Design of non-anisometric and non-amphiphilic liquid crystals: liquid-crystalline tetrahedra

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Tetrahedral pentaerythritol tetra(3,4-dialkoxybenzoates) and tetra(3,4,5-trialkoxybenzoates) can display columnar liquid-crystalline phases despite the fact that they are neither disc-like nor amphiphilic.

There are two well accepted structural guidelines in the design of liquid crystals. They may be formed either by anisometric molecules (calamitic or discotic) or by amphiphilic compounds. However, more recently columnar mesophases were also found for other molecular architectures which have a low aspect ratio such as octahedral metallomesogens,[1,2] diabolo liquid crystals[3] and even some open-chain and branched oligoethyleneamide derivatives.[4–6]

Here we report on the first examples of a novel type of non-anisometric liquid-crystalline compounds. These are spherical molecules **1–3** in which four, eight or twelve aliphatic chains are fixed *via* benzoate linking units to a tetrahedral central unit (Fig. 1).†‡

Despite the fact that these molecules are neither anisometric nor typical amphiphilic, some can display liquid-crystalline properties. For example the 3,4-didecyloxybenzoate **2d** (*n* = 10) forms a monotropic hexagonal columnar mesophase on cooling below 47 °C (transition enthalpy 5.4 kJ mol^{-1}). A typical spherulitic texture is observed by microscopic investigation between crossed polarisers (Fig. 2).

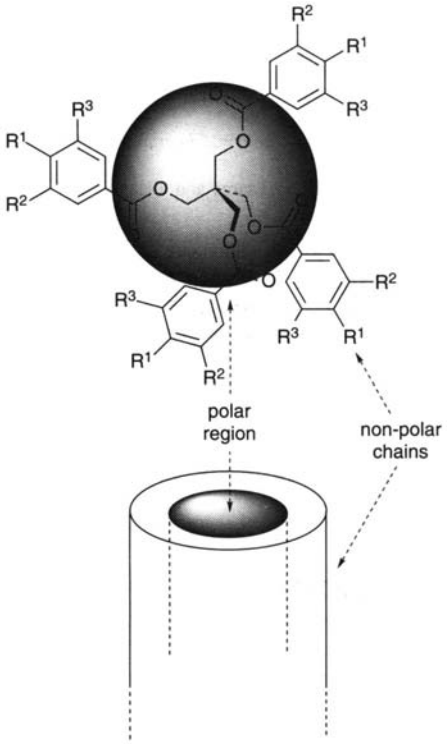

Fig. 1 Structures of the tetrahedral compounds in this work and model of their arrangement in the columnar mesophase (hatched areas indicate polar regions, the molecules are not disc-shaped)

Also X-ray scattering results are typical of a hexagonal columnar phase (three sharp reflections in the small-angle region with ratio of positions of $1:\sqrt{3}:2$; $a_{\text{hex}} = 33.05$ Å and a diffuse scattering in the wide-angle region). The liquid-crystalline state can be supercooled to −30 °C without crystallisation. Slow crystallisation occurs only after prolonged storage at room temperature (mp 54 °C, melting enthalpy 102.2 kJ mol^{-1}).

The appearance of liquid-crystalline phases strongly depends on the number of chains and on their length (Table 1).

3,4-Dialkoxybenzoates with eight aliphatic chains form the most stable phases and introduction of additional alkyl chains

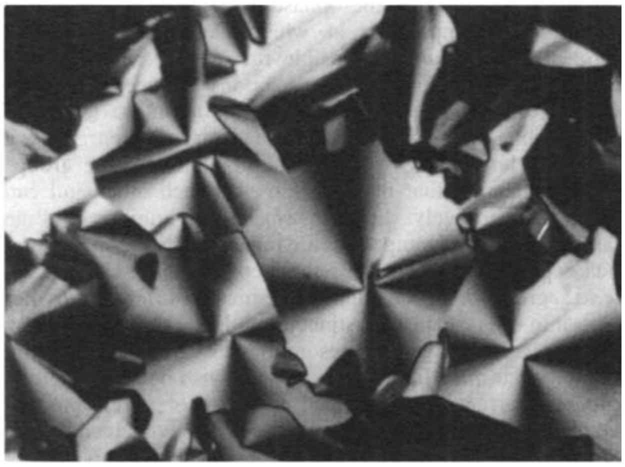

Fig. 2 Optical texture of compound **2d** (*n* = 10) as seen between crossed polarisers at 45 °C

