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Molecular conformation and packing of smectogenic dimeric liquid crystals in the crystalline state

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Molecular conformation and packing of smectogenic dimeric liquid crystals in the crystalline state

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The crystal structures of α,ω-bis(4-*n*-pentylanilinebenzylidene-4′-oxy)butane and α,ω-bis(4-*n*-pentylanilinebenzylidene-4′-oxy)pentane have been determined by single crystal X-ray analysis. These molecules have even and odd chain length spacers linking two mesogenic groups, respectively, and are members of a family of symmetric liquid crystal dimers which possess a rich smectic phase polymorphism, as well as pronounced odd–even effects in the transitional properties as the parity of the central spacer is varied.

1. Introduction

Dimeric liquid crystals such as the α,ω-bis(4′-cyanobiphenyl-4-yloxy)alkanes (CBO*n*OCB) have been extensively studied, partly as simpler models for semi-flexible main chain liquid crystalline polymers, and also because their phase behaviour is quite different from that of monomeric low molar mass mesogens. In particular, they show striking odd–even effects on the transitional properties as the parity of the linking spacer chain is varied, with the even members having much larger values of T_{NI} and $\Delta S_{NI}/R$ [1]. The alternation in T_{NI} is as much as 100°C, but attenuates as the linking chain becomes longer; the values of $\Delta S_{NI}/R$ alternate by a factor of two to four, and show relatively little attenuation. It is expected that on average the *para*-axes of the two biphenyl groups are essentially collinear for even members, but subtend an angle of approximately 109° for the odd members [2]. A simplistic explanation of the odd–even effect is that it arises because the average molecular shape in the all *anti*-conformation (many researchers in the field use the term *trans* synonymously with *anti*) alternates between bent and linear as the linking group parity varies between odd and even. In reality the situation is, of course, more complicated, and a recent generic model shows that the odd–even effect arises from the presence of both bent and linear conformers, and a coupling between the molecular conformation and the orientational order of the nematic phase [3].

The crystal structure of one member of the above dimeric series (CBO7OCB) has been reported [4]. The spacer chain is in a fully extended all-*anti*-conformation, and the phenoxy groups lie in the same plane. Each terminal phenyl group is twisted by approximately 39° with respect to the phenoxy group. The principal axes of the cyanobiphenyl mesogenic groups (i.e., the vector between the CN bond and the phenoxy bond) are inclined by *c*. 17° to the spacer chain axis, giving an angle between the mesogenic units of 34°. This compares with the expected value in the extended conformation of 50–60°, the difference arising from an enlargement of the aliphatic C–C–C bond angles in the spacer chain.

Although the single crystal X-ray structures of a range of low molar mass mesogens have been determined, with the exception of the above-mentioned dimer CBO7OCB, all of these are monomeric, and have a semi-rigid central core with varying chain length termini. While it is not necessarily possible to extrapolate directly from the single crystal data (molecular conformation and packing) to the structure and transitional properties of the various liquid crystalline phases, such data are invaluable for modelling various features of liquid crystals and for interpreting certain experiments. For example, detailed calculations of single-molecule scattering (accessible via isotope labelling neutron scattering experiments) ideally use the atomic coordinates from the crystal structure [5]. Furthermore, although it is clear that the molecule need not necessarily be in the fully extended conformation in the liquid crystalline phases, calculations of the average shape of conformationally disordered dimers do show a remarkable similarity to the fully extended shapes [6, 7].

