Investigation of the crystal structure of two amphiphilic diols

D. Joachimi[a]; G. Latterman[b]; M. Schellhorn[b]; C. Tschierske[a]; P. Zugenmaier[c]

[a] Martin-Luther-University Halle, Institute of Organic Chemistry, Halle, Germany [b] University Bayreuth, Makromolekular Chemistry I, Bayreuth, Germany [c] Technical University Clausthal, Institute of Physical Chemistry, Clausthal-Zellerfeld, Germany

PLEASE SCROLL DOWN FOR ARTICLE

Investigation of the crystal structure of two amphiphilic diols

by D. JOACHIMI†, G. LATTERMANN§, M. SCHELLHORN§,
C. TSCHIERSKE*† and P ZUGENMAIER‡

† Martin-Luther-University Halle, Institute of Organic Chemistry, Weinbergweg 16,
D-06015 Halle, Germany
‡ Technical University Clausthal, Institute of Physical Chemistry,
Arnold-Sommerfeld-Str. 4, D-38678 Clausthal-Zellerfeld, Germany
§ University Bayreuth, Makromolekular Chemistry I, D-95440 Bayreuth, Germany

The crystal and molecular structures of (R)-4'-(2,3-dihydroxypropyloxy)-4-cyanobiphenyl, 1 and 4'-(cis-cis-3,5-dihydroxycyclohexyloxy)-4-cyanobiphenyl, 5 have been determined. The packing of compound 1 occurs in sheets, with a dense hydrogen bonding network within the layer of one sheet and to the next sheet, whereby the cyano groups are incorporated into the hydrogen bonding network. The hydrogen bonding scheme of compound 5 involves a water molecule; there is some disorder with regard to the hydrogen atoms bound to the water molecules.

1. Introduction

The investigation of the crystal structures of mesogenic compounds may provide information on the supermolecular arrangement of the molecules within the liquid crystalline phases. Especially if certain interactions play an important role in the liquid crystalline state as well as in the crystalline state, an investigation of the crystal structure may lead to a better understanding of the molecular order in the liquid crystalline phase [1]. For (R)-4'-(2,3-dihydroxypropyloxy)-4-cyanobiphenyl, 1 the existence of a cholesteric phase in addition to the crystalline state has recently been proved by thermal analysis [2]. On the one hand, this compound is a derivative of the well-known nematogenic 4'-propyloxy-4-cyanobiphenyl, 2 [3]. On the other hand, compound 1 may be regarded as an amphiphilic diol mesogen, a type of material which usually forms smectic mesophases [4]. In figure 1, it is shown that the stability of the nematic phase is raised considerably by the introduction of a 1,2-diol unit into the alkyl chain of the 4'-propyloxy-4-cyanobiphenyl, 2.

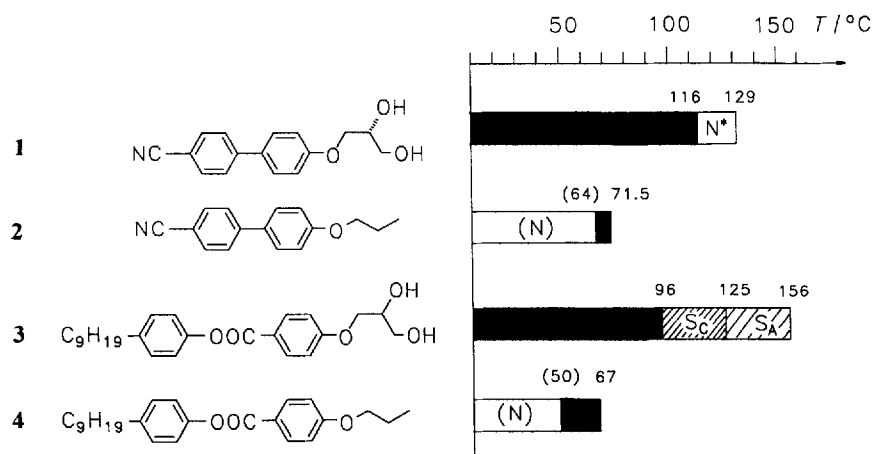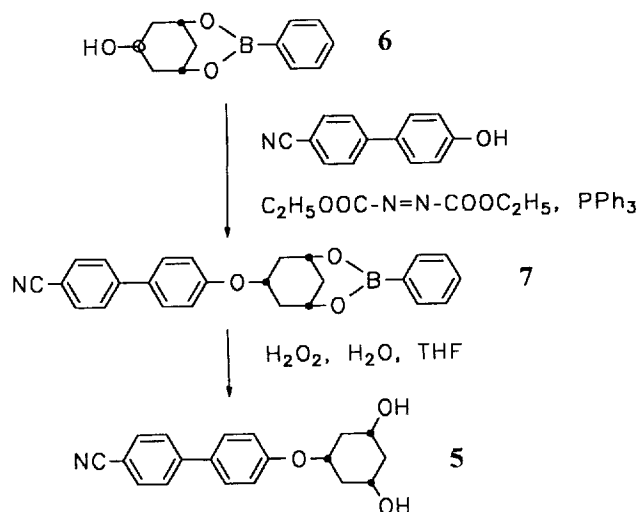Surprisingly, in this case the diol group does not induce

