pyridine, which had been dried over molecular sieve. After the addition of 12 g III the reaction mixture was stirred for two hours at room temperature. After than, pyridine was evaporated. The white residue was refluxed in 50 ml toluene and then the mixture was filtered hot. After washing the remaining pyridinium hydrochloride with 10 ml hot toluene, the solvent was evaporated. The resulting product, a yellowish oil which solidifies in the refrigerator, was used without further purification. Yield: 14.6 g (94 per cent); m.p. 27–29°C. The product was characterized by means of ¹H N.M.R., I.R., M.S., G.P.C.

V

10.6 g IV were stirred with 10 ml H₂O₂ (30 per cent) and 50 ml THF for two hours at room temperature. After that, the mixture was poured into 50 ml ice water with 1 ml triethylamine added and the whole was stirred for a further 30 minutes. Then the product was extracted with ether, the organic phase was washed with aqueous NaHSO₃ to destroy H₂O₂, and a small amount of water. After drying the organic phase with anhydrous Na₂SO₄, the solvent was evaporated and the residue purified by two-fold recrystallization from toluene. The product was freeze dried in benzene and kept under a dry argon atmosphere.

Yield: 6.3 g (67 per cent), colourless, waxy. G.P.C.: Single peak $V_e = 29.8$ ml; M.S. m/e: 704. The I.R. spectrum confirms the structure. ¹H N.M.R. (CDCl₃): δ (ppm) = 0.89 (t; 9H), 1.27 (s; 36H), 1.49 (m; 6H), 1.60 (q; 2H), 1.83 (m; 6H), 2.32 (m; 4H), 2.61 (s; 2H), 3.84 (m; 2H), 4.03 (t; 6H), 4.98 (m; 1H), 7.30 (s; 2H). C₄₃H₇₆O₇ (704.61) Calculated: C 72.23 per cent H 10.87 per cent O 15.89 per cent; Found C 73.21 per cent H 10.85 per cent O 15.86 per cent.

Esterification reactions

Undecanoic acid chloride, obtained from undecanoic acid, 4-decyloxybenzoic acid chloride and 3,5-bis(decyloxy)benzoic acid chloride, both obtained according to the literature [14] from 4-hydroxybenzoic acid methylester and 3,5-dihydroxybenzoic acid methylester respectively, were reacted with V.

VI

The product was purified by M.P.L.C. (hexane/THF 5:1). Yield: 71 per cent, white powder. The I.R. spectrum confirms the structure. G.P.C.: Single peak $V_e = 27.6$ ml; M.S. m/e: 1040. ¹H N.M.R. (CDCl₃): δ (ppm) = 0.87 (m; 15H), 1.29

(m; 64H), 1.49 (m; 6H), 1.63 (m; 4H), 1.84 (m; 9H), 2.31 (t; 4H), 2.47 (m; 3H), 4.03 (m; 6H), 4.90 (m; 2H), 5.11 (m; 1H), 7.22 (s; 2H). $C_{65}H_{116}O_9$ (1040.93) Calculated: C 74.93 per cent H 11.23 per cent O 13.83 per cent; Found: C 74.92 per cent H 11.16 per cent O 13.79 per cent.

VII

Recrystallized from acetone and twice from toluene. Yield: 64 per cent, white powder, $T_m = 46^\circ\text{C}$. The I.R. spectrum confirms the structure. G.P.C.: Single peak $V_e = 27.5$ ml; M.S. m/e: 1225. ^1H N.M.R. (CDCl_3): $\delta(\text{ppm}) = 0.85$ (t; 15H), 1.28 (m; 60H), 1.42 (m; 10H), 1.78 (m; 13H), 2.61 (m; 3H), 3.97 (t; 10H), 5.16 (m; 3H), 6.85 (d; 4H), 7.20 (s; 2H), 7.93 (d; 4H). $C_{77}H_{124}O_{11}$ (1224.99) Calculated: C 75.43 per cent H 10.20 per cent O 14.37 per cent; Found: C 75.54 per cent H 10.32 per cent O 14.36 per cent.

VIII

The product was purified by M.P.L.C. (hexane/THF 9: 1). Yield: 53 per cent, oil. The I.R. spectrum confirms the structure. G.P.C.: Single peak $V_e = 26.9$ ml; M.S. m/e: 1537. ^1H N.M.R. (CDCl_3): $\delta(\text{ppm}) = 0.88$ (t; 21H), 1.27 (s; 84H), 1.47 (m; 17H), 1.80 (m; 14H), 2.66 (m; 3H), 3.83 (m; 1H), 3.97 (t; 14H), 5.16 (m; 2H), 6.63 (t; 2H), 7.15 (d; 4H), 7.25 (s; 2H). $C_{97}H_{164}O_{13}$ (1537.31) Calculated: C 75.72 per cent H 10.75 per cent O 13.53 per cent; Found: C 75.84 per cent H 10.78 per cent O 13.44 per cent.