We have previously synthesized and studied the phase behaviour of the α,ω-bis(4-*n*-alkylanilinebenzylidene-4′-oxy)alkanes, a family of Schiff's base dimers containing terminal alkyl chains [8]. These are the dimeric analogues of the extensively studied *N*-(4-*n*-alkyloxybenzylidine)-4′-*n*-alkylanilines (*n*O.*m*), and so are given the mnemonic *m*.O*n*O.m. We found that these compounds exhibit a rich smectic phase polymorphism. Furthermore, in addition to

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the pronounced odd–even effects on the transitional properties, these compounds also show an alteration in the translational ordering in the smectic phases, in particular in the S_A phase, upon varying the length of the central spacer. Crystal structure data are available for six of the monomeric *n*O.*m* Schiff's base compounds [9–14]. Here we report the crystal structures of two members of the *m*.O*n*O.*m* dimers, with $m = 5$ and $n = 4$ or 5. The phase sequences of these two compounds are as follows [8]:

1. (5.O4O.5): $C \xleftrightarrow{133^\circ C} S_B \xleftrightarrow{162^\circ C} S_A \xleftrightarrow{218^\circ C} I$

2. (5.O5O.5): $C \xleftrightarrow{113^\circ C} S_A \xleftrightarrow{134^\circ C} I$

These structural studies have been carried out to investigate both the chain conformations and the packing motifs of these two examples of the smectogenic Schiff's base dimers, which we anticipated should shed useful light on the liquid crystalline behaviour of these molecules, and on the underlying reasons for the striking odd–even effects.

2. Experimental

The synthesis of the α,ω-bis(4-*n*-alkylanilinebenzylidene-4′-oxy)alkanes has been previously described [8]. Single crystals suitable for X-ray analysis were obtained by slow crystallization from ethyl acetate.

2.1. *X-ray diffraction*

Crystal data. **1**: $C_{40}H_{48}N_2O_2$, $M = 588{\cdot}8$, triclinic, $a = 6{\cdot}168(3)$, $b = 11{\cdot}112(4)$, $c = 25{\cdot}511(9)$ Å, $\alpha = 93{\cdot}06(2)$, $\beta = 91{\cdot}90(2)$, $\gamma = 96{\cdot}20(2)^\circ$, $U = 1735(1)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1{\cdot}13\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{CuK}_\alpha) = 5{\cdot}3\,\mathrm{cm^{-1}}$, $F(000) = 636$, crystal dimensions $0{\cdot}43 \times 0{\cdot}21 \times 0{\cdot}03$ mm. **2**: $C_{41}H_{50}N_2O_2$, $M = 602{\cdot}8$, monoclinic, $a = 5{\cdot}988(2)$, $b = 15{\cdot}066(3)$, $c = 39{\cdot}347(14)$ Å, $\beta = 92{\cdot}60(2)^\circ$, $U = 3546(2)$ Å^3, space group $P2_1$, $Z = 4$ (2 crystallographic independent molecules), $D_c = 1{\cdot}13\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{CuK}_\alpha) = 5{\cdot}3\,\mathrm{cm^{-1}}$, $F(000) = 1304$, crystal dimensions $0{\cdot}60 \times 0{\cdot}30 \times 0{\cdot}02$ mm.

Data for compound **1** were measured on a Siemens P4/RA diffractometer ($2\theta < 125^\circ$), and for compound **2** on a Siemens P3/PC diffractometer ($2\theta < 116^\circ$), with CuK_α radiation (graphite monochromator) using ω-scans. For compounds **1** and **2**, 5533 and 4956 independent reflections, respectively were measured, and of these 3215 and 2062 respectively had $|F_0| > 4\sigma(|F_0|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors; no absorption corrections were applied. Both structures were solved by direct methods. For compound **1**, all the non-hydrogen atoms were refined anisotropically. The terminal pentyl chains in **1** were poorly defined; their geometries were therefore optimized and they were refined subject to refined distance and angle constraints. For compound **2**, because of the shortage of observed data, only the nitrogen and oxygen atoms were refined anisotropically; the carbon atoms were refined isotropically. In both structures the positions of the hydrogen atoms were idealized C–H = 0·96 Å, assigned isotropic thermal parameters $U(\mathrm{H}) = 1{\cdot}2\,U_{\mathrm{eq}}(\mathrm{C})$, and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares to give for **1**, $R = 0{\cdot}113$, $R_w = 0{\cdot}124$ $(w^{-1} = \sigma^2(F) + 0{\cdot}0005F^2)$, and for **2**, $R = 0{\cdot}093$, $R_w = 0{\cdot}089$ $(w^{-1} = \sigma^2(F) + 0{\cdot}0005F^2)$. The maximum residual electron densities in the final ΔF maps were 0·75 and $0{\cdot}23\,\mathrm{e\,Å^{-3}}$ for **1** and **2**, respectively. Computations were carried out on a 486 PC using the SHELXTL-PC program system. Fractional atomic coordinates for **1** are listed in table 1 and selected torsion angles in table 2. Fractional atomic coordinates for **2** are listed in table 3 and selected torsion angles in table 4. The bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. *5.O4O.5*