Figure 1. Comparison of the mesomorphic properties of amphiphilic diols **1** [2] and **3** [4] and non-amphiphilic mesogens **2** [3] and **4** [5].

* Author for correspondence.

Scheme. Synthesis of 4'-(*cis-cis*-3,5-dihydroxycyclohexy-loxy)-4-cyanobiphenyl **5**.

a smectic mesophase. This is in contradiction to our experience with diol mesogens containing calamitic structural units different from the cyanobiphenyl system (compare compounds **3** [4] and **4** [5] in figure 1). Also the cyanobiphenyl derivative **5**, which differs from **1** in the structure of the hydrophilic diol group, exhibits a monotropic nematic phase.
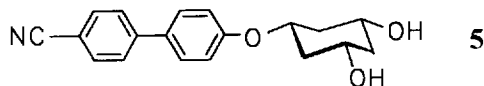
We assume, that the terminal CN-groups of both compounds must be incorporated in the hydrogen bonding networks [6] of their diol groups, causing the breakdown of the layer structure. To support this hypothesis we were interested in an investigation of the crystal structures of the two diols, **1** and **5**, with a common 4-cyanobiphenyl moiety.

2. Synthesis and properties

The homochiral compound **1** exhibits a cholesteric mesophase between 116°C and 129°C [2]. The synthesis was performed from 4'-hydroxy-4-cyanobiphenyl and (*S*)-1,2-O-isopropylideneglycerol by a Mitsunobu etherification, followed by acidolytic deprotection of the diol group [2]. Compound **5**, a novel material has a melting point of 181°C ($\Delta H = 38\cdot8\,\mathrm{kJ\,mol^{-1}}$) and is easily supercooled. On cooling to 112°C ($\Delta H = -1\cdot8\,\mathrm{kJ\,mol^{-1}}$), the appearance of a monotropic nematic phase is detected.

The synthesis of compound **5**, outlined in the scheme, was carried out according to the following procedure: 3-Phenyl-2,4-dioxa-3-bora-bicyclo[3.3.1]nonan-7-β-ol, **6**, synthesized according to the literature [7,8] (2·0 mmol, 0·43 g), 4-cyano-4'-hydroxy-biphenyl [9] (1·5 mmol, 0·29 g) and triphenylphosphine (1·5 mmol, 0·39 g) were

dissolved in anhydrous tetrahydrofuran (30 ml). The solution was cooled in an ice/water bath and diethyl azodicarboxylate (1·5 mmol, 0·26 g) was added with a syringe via a septum inlet over a 5 min period. The mixture was stirred at 0–5°C for 30 min; stirring was continued after the solution had reached ambient temperature and for a further 24 h. After most of the tetrahydrofuran had been distilled off using a rotary evaporator, an oily residue was obtained. This was dissolved in boiling aqueous methanol (10 per cent water) to remove the triphenylphosphine oxide. Upon cooling, the dioxaborinane, **7** crystallized out, affording 0·57 g (96·2 per cent) of product, which was pure according to TLC and was used in the following reaction step without further purification.