Table 1 Phase transition temperatures (T/°C)[a] of compounds **1–3**

Compound	R^1	R^2	R^3	K		Col		I
1a	$OC_{10}H_{21}$	H	H	·	<20	—	—	·
1b	$OC_{16}H_{33}$	H	H	·	72	—	—	·
2a	OC_6H_{13}	OC_6H_{13}	H	·	45	—	—	·
2b	OC_8H_{17}	OC_8H_{17}	H	·	55	(·	31)	·
2c	OC_9H_{19}	OC_9H_{19}	H	·	55	(·	42)	·
2d	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H	·	54	(·	47)	·
2e	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	·	24	·	53	·
2f	$OC_{16}H_{33}$	$OC_{16}H_{33}$	H	·	58	—	—	·
3a	OC_6H_{13}	OC_6H_{13}	OC_6H_{13}	·	<20	—	—	·
3b	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$	·	41	(·	8)	·
3c	$OC_{16}H_{33}$	$OC_{16}H_{33}$	$OC_{16}H_{33}$	·	50	—	—	·

[a] Phase transition temperatures were determined by optical microscopy between crossed polarisers using a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot-2 polarising microscope; abbreviations: K = crystalline solid, Col = columnar mesophase, I = isotropic liquid.

decreases the mesophase stability. On cooling the 3,4,5-tridecyloxybenzoate **3b** (n = 10) to 8 °C a liquid-crystalline phase is formed with the same optical texture as that of the compounds **2b–e**. In contrast to the corresponding double- and triple-chain derivatives the single-chain 4-decyloxybenzoate **1a** (n = 10) is not mesomorphic. Liquid-crystalline properties are also absent if the chains are too long or short. The hexyl derivatives are oily liquids whereas the hexadecyl derivatives of **1–3** are crystalline solids. These results indicate that an appropriate ratio between the polar groups and the aliphatic chains has to be maintained.

The rather unexpected formation of liquid-crystalline phases in these non-anisometric and non-amphiphilic compounds cannot be explained simply on the basis of the taper-shaped structures of the four 3,4-dialkoxbenzoyl units alone. As is evident from CPK models, the tetrahedral linking unit inhibits flat disc-like organisation of these units; therefore, we assume an additional driving force for their self organisation. Because the polar carboxyl groups are fixed close to each other by the central linking unit it seems reasonable that the accumulation of the polar carboxyl groups gives rise to a distinct polar region. By assembling the individual molecules in columns the polar and non-polar regions can segregate into separate microdomains. This obviously promotes the arrangement of the individual molecules into columns with the polar groups assembled in the centre. The hydrophobic parts of the individual molecules have to be large enough to efficiently surround these polar regions and thus allow the separation of the polar and non-polar regions.

In this respect the liquid-crystalline phases of these compounds are related to the mesophases of ionic amphiphiles and multihydroxy compounds, in which Coulombic forces or hydrogen bonding are responsible for mesophase formation. However, the dipole–dipole interactions between the ester groups are much weaker than either Coulombic forces or hydrogen bonding. Therefore it is necessary to preorganise a sufficiently large number of these non-operative[7] ester groups in such a manner that they are close to each other and can interact cooperatively. In this respect the liquid-crystalline phases of these new compounds are related to the mesophases of block copolymers, where the same incompatibility effect gives rise to segregation of the slightly chemically different polymer blocks into well organised distinct microdomains.[8] Additionally these results reveal that the mesomorphism of non-amphiphilic low molecular mass liquid crystals could also be influenced by segregation effects. For example, it is often observed, but still unexplained, that columnar mesophases can be obtained if non-polar groups in the centre of disc-like molecules are replaced by more polar ones. For example, the all-*trans*-hexaalkylcyclohexanes,[9] hexakis(alkylthio)benzenes[10] and alkylated azamacrocycles[11,12] are non-mesomorphic compounds. In these molecules only weak polar groups are incorporated. If the polarity is increased (*e.g.* inositol ethers and esters,[13,14]§ hexakis(alkylsulfono)benzenes[15] and acylated,[16]¶ protonated[17] or complexed[11] azamacrocycles) the intramolecular polarity contrast is increased and columnar mesomorphic properties can be obtained. This means that in these cases also the insetting microdomain segregation aids in the formation of columnar supermolecular structures.

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Footnotes

† Obtained by esterification of pentaerythritol with an excess of the appropriately substituted carboxylic acids in the presence of a water-soluble carbodiimide. All analytical data are in accordance with the proposed structures, *e.g.* **2d**: $C_{113}H_{188}O_{16}$ requires (found) C, 75.33 (75.29) H, 10.44 (10.51%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, $SiMe_4$): δ 7.55 (d, J 8.3 Hz, 4 H, arom. H), 7.47 (s, 4 H, arom. H), 6.77 (d, J 8.3 Hz, 4 H, arom. H), 4.60 (s, 8 H, CO_2CH_2), 3.96–4.01 (m, 16, CH_2O), 1.76–1.83 (m, 16 H, CH_2), 1.42–1.47 (m, 16 H, CH_2), 1.25–1.34 (m, 96 H, CH_2), 0.84–0.87 (m, 24 H, CH_3). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1701 (C=O), absence of ν_{O-H}.