5.O4O.5 crystallizes in the centrosymmetric space group $P\bar{1}$. The X-ray analysis of 5.O4O.5 shows the molecules to adopt an essentially extended (near-linear) conformation (see figure 1), with a distance of approx. 39 Å between the terminal hydrogen atoms, and a corresponding effective molecular length of approx. 41 Å, when 1 Å is added to each end to allow for the van der Waal's radius of the hydrogens. The two mesogenic units at the two ends of the spacer adopt different conformations. The normals to rings C6–C11 and C14–C19 are rotated by approx. 33° with respect to each other. The principal torsional twist of 31° (see table 2) takes place about the C9–N12 bond, the rotations about the N12–C13 and C13–C14 bonds being small, at 8° and 2°, respectively. Rings C26–C31 and C34–C39 are closer to coplanarity, with a dihedral angle of 15° between the ring planes. In contrast to the other mesogenic unit, this twist between the two rings is made up of two torsional twists of opposite sign, with a rotation of -10° about C29–C32 and of $+25^\circ$ about N33–C34; there is no significant rotation about C32–N33. Despite these marked conformational differences, a least squares fit of the two mesogenic units (see figure 2) reveals an rms deviation of only 0·42 Å and a maximum deviation of 0·61 Å. Thus the overall molecular envelope is not dramatically changed as a consequence of these significant differences in the conformations of the mesogenic units.

The most striking feature of the central $\mathrm{O{-}(CH_2)_4{-}O}$ spacer conformation is its non-planarity. The chain from C21–C26 adopts a 'normal' all-*anti*-geometry, but the geometry about the C21–C22 bond is *gauche*, with an O20–C21–C22–C23 torsion angle of 62·5°. The effect of

Table 1. Atomic coordinates (× 10^4) and equivalent isotropic displacement factors (Å^2 × 10^3) for 5.O4O.5.

