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 Praefcke, Klaus , Psaras, Panicos and Eckert, Andreas(1993) 'Bis-1,3-diol type liquid crystals from pentaerythritol [1]', Liquid Crystals, 13: 4, 551 — 559
To link to this Article: DOI: 10.1080/02678299308026327
URL: http://dx.doi.org/10.1080/02678299308026327

LIQUID CRYSTALS, 1993, VOL. 13, NO. 4, 551–559

Bis-1,3-diol type liquid crystals from pentaerythritol [1]

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(*Received 26 October 1992; accepted 4 January 1993*)

Several esters and ethers of pentaerythritol have been prepared. Four of them, containing each a 1,4-*trans*-disubstituted cyclo-hexane unit and three hydroxyl functions, emerge as examples of a novel type of thermotropic, intermolecularly hydrogen bridge-supported multiol mesogens exhibiting the smectic A phase. A new case of a heteroatom effect preventing mesophase formation by causing stable intramolecular hydrogen bonding situations will also be discussed.

1. Introduction

Our interest in hydroxyl group-containing liquid crystal materials derived from various kinds of synthetic or naturally occurring multiols [2] gave rise to the question as to whether appropriate derivatives of pentaerythritol (**1**), which we considered to be an interesting tris-1,3-diol which had not yet been investigated in this field, might exhibit thermotropic mesomorphic properties. Depending on the number of functions attached, mono-ols, 1,3-diols, or bis-1,3-diols, all primary in character, are synthetically possible. For the latter, two types of esters and ethers (**7**, **8**, and **13**) having at least two hydrogen groups left and with side-arms of optimal shape, it would be conceivable to expect the formation of thermotropic mesophases based on (intermolecularly) hydrogen-bonded networks, processes which we like to call multimerizations of pro-mesogenic molecules supported by hydrogen bridges. Indeed, it has recently been shown [3, 4] that 1,3-diols too, both cyclic [3], i.e. *cis, cis*-phloroglucitol benzoates, and acyclic [4], i.e. 2-substituted propane-1,3-diols, in structure, may exhibit thermotropic mesophases because of such multimerizations.

An overview of our synthetic work on new and in part thermomesogenic (**7 a** and **b**, and **8 a** and **b**) pentaerythritol esters and ethers is given in the scheme. The differences in liquid crystalline behaviour observed for the three families (**7**, **8** and **13**) of multiols are indeed strongly determined by the make-up and number of their side arms. A new example has also been found of a heteroatom effect causing the intramolecular formation of six-membered rings by hydrogen bridges [5] and, hence, in case of the 1,3-diol **13** totally disturbing the self organization of this amphiphile. Details of our study are now discussed.

2. Results and discussion

Starting from pentaerythritol (**1**) via the cyclic orthoester **2** [6] and its derivatives **5** or **6** (not isolated), five bis-1,3-diol type mono-esters (**7a** and **b**) and -esters (**8 a** and **b**), of which the two pairs **7 a** and **b** and **8 a** and **b** are novel thermotropic liquid crystal materials, have been prepared by classical routes, along with some of their derivatives