The hydrolysis of the dioxaborinane, **7**, was carried out according to the literature [10]: a mixture of compound **7** (1·0 mmol, 0·39 g), 30 per cent hydrogen peroxide solution (2 ml), and tetrahydrofuran (15 ml) was stirred at room temperature until the starting material was no longer detectable by TLC (4 h). The reaction mixture was then poured into ice/water (100 ml) and shaken with ethyl acetate several times. The combined extracts were washed with sodium hydrogen sulphite solution to destroy the excess of hydrogen peroxide and dried over sodium sulphate. Evaporation of the solvent gave a solid off-white residue which was recrystallized several times from heptane/propanol to yield compound **5** as a colourless crystalline material. The yield was 0·25 g (80·9 per cent). ^{1}H NMR (200 MHz, acetone-d_6): 7·89 (m, 4 H, H-arom.), 7·78 (m, 2 H, H-arom.), 7·19 (m, 2 H, H-arom), 4·51 (m, 1 H, H–C(13)), 4·07 (d, 2 H, OH), 3·88–3·68 (m, 2 H, C$\underline{H}$-OH), 2·59–2·45 (m, 2 H, H_{ax}–C(14), H_{ax}–C(18)), 2·41–2·28 (m, 1 H, H_{ax}–C(16)), 1·57–1·29 (m, 3 H, H_{eq}–C(14), H_{eq}–C(16), H_{eq}–C(18)).

3. Structure solution and refinement

Suitable crystals of sufficient size for the X-ray investigations of compound **1** were obtained by vapour diffusion of hexane into a chloroform solution. Crystals of compound **5** were grown by slow crystallization from a dilute heptane/propanol solution.

Preliminary examination and data collection were performed with MoK$_{\alpha_1}$ radiation for compound **1** and CuK$_{\alpha_1}$ for compound **5** using an Enraf-Nonius CAD 4 computer-controlled kappa axis diffractometer equipped with a graphite crystal incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least squares refinement using setting angles from up to 25 reflections; the number of reflections, scanning ranges and other crystallographic data are summarized in table 1. The determination and refinement of the structure was performed on a VAX computer with the MolEN package [11]. The structures were solved by direct methods. The hydrogen atoms of the hydroxyl

Table 1. Selected crystallographic data.

Compound	1	5
Formula weight/g mol^{-1}	269·30	327·38
Radiation	MoK$_{\alpha 1}$	CuK$_{\alpha 1}$
Unit cell	Monoclinic	Monoclinic
Space group	P2$_1$	P2$_1$/c
a/Å	5·331 (1)	10·685 (2)
b/Å	8·518 (1)	10·040 (1)
c/Å	15·295 (4)	16·365 (2)
α; β; γ/°	90; 99·69 (1); 90	90; 99·277 (7); 90
D_c/g cm^{-3}	1·31	1·255
μ/cm^{-1}	0·8	6·8
Number of reflections used for lattice paramater refinement	25 $6° < \Theta < 21°$	21 $22° < \Theta < 52°$
Number of measured reflections	1020	2912
Number of independent reflections	907	2748
Scanning range	$1° < \Theta < 22°$	$1° < \Theta < 60°$
$I_0 > 3\sigma$	593	2136
Refined parameters	180	283
$F(000)$	284	696
$R(R_W$ with $W = 1/\sigma^2)$	0·035 (0·038)	0·052 (0·065)

Table 2. Fractional coordinates and isotropic equivalent displacement parameters B_{eq} for compound 1 and their estimated standard deviations [†].