Atom	*x*	*y*	*z*	*U*(eq)†
C(1)	11422 (18)	6114 (13)	631 (5)	274 (2)
C(2)	11012 (18)	5228 (13)	987 (6)	348 (2)
C(3)	9012 (14)	5316 (13)	1205 (6)	375 (2)
C(4)	8909 (15)	4713 (15)	1667 (4)	396 (2)
C(5)	6851 (17)	4112 (12)	1709 (4)	223 (2)
C(6)	5736 (14)	3325 (6)	2101 (3)	138 (2)
C(7)	6218 (12)	2132 (6)	2128 (3)	127 (2)
C(8)	5090 (10)	1359 (4)	2464 (3)	84 (1)
C(9)	3461 (9)	1776 (4)	2770 (2)	65 (1)
C(10)	2987 (10)	2971 (5)	2745 (3)	81 (1)
C(11)	4156 (12)	3753 (4)	2420 (3)	110 (1)
N(12)	2442 (9)	946 (5)	3119 (2)	62 (1)
C(13)	456 (11)	965 (6)	3237 (3)	59 (1)
C(14)	− 492 (10)	250 (6)	3641 (3)	59 (1)
C(15)	670 (10)	− 570 (6)	3896 (3)	60 (1)
C(16)	− 93 (10)	− 1143 (6)	4308 (3)	66 (1)
C(17)	− 2158 (10)	− 949 (6)	4502 (3)	56 (1)
C(18)	− 3386 (10)	− 168 (6)	4253 (3)	62 (1)
C(19)	− 2553 (10)	415 (6)	3828 (3)	61 (1)
O(20)	− 3059 (7)	− 1473 (4)	4924 (2)	65 (1)
C(21)	− 1818 (10)	− 2239 (6)	5216 (3)	66 (1)
C(22)	− 3128 (10)	− 2645 (6)	5670 (3)	63 (1)
C(23)	− 5309 (10)	− 3391 (6)	5505 (3)	63 (1)
C(24)	− 6527 (10)	− 3902 (6)	5941 (3)	68 (1)
O(25)	− 8415 (7)	− 4614 (4)	5714 (2)	72 (1)
C(26)	− 9841 (11)	− 5225 (6)	6039 (3)	60 (1)
C(27)	− 9491 (11)	− 5256 (7)	6567 (3)	71 (1)
C(28)	− 11075 (11)	− 5945 (6)	6850 (3)	71 (1)
C(29)	− 12933 (10)	− 6537 (6)	6605 (3)	60 (1)
C(30)	− 13208 (11)	− 6489 (6)	6070 (3)	66 (1)
C(31)	− 11690 (11)	− 5825 (6)	5783 (3)	63 (1)
C(32)	− 14605 (11)	− 7215 (6)	6905 (3)	70 (1)
N(33)	− 14489 (9)	− 7160 (5)	7406 (3)	73 (1)
C(34)	− 16116 (7)	− 7823 (6)	7697 (2)	74 (1)
C(35)	− 15461 (7)	− 8050 (7)	8208 (2)	95 (1)
C(36)	− 16903 (10)	− 8705 (9)	8525 (2)	120 (2)
C(37)	− 19015 (9)	− 9116 (8)	8335 (3)	109 (1)
C(38)	− 19693 (7)	− 8853 (7)	7830 (2)	96 (1)
C(39)	− 18246 (8)	− 8204 (6)	7513 (2)	75 (1)
C(40)	− 20569 (15)	− 9746 (11)	8695 (5)	197 (2)
C(41)	− 20596 (18)	− 10828 (10)	8942 (6)	287 (2)
C(42)	− 22338 (19)	− 10929 (9)	9273 (5)	293 (2)
C(43)	− 22509 (23)	− 12045 (10)	9490 (7)	476 (2)
C(44)	− 24129 (20)	− 12092 (12)	9855 (6)	309 (2)

† Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

this *gauche* geometry is to produce an approximately 60° rotation of the two mesogenic cores relative to each other about the spacer axis (see figure 3), thus producing the near-linear extended conformation observed for the molecule as a whole.

Table 2. Selected torsion angles (°) for 5.O4O.5, with the e.s.d.'s in parentheses.

Atoms	
C8–C9–N12–C13	− 148·6 (0·6)
C10–C9–N12–C13	35·0 (0·8)
C9–N12–C13–C14	− 171·3 (0·6)
N12–C13–C14–C15	− 5·2 (1·0)
N12–C13–C14–C19	169·5 (0·6)
C16–C17–O20–C21	3·1 (0·9)
C18–C17–O20–C21	− 176·6 (0·5)
C17–O20–C21–C22	177·3 (0·5)
O20–C21–C22–C23	61·8 (0·7)
C21–C22–C23–C24	174·3 (0·6)
C22–C23–C24–O25	− 176·7 (0·5)
C23–C24–O25–C26	178·6 (0·6)
C24–O25–C26–C27	− 4·4 (1·0)
C24–O25–C26–C31	176·0 (0·6)
C28–C29–C32–N33	7·9 (1·1)
C30–C29–C32–N33	− 172·4 (0·7)
C29–C32–N33–C34	− 179·9 (0·6)
C32–N33–C34–C35	158·0 (0·7)
C32–N33–C34–C39	− 24·0 (1·0)

A search [15] for other compounds containing the Ph–O–$(CH_2)_4$–O–Ph unit revealed only one other example, 1,4-bis(*p*-bromophenoxy)butane [16]. This molecule also has an extended near linear conformation, with the phenyl rings rotated by *c.* 20° with respect to each other about the chain axis. However, the conformation of the O–$(CH_2)_4$–O chain is different, there being two out-of-plane *gauche* torsional rotations of opposite sense about two of the CH_2–CH_2 bonds.