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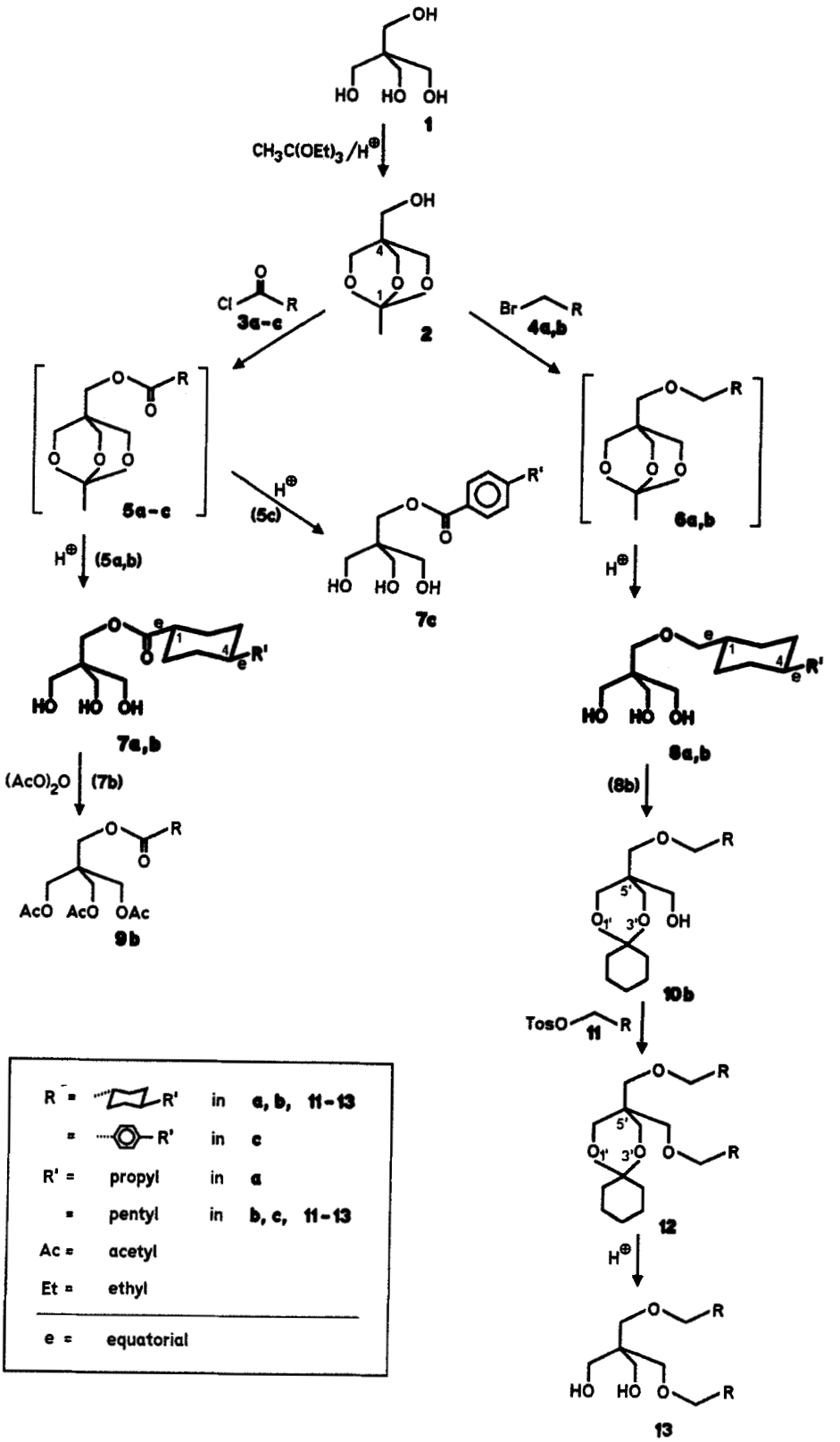


(**9 b, 10 b, 12** and **13**). Details of the synthetic work and the applied analytical methods, as well as the elementary and assigned spectroscopic data providing the various molecular structures of the twelve new colourless compounds are compiled in the Experimental section. The phase transition data for the six target compounds (**7 a–c, 8 a** and **b**, and **13**) of this study are however listed in the table. As expected, with respectively identical alkyl groups in the 4-position of their cyclohexane part the esters **7 a** and **b** form enantiotropic and much more stable liquid crystals—wide range smectic A phases—than the corresponding two ethers **8 a** and **b**; **8 a** forms only a monotropic phase.

Suprisingly, the aromatic ester analogues **7 a** show no thermomesomorphic behaviour at all. The same is true for derivatives of both series, for the tris-actate **9 b**, for the mono-ol **10 b, 12,** and—not obvious at first glance—also for the 1,3-diol **13** (see below).

The smectic A character of the four triol or bis-1,3-diol type liquid crystal materials could clearly be established by extensive texture and miscibility studies (contact method) using three compounds definitely exhibiting this mesophase: (1) octyl 1-*O*-*β*-D-glucopyranoside [7], (ii) octyl 1-*S*-*β*-D-thioglucopyranoside [8], or (iii) 3,4-di-*O*-hexyl-L-(-)-chiro-inositol [9]. The texture of **7** and and **8** are similar to that shown in a photomicrograph of the smectic A phase of another kind of multiol published recently [10]. The new compounds proved be miscible mutually and with the three comparison materials mentioned above. On the other hand, exhaustive tests of D-arabinose -*S*, *S*-dioctylacetal [11, 12] which exhibits the hexagonal columnar phase, in contact preparations with the ester **7 a** or with the ether **8 b**, unambiguously showed no miscibility within these two pairs of compounds.