Analytic methods

I.R.: Philips Pye-Unicam SP 3-300. ^1H N.M.R.: Bruker 300 MHz; ^{13}C N.M.R.: Jeol FX 90. M.S.: Varian 312. G.P.C.: Waters ALC 200, RI-detector. Melz LCD 201, two 0.5 m PL-gel columns (Polymer Laboratories, 5 μm particle diameter, 10 and 20 nm pore width), eluent THF, elution rate 0.5 ml/min. M.P.L.C.: Labomatic, gradient system Labomat VS-200, pump Labomat MD 80/100, U.V. detector, 1 \times 539 mm column (Labochrom, gel, 20-45 μ particle size, 60 \AA pore width). D.S.C.: Perkin Elmer, DSC 7; temperatures were taken from peak maxima. Polarizing microscopy: Leitz, Laborlux 12-Pol, Mettler hot stage FP 82, photoautomat Wild MPS 45/51 S. Both D.S.C. measurements and polarizing microscopy of the diol compounds were performed with the most complete exclusion of humidity possible. Therefore, the D.S.C. pans were weighed empty in a small glass vessel under argon, filled in a desiccator under argon, and weighed again in the glass vessel under argon. Then the D.S.C. pans were closed as quickly as possible.

With respect to polarizing light microscopy, the dry product was brought under dry atmosphere between the glass plates and introduced as quickly as possible in the hot stage above the clearing temperature. The product melted instantaneously and spread between the glass plates. Therefore, the inner part of the substance under glass was protected against humidity from air.

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References

- [1] DEMUS, D., DEMUS, H., and ZASCHKE, H., 1974, *Flüssige Kristalle in Tabellen* (VEB Deutscher Verlag für Grundstoffindustrie).
- [2] DEMUS, D., and ZASCHKE, H., 1984, *Flüssige Kristalle in Tabellen*, Vol. II (VEB Deutscher Verlag für Grundstoffindustrie).
- [3] GILBERT, R. D., and PATTON, P. A., 1983, *Prog. Polym. Sci.*, **9**, 115.
- [4] JEFFREY, G. A., 1984, *Molec. Crystals liq. Crystals*, **110**, 221.
- [5] GOODBY, J. W., 1984, *Molec. Crystals liq. Crystals*, **110**, 205.
- [6] JEFFREY, G. A., 1986, *Accts chem. Res.*, **19**, 168.
- [7] DIELE, S., GEISSLER, E., VORBRODT, H. M., and ZASCHKE, H., 1984, *Molec. Crystals liq. Crystals Lett.*, **102**, 181.
- [8] GRAY, G. W., 1974, *Liquid Crystals and Plastic Crystals*, Vol. 1, edited by G. W. Gray and P. A. Winsor (Ellis Horwood), p. 109 f.
- [9] LARSSON, K., 1964, *Ark. Kemi*, **23**, 23. LARSSON, K., 1967, *Z. phys. Chem. N.F.*, **56**, 173.
- [10] PFANNEMÜLLER, B., WELTE, W., CHIN, E. and GOODBY, J. W., 1986, *Liq. Crystals*, **1**, 357.
- [11] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals*, (Leonard Hill), p. 143.
- [12] STETTER, H., and STEINACKER, K. H., 1952, *Chem. Ber.*, **85**, 451.
- [13] STRONG, P. N., and KEANA, J. F. W., 1975, *J. org. Chem.*, **40**, 956.
- [14] MALTHÊTE, J., LEVELUT, A. M. and NGUYEN, HUU TINH, 1985, *J. Phys. Lett., Paris*, **46**, L 875.
- [15] NAGATA, W., OKADA, K., and AOKI, T., 1979, *Synthesis*, 365.
- [16] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals* (Leonard Hill), plate 83.
- [17] DEMUS, D., and RICHTER, L., 1987, *Textures of Liquid Crystals* (Verlag Chemie), p. 127.
- [18] COBURN, W. C., JR and GRUNWALD, E., 1958, *J. Am. chem. Soc.*, **80**, 1318.
- [19] LATTERMANN, G., STAUFER, G., WENDORFF, J. H., and EBERT, M. (in preparation).
- [20] WINSOR, P. A., 1974, *Liquid Crystals and Plastic Crystals*, Vol. 1, edited by G. W. Gray and P. A. Winsor (Ellis Horwood), p. 252.
- [21] GUILLON, D., SKOULIOS, A., and MALTHÊTE, J., 1987, *Europhys. Lett.*, **3**, 67.
- [22] LEVELUT, A. M., MALTHÊTE, J., DESTRADE, C., and NGUYEN HUU TINH, 1987, *Liq. Crystals*, **2**, 877.
- [23] WINSOR, P. A., 1974, *Liquid Crystals and Plastic Crystals*, Vol. 1, edited by G. W. Gray and P. A. Winsor (Ellis Horwood), p. 225 f.
- [24] BUNNING, J. D., LYDON, J. E., EABORN, C., JACKSON, P. M., GOODBY, J. W., and GRAY, G. W., 1982, *J. chem. Soc. Faraday Trans. I*, **78**, 713.
- [25] RINGSDORF, H., SCHLARB, B., and VENZMER, J., 1988, *Angew. Chem. Int. Ed. Engl.*, **27**, 113.
- [26] LATTERMANN, G., 1987, *Liq. Crystals*, **2**, 723.
- [27] DAHLHOFF, W. V., 1987, *Z. Naturf.*, **42b**, 661.
- [28] Note added after submitting this paper: Further liquid crystalline carbohydrate dithioacetals with two alkyl chains per molecule are described in: ECKERT, A., KOHNE, B., and PRAEFCKE, K., 1988, *Z. Naturf. (b)* **43b**, 878. VAN DOREN, H., KELLOG, R. M., and WYNBERG, H., *J. chem. Soc. Chem. Commun.* (to be published), as mentioned in Preprints of the 12th International Liquid Crystal Conference, Freiburg, 1988.