Atom	x	y	z	B_{eq}(Å^2)
O1	1·1638 (6)	0·241	0·2346 (2)	4·30 (8)
O2	1·5041 (6)	0·3548 (5)	0·3899 (2)	4·68 (9)
O3	1·502 (1)	0·0716 (6)	0·4821 (3)	9·4 (1)
N1	−0·0461 (9)	0·2282 (7)	−0·4245 (3)	6·3 (1)
C1	0·2632 (9)	0·2627 (7)	−0·2756 (3)	4·1 (1)
C1'	0·094 (1)	0·2444 (8)	−0·3589 (3)	4·9 (1)
C2	0·474 (1)	0·1645 (8)	−0·2566 (3)	4·6 (1)
C3	0·6251 (9)	0·1699 (7)	−0·1742 (3)	4·3 (1)
C4	0·5729 (8)	0·2731 (6)	−0·1087 (3)	3·5 (1)
C5	0·3641 (9)	0·3728 (7)	−0·1306 (3)	4·1 (1)
C6	0·2134 (9)	0·3677 (7)	−0·2124 (3)	4·5 (1)
C7	0·7289 (8)	0·2712 (6)	−0·0192 (3)	3·0 (1)
C8	0·9566 (9)	0·1878 (7)	0·0004 (3)	3·8 (1)
C9	1·0979 (9)	0·1817 (7)	0·0840 (3)	3·9 (1)
C10	1·0131 (8)	0·2571 (7)	0·1530 (3)	3·5 (1)
C11	0·7880 (9)	0·3398 (7)	0·1382 (3)	4·2 (1)
C12	0·6512 (8)	0·3461 (7)	0·0521 (3)	4·0 (1)
C13	1·0784 (9)	0·3076 (7)	0·3099 (3)	4·5 (1)
C14	1·2760 (9)	0·2706 (7)	0·3910 (3)	4·5 (1)
C15	1·332 (1)	0·1013 (8)	0·4006 (4)	7·8 (2)
H-O2	1·456	0·457	0·436	8·0‡
H-O3	1·593	0·170	0·512	8·0‡
H = O3	1·629	0·048	0·439	8·0‡

† Anisotropically refined B_{eq}s are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (3/4) \times [a^2 \times B(1,1) + b^2 \times B(2,2) + c^2 \times B(3,3) + ab(\cos \gamma) \times B(1,2) + ac(\cos \beta) \times B(1,3) + bc(\cos \alpha) \times B(2,3)]$.
‡ Atoms were not refined.

Table 3. Fractional coordinates and isotropic equivalent displacement parameters B_{eq} for compound 5 and their estimated standard derivations [†].

Atom	x	y	z	B_{eq}(Å^2)
O-1W	0·0471 (2)	1·2417 (2)	0·0718 (1)	7·18 (4)
O1	0·3459 (1)	0·9303 (1)	0·4044 (1)	5·41 (3)
O2	0·0598 (1)	1·2923 (1)	0·40911 (8)	5·44 (3)
O3	0·0202 (2)	1·0264 (1)	0·16640 (8)	6·06 (4)
N1	0·7727 (2)	−0·0565 (2)	0·3467 (1)	6·18 (5)
C1'	0·7232 (2)	0·0425 (2)	0·3535 (1)	5·07 (5)
C1	0·6636 (2)	0·1689 (2)	0·3626 (1)	4·55 (4)
C2	0·7265 (2)	0·2649 (2)	0·4136 (1)	5·26 (5)
C3	0·6707 (2)	0·3864 (2)	0·4216 (1)	5·07 (5)
C4	0·5504 (2)	0·4163 (2)	0·3790 (1)	4·19 (4)
C5	0·4893 (2)	0·3183 (2)	0·3271 (2)	5·41 (5)
C6	0·5438 (2)	0·1954 (2)	0·3186 (2)	5·54 (5)
C7	0·4926 (2)	0·5486 (2)	0·3872 (1)	4·18 (4)
C8	0·5671 (2)	0·6601 (2)	0·4119 (1)	5·19 (5)
C9	0·5156 (2)	0·7835 (2)	0·4174 (2)	5·21 (5)
C10	0·3850 (2)	0·8023 (2)	0·3972 (1)	4·39 (4)
C11	0·3082 (2)	0·6934 (2)	0·3735 (1)	4·29 (4)
C12	0·3617 (2)	0·5686 (2)	0·3691 (1)	4·16 (4)
C13	0·2164 (2)	0·9663 (2)	0·3748 (1)	3·95 (4)
C14	0·2004 (2)	1·1034 (2)	0·4110 (1)	4·31 (4)
C15	0·0692 (2)	1·1583 (2)	0·3817 (1)	4·04 (4)
C16	0·0354 (2)	1·1565 (2)	0·2889 (1)	4·69 (4)
C17	0·0526 (2)	1·0187 (2)	0·2540 (1)	4·08 (4)
C18	0·1863 (2)	0·9698 (2)	0·2813 (1)	4·30 (4)
H-W1	0·124 (2)	0·190 (2)	0·074 (1)	5·0‡
H-W2	0·035 (2)	0·157 (2)	0·109 (1)	8·1‡
H-W3	0·108 (2)	1·314 (2)	0·107 (2)	8·3‡
H-O2	0·060 (2)	1·292 (2)	0·459 (1)	7·1‡
H-O3	−0·006 (2)	0·947 (2)	0·146 (1)	6·8‡