The totally different properties of the triols **7** and **8** on the one hand and of the diol **13** on the other lead us to make some comments on the importance of certain structural elements or hetero-atom effects [5] present in these two kinds of derivatives of pentaerythritol (see the figure). Both drawings show the intramolecular possibilities for hydrogen bond formation, each directed away from the 'spiro'-type molecular centre at position 2. In the case of **13** the two ether oxygen atoms in the hydrophobic main chain tie up both hydroxyl functions and relatively stable 6-membered rings are formed, blocking completely any chance of molecular multimerization which most probably is

Phase transition temperatures (°C)† and enthalpies (kJ mol^{-1})‡ for the six pentaerythritol esters (**7a–c**) and ethers (**8a, b**, and **13**).

Ester/ether	C		S_A		I
7a§	●	— 82·4/ — 82·3 (27·2)	●	118·1/117·9 (1·4)	●
b§‖	●	88·7; 100·8/88·0 (14·1); 100·7 (6·6)	●	160·7/159·8 (10·8)	●
c	●	— 59·2/ — 61·1 (30·4)	—		●
8a	●	— 75·8/ — 76·5 (43·8)	{●	53·8/51·7 (1·9)	●}¶
b	●	— 75·6/ — 75·9 (41·1)	●	82·4/81·2 (2·2)	●
13‖	●	62·8; 64·2/61·8 (15·4); 64·6 (17·3)	—		●

† Temperatures obtained by polarizing microscopy and differential scanning calorimetry (heating rates: 5 K min^{-1}): PM/DSC.

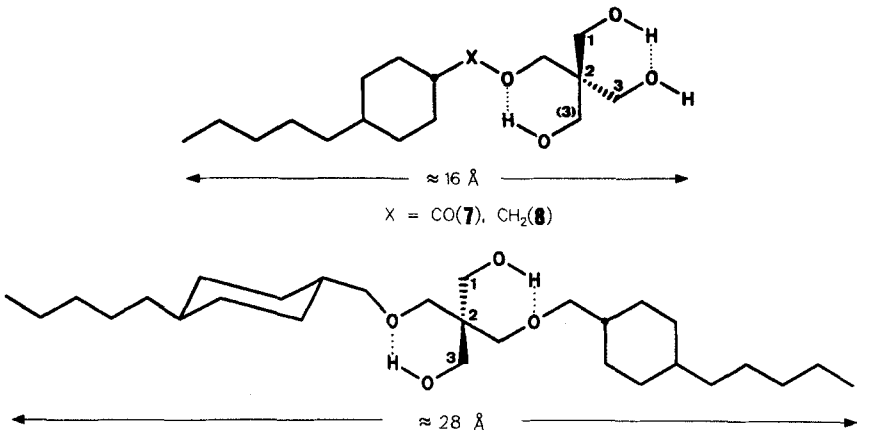
‡ Given in brackets.

§ Decomposes above the clearing point.

‖ Two crystal modifications are observed both by PM and DSC.

¶ Values obtained on cooling from the isotropic phase.

{ } A monotropic transition.



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The structure of the triols (or bis-diols) **7** and **8** as well as of the diol **13** in their extended conformations of about 16 Å (top) or 28 Å length from Dreiding models. Here, the numbering in both formulae emphasizes the 1,3-arrangements of the hydroxy functions. The constitutional situations giving rise to the intramolecular formation of additional, hydrogen bridge-supported 6-membered rings are also depicted.

essential [13, 14] for the generation of a mesophase by multiol types of material. The increase in rigidity in the middle section of compound **13** by this strong hydrogen bonding network, however, also disfavours the formation of a mesophase due most likely to the twist of 90° caused at the 'spiro' -type centre of the molecule which is about 28 Å in length.

In the triols **7** and **8**, only one hydroxyl function is intramolecularly involved in the manner described above; the remaining two are available for other, mainly smectic A phase promoting intermolecular interactions.

Regarding both structures of **7** and **8** or **13**, respectively, shown in the figure, we feel it is also worth mentioning that each cyclohexane unit can be in plane with the hydrogen bridge supported 6-membered ring next to it, as Dreiding models reveal.