‡ Other liquid crystals obtained from pentaerythritol are oligomesogens in which four rigid calamitic cores are fixed *via* spacers to a pentaerythritol connecting unit. However their mesomorphic properties mainly arise from the parallel arrangement of the rigid calimitic mesogenic units.[18,19] Also some calamitic diol type liquid crystals have been obtained from pentaerythritol.[20]

§ Segregation of polar and non-polar regions was already mentioned as one possible explanation of the role of heteroatoms in the side chains of all-*trans*-hexasubstituted cyclohexane derivatives.[14]

¶ Up to now only the rigidity of the amide group in contrast to alkylamines has been taken into account to explain the different mesomorphic properties of acylated and alkylated azacrowns.[11,12]

References

1 A.-M. Giroud-Godquin and A. Rassat, *C. R. Acad. Sci. Paris*, 1982, **294**, 241.
2 H. Zheng and T. M. Swager, *J. Am. Chem. Soc.*, 1994, **111**, 761; T. M. Swager and H. Zheng, *Mol. Cryst. Liq. Cryst.*, 1995, **260**, 301.
3 J. Malthete and A. M. Levelut, *Adv. Mater.*, 1991, **3**, 94.
4 U. Stebani, G. Lattermann, M. Wittenberg, R. Festag and J. H. Wendorff, *Adv. Mater.*, 1994, **6**, 572; H. Fischer, S. Ghosh, P. A. Heiny, N. C. Maliszewskyj, T. Plesnivy, H. Ringsdorf and M. Seitz, *Angew. Chem.*, 1995, **107**, 879; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 795.
5 U. Stebani, G. Lattermann, R. Festag, M. Wittenberg and J. H. Wendorff, *J. Mater. Chem.*, 1995, **5**, 2247.
6 U. Stebani and G. Lattermann, *Adv. Mater.*, 1995, **7**, 578.
7 R. G. Laughlin, *Adv. Liq. Cryst.*, 1978, **3**, 42.
8 A. E. Skoulios, in *Developments in Block Copolymers*, ed. I. Goodman, Applied Science Publishers, London, 1982, vol. 1, p. 81; A. Skoulios, *Adv. Liq. Cryst.*, 1975, **1**, 169.
9 K. Praefcke, P. Psaras and B. Kohne, *Chem. Ber.*, 1991, **124**, 2523.
10 W. Poules and K. Praefcke, *Chem. Zeit.*, 1983, **107**, 310.
11 A. Liebmann, C. Mertesdorf, T. Plesnivy, H. Ringsdorf and J. H. Wendorff, *Angew. Chem.*, 1991, **103**, 1358; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1375.
12 G. Lattermann, S. Schmidt, R. Kleppinger and J. H. Wendorff, *Adv. Mater.*, 1992, **4**, 30.
13 B. Kohne and K. Praefcke, *Angew. Chem.*, 1984, **96**, 70; *Angew. Chem., Int. Ed. Engl.*, 1995, **23**, 82.
14 K. Praefcke, B. Kohne, P. Psaras and J.Hempel, *J. Carbohydr. Res.*, 1991, **10**, 523.
15 K. Praefcke, W. Poules, B. Scheuble, R.Poupko and Z. Luz, *Z. Naturforsch., Teil B*, 1984, **39**, 950.
16 J. M. Lehn, J. Malthete and A. M. Levelut, *J. Chem. Soc., Chem. Commun.*, 1985, 1794; C. Mertensdorf and H. Ringsdorf, *Liq. Cryst.*, 1989, **5**, 1757; G. Lattermann, *Liq. Cryst.*, 1989, **6**, 619.
17 G. Lattermann, S. Schmidt and B. Gallot, *J. Chem. Soc., Chem. Commun.*, 1992, 1091.
18 R. Eidenschink, F. H. Kreutzer and W. H. De Jeu, *Liq. Cryst.*, 1990, **8**, 879.
19 K. Zab, D. Joachimi, O. Agert, B. Neumann and C. Tschierske, *Liq. Cryst.*, 1995, **18**, 489; J. Andersch, S. Diele, D. Lose and C. Tschierske, *Liq. Cryst.*, 1996, **21**, 103.
20 K. Praefcke, P. Psaras and A. Eckert, *Liq. Cryst.*, 1993, **13**, 551.

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