† Anisotropically refined B_{eq}s are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (3/4) \times [a^2 \times B(1,1) + b^2 \times B(2,2) + c^2 \times B(3,3) + ab(\cos \gamma) \times B(1,2) + ac(\cos \beta) \times B(1,3) + bc(\cos \alpha) \times B(2,3)]$.
‡ Atoms were refined isotropically with fixed B.

groups were found by difference Fourier Transformation. The coordinates of the hydrogens of compound 5 were refined; those of compound 1 were added at appropriate bond lengths and angles.

4. Molecular and crystal structure

The fractional coordinates and isotropic equivalent displacement parameters B_{eq} for the two compounds are listed in tables 2 and 3. Figures 2 and 3 represent the molecular conformations. The twist of the least squares planes of the two phenyl rings is 13° for compound 1 and 23° for compound 5.

The packing of compounds 1 (see figure 4) and 5 (see figure 5) occurs in sheets with a dense hydrogen bonding network between adjacent sheets (see table 4). The hydrogen bonding scheme of compound 5 involves a water molecule which exhibits some disorder with partial occupancy of the hydrogens at three sites, all included in the hydrogen bonding scheme (see table 4). The shortest
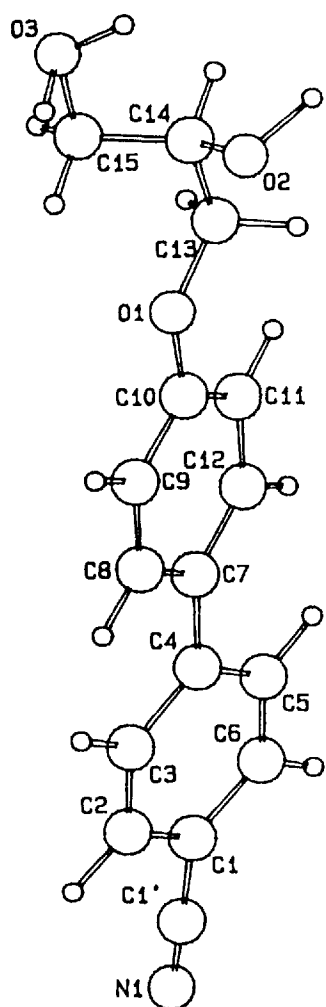
D. Joachimi *et al.*

Figure 2. Molecular structure and atom labelling of diol 1.

Figure 3. Molecular structure and atom labelling of diol 5.

intermolecular distances between hydroxyl hydrogen atoms are 1·90 Å (HW1–HO2), 2·32 Å (HO3–HO2) for compound 5 and 2·02 Å (HO3–HO2), 2·18 Å (H = O3–HO2) for compound 1. The packing of compound 5, represented in figure 5, shows a tilt of the molecular axis out of the *a*, *c*-plane, since the molecules are much longer than the a dimension.