3. Experimental

Polarizing microscopy (PM): Leitz Laborlux 12 Pol, Mettler hot stage FP 80 heating/cooling rate 1 K min^{-1}. Differential Scanning Calorimetry (DSC): Mettler TA 3000/DSC 30 S with GraphWare TA 72. IR: Beckmann IR 9. ^{1}H NMR: Bruker WM 400. ^{13}C NMR: Bruker WH 270. MS: Varian MAT 711. Combustion analyses: Hewlett–Packard 185. All chemicals and starting materials used in this study are commercially available.

4-(Hydroxymethyl)-1-methyl-2,6,7-trioxabicyclo-[2,2,2]octane (**2**) [6], the widely known acid chlorides **3a–c**, as well as the two *trans*-4-substituted cyclohexylmethyl bromides **4a** and **b** were synthesized in good yields (for example **2**: 86 per cent) by well-established procedures.

3.1. *trans (4-Pentyl-1-tosyloxymethyl) cyclohexane* (**11**)

A solution of 39·7 g (0·2 mol) of *trans*-4-pentylcyclohexane-1-carboxylic acid in 200 ml of dry diethyl ether was added dropwise to a suspension of 15·18 g (0·4 mol) of

lithium aluminium hydride in 300 ml of this ether. While stirring, this mixture was heated under reflux for 2 h and then kept at room temperature overnight. A normal work-up procedure, including concentration by rotary evaporation at 400 to 800 mbar at 40°C (bath temperature), produced a yellowish liquid. This was dissolved in 64 ml of pyridine, and thereafter reacted with 41·95 g (0·22 ml) of tosyl chloride, added in batches with ice cooling, and subsequent stirring for 2 h at room temperature and then 3 h at 50°C, and finally overnight again at room temperature. Eventually the reaction mixture was poured into ice water, acidified with 200 ml of concentrated aqueous hydrogen chloride, and shaken several times with chloroform. After washing the organic extracts with saturated aqueous solutions of sodium hydrogen carbonate and sodium chloride drying them over magnesium sulphate, and concentrating them by rotary evaporation (about 500 mbar) at 40°C bath temperature, a yellowish oil resulted which crystallized. Recrystallization from ethanol yielded 48·05 g (71 per cent) of colourless crystals, mp 57°C (electrothermal). ^{1}H NMR ($CDCl_3$): selected aliphatic resonances, δ 3·80 (d, $J \approx 6{\cdot}5$ Hz; CH_2–OSO_2), 2·45 and 0·86 p.p.m. (s and t, $J \approx 7$ Hz; $2\,CH_3$); others appear in several broad multiplets between about 2·0 or 1·8 and 0·8 p.p.m. as they do also for **7** or **8–13**, respectively. ^{13}C NMR ($CDCl_3$): selected aliphatic resonances, δ 75·37 (t; CH_2–OCO_2), 37·31 and 37·26 (2 d; 2 tertiary cyclohexane ring C_s, ratio 1 : 1), 21·52 and 13·99 p.p.m. (2 q; $2\,CH_3$). MS (150°C) *m/e* (per cent): 338 (<0·1) (M^+, 166 (30) $[M-C_7H_8O_3S]^+$, 100 (40), 95 (100). $C_{19}H_{30}O_3S$ (338·5). Calculated: C, 67·42 per cent H, 8·93 per cent. Found: C, 67·08 per cent H, 8·80 per cent.

3.2. *Ester- and etherification reactions: general description for reactions 3.3 to 3.8*

The trioxabicyclononane **2** [6], in amounts between 1·6 g (10 mmol) and 8·0 g (50 mmol), was interacted with stirring during 2 h at room temperature with sodium hydride (80 per cent, an excess of 10 per cent) suspended in *N*, *N*-dimethylformamide (30 to 150 ml, depending on the size of the trial). After the corresponding carboxylic acid chlorides **3a–d** or the substituted methyl bromides **4a** or **b**, respectively (each in an excess of 10 per cent) had been added neat and dropwise, the reaction mixtures were stirred for 5 h at 50°C and then overnight at room temperature before they were poured into ice water and extracted three times with methyl *t*-butyl ether. A normal work-up consisting of washing, drying and concentration (see above) yielded the intermediate (not characterized) crude products **5a–d**, **6a** or **b**, respectively, each of which was dissolved in distilled methanol (between 5 and 32 ml), and stirred for 1 h at room temperature after adding 0·01 M aqueous hydrogen chloride (between 19 and 128 ml). Another work-up procedure was started with the addition of sodium hydrogen carbonate powder (between 0·7 and 4·65 g corresponding to the scale of the trials). The mixtures were stirred for 1 h at room temperature, and then concentrated by rotary evaporation (about 100 mbar) using 40°C as the bath temperature. Thereafter, some methanol was added and the trial runs were concentrated again by evaporation. Each of the residues was now taken up in chloroform and this solvent removed (around 500 mbar and the same bath temperature) as described before. The remaining colourless materials were crystallized from heptane, furnishing the products in yields between 6 and 35 per cent.

3.3. *Pentaerythritol mono-[trans-4-propylcyclohexane]-1-carboxylate* (**7a**)

Yield: 288 mg (10 per cent) starting from 1·6 g (10 mmol) of **2**; colourless crystals with phase transition temperatures as summarized in the table. IR ($CHCl_3$): ν 3680, 3620 and

3460 (broad) hydroxyl, 1720 carbonyl. ^{1}H NMR ($CDCl_3$): selected resonances, δ 4·15 (s; CH_2–OCO), 3·60 (s, broad; 3 CH_2-hydroxyl), 2·28 (tt, $J \approx 12{\cdot}5$ and 3·5 Hz; cyclohexyl-CH–CO_2), 0·88 p.p.m. (t, $J \approx 7$ Hz; CH_3). ^{13}C NMR ($CDCl_3$): selected resonances, δ 177·40 (s; CO), 62·48 (t; 3 CH_2-hydroxyl and CH_2-OCO), 45·47 (s; quaternary C), 43·60 and 36·88 (2 d; 2 tertiary ring C_s, ratio 1 : 1), 14·06 p.p.m. (q; CH_3). MS (170°C) *m/e* per cent) 288 ($\ll$1) M^+, 199 (100). $C_{15}H_{28}O_5$ (288·4). Calculated: C, 62·47 per cent H, 9·79 per cent. Found: C, 61·91 per cent H, 9·57 per cent.

3.4. *Pentaerythritol mono-[trans-4-pentylcyclohexane]-1-carboxylate* (**7b**)

Yield: 2·95 g (19 per cent) starting from 8·0 g (50 mmol) of **2**; colourless crystals with phase transition temperatures as summarized in the table. IR ($CHCl_3$): ν 3680, 3610 and 3440 (broad) hydroxyl, 1740 cm^{-1} carbonyl. ^{1}H NMR ($CDCl_3$): selected resonances, δ 4·22 (s, CH_2–OCO), 3·63 (s, broad; 3 CH_2-hydroxyl, decoupled: d, $J \approx 5$ Hz), 2·49 (decoupled: t, broad, $J \approx 5$ Hz; OH), 2·29 (tt, $J \approx 12$ and 3·5 Hz; cyclohexyl -CH–CO_2), 0·88 p.p.m. (t, $J \approx 7$ Hz; CH_3). ^{13}C NMR ($CDCl_3$): selected resonances, δ 177·47 (s; CO), 63·31 (t; 3 CH_2-hydroxyl), 62·40 (t; CH_2–OCO), 45·43 (s; quaternary C), 43·60 and 36·82 (2 d; 2 tertiary ring C_s, ratio 1 : 1), 14·06 p.p.m. (q; CH_3). MS (200°C) *m/e* (per cent): 316 ($\ll$1) M^+, 199 (100). $C_{17}H_{32}O_5$ (316·4). Calculated: C, 64·53 per cent H, 10·19 per cent. Found: C, 64·00 per cent H, 10·18 per cent.

3.5. *Pentaerythritol mono-(4-pentylbenzoate)* (**7c**)

Yield: 2·19 g (35 per cent), starting from 3·2 g (20 mmol) of **2**; colourless crystals; purity 99·38 per cent (DSC). The melting data are in the table. IR ($CHCl_3$): ν 3690, 3620 and 3490 (broad) hydroxyl, 1720 cm^{-1} carbonyl. ^{1}H NMR ($CDCl_3$): selected resonances, δ 4·23 (s; CH_2–OCO), 3·67 (d, $J \approx 6{\cdot}5$ Hz; 3 CH_2-hydroxyl) 2·84 (t, $J \approx 6{\cdot}5$ Hz; 3 OH), 0·89 p.p.m. (t, $J \approx 7$ Hz; CH_3). ^{13}C NMR ($CDCl_3$; selected resonances, δ 171·66 (s; CO), 62·71 and 62·47 (2 t; CH_2–OCO and CH_2-hydroxyl, ratio 1 : 3), 45·03 (s; quaternary C), 13·93 p.p.m. (q; CH_3). MS (130°C) *m/e* (per cent): no M^+, 175 (100), 4-pentylbenzoyl by α-cleavage. $C_{17}H_{26}O_5$ (310·4). Calculated: C, 65·78 per cent H, 8·44 per cent. Found: C, 65·63 per cent H, 8·38 per cent.