5. Discussion

As expected, diol 1 crystallizes in an enantiomorphous space group, P2$_1$, and diol 5 in a centrosymmetric space group, P2$_1$/c. The CN-groups of both compounds are incorporated into the hydrogen bonding networks of the diol groups. The crystal structure of compound 1 reveals that this produces an antiparallel arrangement of the molecules within the layers, resulting in a 'pseudo-head-to-tail-arrangement' of the molecules in neighbouring layers. This means that in the crystalline state, a bilayer structure (head-to-head-arrangement) is not favourable.
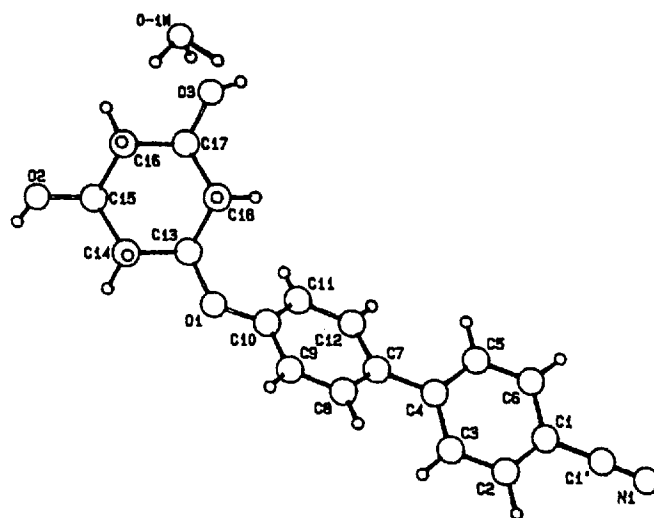

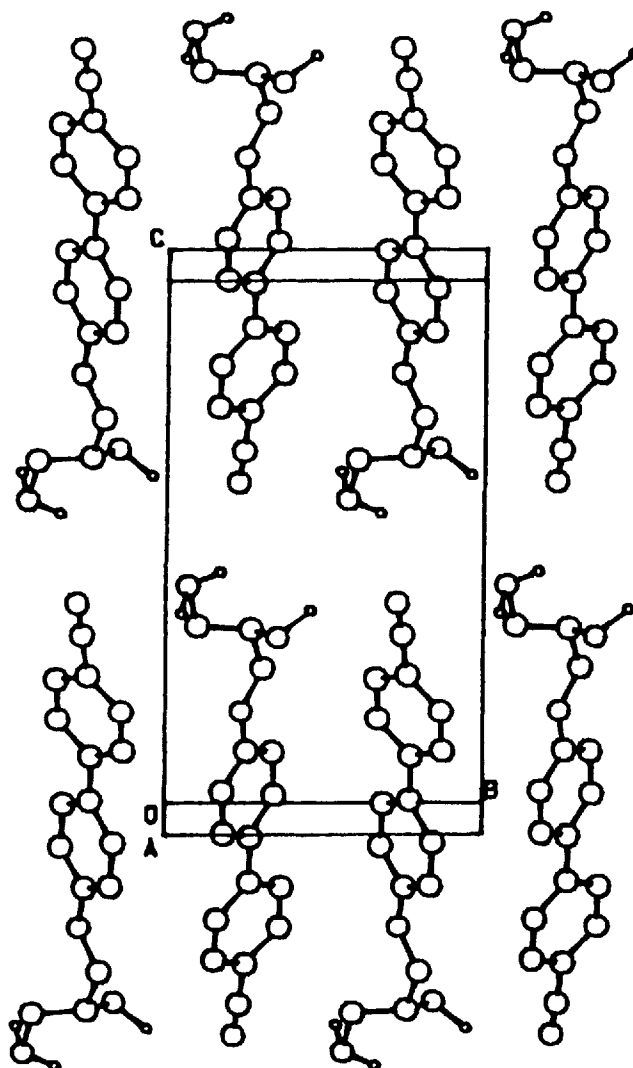Figure 4. Molecular packing of diol 1.

Figure 5. Molecular packing of diol **5**.