3.6. *Pentaerythritol mono-nonanoate*

Unfortunately, various attempts under different conditions to prepare this compound analogously to **7a–c** were unsuccessful as its precursor, the corresponding trioxabicyclononylmethyl ester, also could not be isolated and characterized.

3.7. *Pentaerythritol mono-[trans-4-propylcyclohexylmethyl] ether* (**8a**)

Yield: 330 mg (6 per cent), starting from 3·2 g (20 mmol) of **2**; colourless crystals; phase transition temperatures are summarized in the table. IR ($CHCl_3$): ν 3670, 3620 and 3480 cm^{-1} (broad) hydroxyl. ^{1}H NMR ($CDCl_3$): selected resonances, δ 3·71 (d, $J \approx 4$ Hz; 3 CH_2-hydroxyl), 3·45 (s; q-C-CH_2-O), 3·23 (d, $J \approx 6{\cdot}5$ Hz; O-CH_2-cyclohexyl), 2·74 (m, broad; OH), 0·87 p.p.m. (t, $J \approx 7$ Hz; CH_3). ^{13}C NMR ($CDCl_3$): selected resonances, δ 77·92 and 73·79 (2 t; CH_2–O–CH_2, not assigned, ratio 1 : 1), 64·33 (t; 3 CH_2–OH), 44·91 (s; quaternary C), 38·02 and 37·41 (2 d; 2 tertiary rings C_s, ratio

1 : 1), 14·35 p.p.m. (q: CH_3). MS (90°C) *m/e* (per cent): 275 (5) $[M+1]^+$, 139 (80) [M − 4-propylcyclohexylmethyl]$^+$, 83 (100). $C_{15}H_{30}O_4$ (274·4). Calculated: C, 65·66 per cent H, 11·02 per cent. Found: C, 65·20 per cent H, 10·87 per cent.

3.8. *Pentaerythritol mono-[trans-4-pentylcyclohexylmethyl] ether* (**8b**)

Yield: 605 mg (10 per cent), starting from 3·2 g (20 mmol) of **2**, colourless crystals; phase transition temperatures are summarized in the table. IR ($CHCl_3$): ν 3670, 3620 and 3470 cm^{-1} (broad) hydroxyl. ^1H NMR, ($CDCl_3$): selected resonances, δ 3·71 (d, $J \approx 5{\cdot}5$ Hz; 3 CH_2-hydroxyl), 3·45 (s; q-C–CH_2–O), 3·23 (d, $J \approx 6{\cdot}5$ Hz; O–CH_2-cyclohexyl), 2·65 (t, broad, $J \approx 5{\cdot}5$ Hz; OH), 0·88 p.p.m. (t, $J \approx 7$ Hz; CH_3). ^{13}C NMR ($CDCl_3$): selected resonances, δ 77·94 and 73·84 (2 t; CH_2–O–CH_2, not assigned, ratio 1 : 1), 64·55 (t; 3 CH_2–OH), 44·89 (s; quaternary C), 38·05 and 37·72 (2 d; 2 tertiary ring C_s, ratio 1 : 1), 14·06 p.p.m. (q; CH_3). MS (120°C) *m/e* (per cent): 303 (10) $[M+1]^+$, 167 (80) [M − 4-pentylcyclohexylmethyl]$^+$, 97 (100). $C_{17}H_3O_4$ (302·5). Calculated: C 67·51 H, 11·33 per cent. Found: C, 67·48 per cent H, 11·64 per cent.

3.9. *Mono-O-[trans-4-pentylcyclohexylcarbonyl-pentaerythritol] triacetate* (**9b**)

A solution of 237 mg (0·75 mmol) of **7b** and 0·5 ml (510 mg = 5 mmol) of ethanoic anhydride in 5 ml of pyridine was heated for 1 h at 100°C. After pouring this mixture into ice water and the usual work-up as described in the case of **11**, 290 mg of a yellowish, semi-crystalline oil were obtained. Recrystallization from heptane yielded colourless crystals, mp 68°C (electrothermal). Yield: 217 mg (66 per cent). IR ($CHCl_3$): ν 1750 cm^{-1} carbonyl. ^1H NMR ($CDCl_3$): selected resonances, δ 4·11 and 4·10 (2 s; 2 CH_2O, ratio 3 : 1), 2·06 (s; acetyl), 0·87 p.p.m. (t; CH_3). ^{13}C NMR ($CDCl_3$): selected resonances, δ 175·51 and 170·44 (2 s; 2 × CO, ratio 1 : 3), 62·27 and 61·82 (2 t; CH_2–OAc and CH_2–OCO, ratio 3 : 1), 43·43 and 36·80 (2 d; 2 tertiary ring C_s, ratio 1 : 1), 41·72 (s; quaternary C), 20·66 and 14·02 p.p.m. (2 q; acetyl and methyl, ratio 3 : 1). $C_{23}H_{38}O_8$ (442·6). Calculated: C, 62·42 per cent H, 8·65 per cent. Found: C, 62·31 per cent H, 9·09 per cent.

3.10. *5'-Hydroxymethol-5'-trans-[4-pentylcyclohexylmethyleneoxy]-methyl-2',2'-cyclopentamethylen-1',3-dioxan* (**10b**)

A solution of 6·05 g (20 mmol) of **8b**, 30 ml of cyclohexanone, and 1 g of 4-toluenesulphonic acid in 60 ml of toluene was placed in a Dean–Stark trap and heated under reflux for 5 h. Aqueous potassium hydroxide (500 ml, 10 per cent) was added; the mixture was worked up in the usual manner, concentrated in a rotary evaporator (about 70 mbar) at 40°C bath temperature, dried *in vacuo*, and the remaining crude orange-yellow product (11·2 g) was purified by flash chromatography (300 ml of silica gel 60, inner diameter of the column used: 60 mm, eluent: light petroleum/ethyl acetate 7 : 1). Yield 7·2 g (94 per cent) of **10b** as a yellowish oil. IR ($CHCl_3$): ν 3490 cm^{-1} (the maximum between 3345 and 3570) hydroxyl. ^1H NMR ($CDCl_3$): selected resonances, δ 3·71 (s; 2 CH_2, dioxan ring), 3·66 (d, broad, $J \approx 5{\cdot}5$ Hz; CH_2-hydroxyl), 3·53 (s; q-C–CH_2–O), 3·14 (d, $J \approx 6{\cdot}5$ Hz; O–CH_2-cyclohexyl), 2·74 (t, broad, $J \approx 5{\cdot}5$ Hz; OH), 0·87 p.p.m. (t, $J \approx 7$ Hz; CH_3): ^{13}C NMR ($CDCl_3$): selected resonances, δ 98·44 (s; spiro-C), 77·82 and 73·94 (2 t; CH_2–O–CH_2, not assigned, ratio 1 : 1), 65·82 (t; CH_2–OH), 62·08 (t; 2 CH_2, dioxan ring), 38·80 (s; quaternary C), 38·06 and 37·71 (2 d; 2 tertiary ring C_s, ratio 1 : 1), 14·06 p.p.m. (t; CH_3). MS (70°C) *m/e* (per cent): 383 (10) $[M+1]^+$, 216 (3) [M − 4-pentylcyclohexylmethyl]$^+$, 67 (100). $C_{23}H_{42}O_4$ (382·6). Calculated: C, 72·71 per cent H, 11·07 per cent. Found: C, 71·90 per cent H, 11·00 per cent.

3.11. *5',5'-Bis-{[trans-4-pentylcyclohexylmethyleneoxy]methyl}-2',2'-cyclopentamethylen-1',3'-dioxan* (**12**)