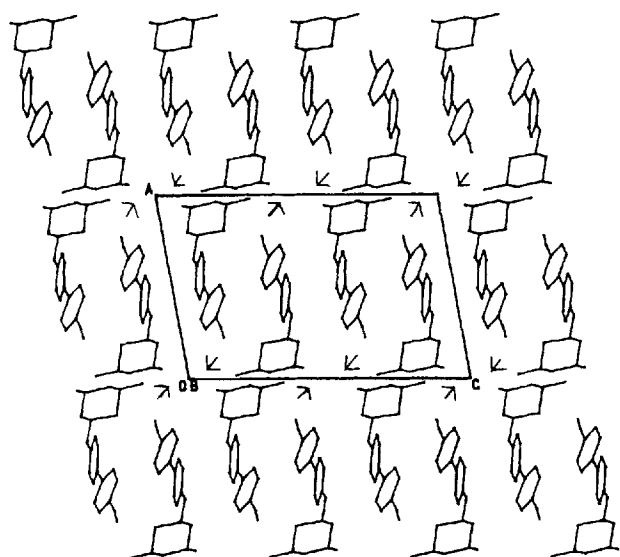Table 4. Intermolecular hydrogen bond lengths for diols **1** and **5**.

Compound	Bond	Length/Å	
1	O3–N1†	2·91	(HO3–N1 2·06), (HO3–N1 2·92)
	O2–O3‡	2·69	(HO2–O3 1·57)
5	O1W–O2§	2·71	(O1W–HO2 1·90), (HW1–O2 2·68)
	O2–O3‖	2·73	(O2H–O3 1·84)
	O1W–O3¶	2·70	(HW2–O3 1·64)
	O1W–N1††	2·96	(HW3–N1 1·89), (HW1–N1 2·99)

†$2 + x, y, 1 + z$. ‡$3 - x, \frac{1}{2} + y, 1 - z$. §$x, \frac{5}{2} - y, -\frac{1}{2} + z$.
‖$-x, \frac{1}{2} + y, \frac{1}{2} - z$. ¶$x, y, z$. ††$1 - x, \frac{3}{2} + y, \frac{1}{2} - z$.

This kind of packing also prevails in diol **5**, with water involved in the hydrogen bonding. Although the distances between N and O atoms are longer than those between two oxygen atoms, indicating a weaker hydrogen bonding interaction between the OH- and the CN-groups, the CN-group obviously acts as proton acceptor. We would expect the hydrogen bonding interactions involving the CN groups to be important also in the liquid crystalline state, in which they would disturb the hydrogen bonding between the diol groups, thus suppressing the formation of a bilayer structure in favour of the more disordered nematic phase.

References

[1] ZUGENMAIER, P., and HEISKE, A., 1993, *Liq. Crystals*, **15**, 835.
[2] JOACHIMI, D., TSCHIERSKE, C., MÜLLER, H., WENDORFF, J. H., SCHNEIDER, L., and KLEPPINGER, R., 1993, *Angew, Chem. Int. Ed. Engl.*, **32**, 1165.
[3] GRAY, G. W., HARRISON, K. J., NASH, J. A., CONSTANT, J., HULME, D. S., KIRTON, J., and RAYNES, E. P., 1974, *Liq. Crystals Ordered Fluids*, **2**, 617.
[4] TSCHIERSKE, C., LUNOW, A., JOACHIMI, D., HENTRICH, F., GIRDZIUNAITE, D., ZASCHKE, H., MÄDICKE, A., BREZESINSKI, G., and KUSCHEL, F., 1991, *Liq. Crystals*, **9**, 821.
[5] WEISSFLOG, W., 1972, Ph. D. Thesis, Halle.
[6] ALLERHAND, A., and SCHLEYER, P. V. R., 1963, *J. Am. chem. Soc.*, **85**, 866.
[7] STETTER, H., and STEINACKER, K. H., 1952, *Chem. Ber.*, **85**, 451.
[8] STRONG, P. N., and KEANA, J. F. W., 1975, *J. org. Chem.*, **40**, 956.
[9] We thank Merck Ltd for the donation of 4-cyano-4'-hydroxybiphenyl.
[10] LATTERMANN, G., and STAUFER, G., 1989, *Liq. Crystals*, **4**, 347.
[11] MolEN, An interactive Structure Solution, Enraf-Nonius, 1990, Delft, The Netherlands.