A solution of 765 mg (2 mmol) of **10b** in 5 ml of dimethylformamide (DMF), was added dropwise to a mixture of 90 mg of sodium hydride (80 per cent, oil dispersion) in 5 ml of DMF and stirred for 2 h at room temperature. After further addition of 5 ml of DMF containing 740 mg (2·2 mmol) of **11**, this trial run was stirred for 5 days at 70–80°C. A similar work-up procedure to that described above produced a yellowish crude oil (1·14 g) which was purified by flash chromatography using 80 ml of silica gel 60 in a column with an inner diameter of 28 mm and elution with light petroleum/ethyl acetate 10:1. Yield: 530 mg (49 per cent) of **12** as a yellowish oil. ^{1}H NMR ($CDCl_3$): selected resonances, δ 3·73 (s; $2\,CH_2$, dioxan ring), 3·36 (s; q-C–CH_2–O), 3·08 (d, $J \approx 6{\cdot}5$ Hz; O–CH_2-cyclohexyl), 0·90 p.p.m. (t; CH_3). ^{13}C NMR ($CDCl_3$): selected resonances, δ 97·94 (s; spiro-C), 77·40 and 70·51 (2 t; $2\,CH_2$–O–CH_2, not assigned), 62·05 (t; $2\,CH_2$, dioxan ring)—the intensity of these $3\,CH_2$ signals is 1:1:1—39·18 (s; quaternary C), 38·16 and 37·83 (2 d; 2 tertiary ring C_s, ratio 1:1), 14·09 p.p.m. (t, $J \approx 7$ Hz; CH_3). MS (90°C) *m/e* (per cent): 549 (6) M^+, 95 (88), 55 (100). $C_{35}H_{64}O_4$ (548·9. Calculated: C, 76·59 per cent H, 11·75 per cent. Found: C, 76·67 per cent H, 11·88 per cent.

3.12. *Pentaerythritol bis-[trans-4-pentylcyclohexylmethyl] ether* (**13**)

The 1,3-diol **13** was obtained by stirring 274 mg (0·5 mmol) of **12** in a mixture of 7 ml of ethanoic acid and 2 ml of concentrated hydrogen chloride for 24 h at 90°C then concentration by rotary evaporation (about 40 mbar, 40°C bath temperature), and drying the product *in vacuo*. This yielded 220 mg of a yellowish crude product. Purification by flash chromatography (cf. **12**) elution with light petroleum/ethyl acetate 4:1) yielded 60 mg of a semi-crystalline oil; after recrystallization from acetonitrile 14 mg (6 per cent) remained as colourless crystals. The melting data are in the table. IR ($CHCl_3$): ν 3680, 3610, and 3490 cm^{-1} (broad) hydroxyl. ^{1}H NMR ($CDCl_3$): selected resonances, δ 3·64 (d, $J \approx 6{\cdot}5$ Hz; CH_2-hydroxly), 3·50 (s; q-C–CH_2–O), 3·23 (d, $J \approx 6{\cdot}5$ Hz; O–CH_2-cyclohexyl), 2·84 (t, $J \approx 6{\cdot}5$ Hz; OH), 0·88 p.p.m. (t, $J \approx 7$ Hz; CH_3). ^{13}C NMR ($CDCl_3$): selected resonances, δ 77·83 and 73·43 (2 t; $2\,CH_2$–O–CH_2, not assigned), 65·48 (t; $2\,CH_2$–OH)—the intensity of these $3\,CH_2$ signals is 1:1:1—44·57 (s; quaternary C), 38·07 and 37·70 (2 d; 2 tertiary ring C_s, ratio 1:1), 14·05 p.p.m. (q; CH_3). MS (150°C) *m/e* (per cent): 468 (< 1) M^+, 266 (50), 167 (100), 97 (100). $C_{29}H_{56}O_4$ (468·8). Calculated: C, 74·31 per cent H, 12·04 per cent. Found: C, 74·22 per cent H, 12·13 per cent.

4. Concluding remarks

The compounds presented and discussed in this report enrich the spectrum of amphiphilic multiols (several hydroxy function-containing materials) in the liquid crystal field. They support earlier statements [13, 14] that apparently at least two hydroxyl functions in simply structured molecules of this kind are necessary for the occurrence of thermotropic mesophases.

K.P. is grateful for the financial support of our liquid crystal work by the Deutsche Forschungsgemeinschaft, Bonn (project C3 of the Sonderforschungsbereich 335 'Anisotrope Fluide'), by E. Merck, Darmstadt, Germany, and by the Technische Universität. We thank Mrs Dipl.-Chem. A. Humke in our group for checking the mesophase characterizations by polarizing microscopy. We are also very grateful to

Professor H. Schumann and Mrs D. Bernhardt, Institute of Inorganic and Analytical Chemistry at our University, for their kind support in performing the combustion analyses.

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