The terminal pentyl chains of 5.O4O.5 are poorly defined in the structure (*vide ut supra*) as a consequence of some disorder in their conformations. Despite this

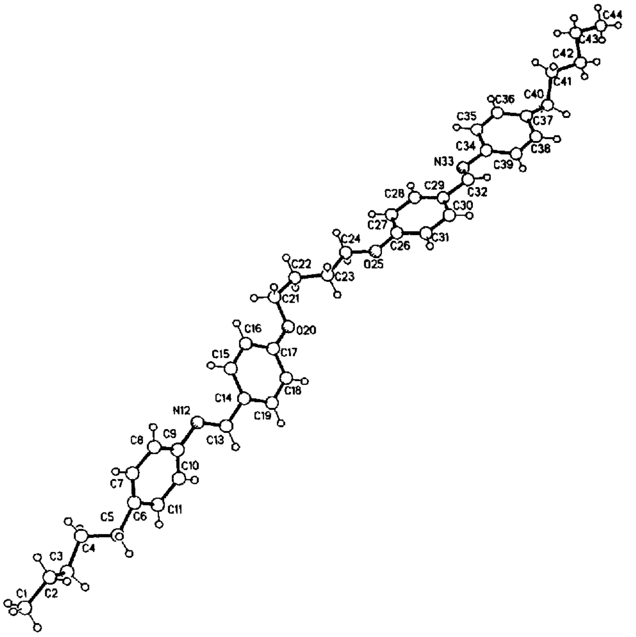

Figure 1. Perspective view of 5.O4O.5 showing the atomic numbering scheme.

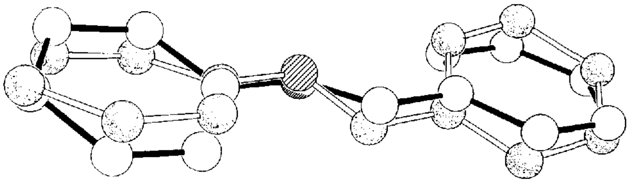

Figure 2. Best fit of the two semi-rigid mesogenic groups in 5.O4O.5 showing the conformational differences.

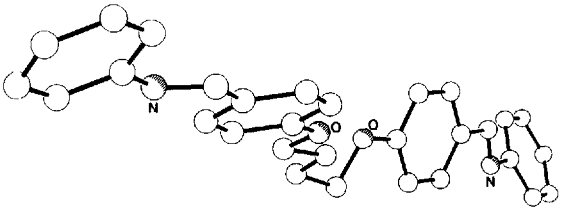

Figure 3. Perspective view of the central core of 5.O4O.5 showing the distinct rotation of one of the mesogenic groups relative to the other about the chain axis.

disorder, it is clear that the planes through both chains are steeply inclined to their associated aromatic groups. This in fact is a common feature in the structures of other alkyl-substituted liquid crystal molecules (see, for example, [9]).

The 5.O4O.5 molecules are packed into strongly tilted monolayers (see figure 4). The molecular long axis is inclined to both the crystallographic a and b axes by 58°, and by 48° to the c axis. The molecules lie within distinct sheets within each monolayer, the sheets extending in the a direction. A view of the packing of the molecules looking along their chain axes (see figure 5) reveals an essentially close-packed hexagonal arrangement, reminiscent of that adopted by many polymer and oligomer molecules [17].

An inspection of the packing fails to reveal any distinctive aromatic–aromatic interactions between adjacent molecules, neither face to face nor edge to face. A search for possible CH ... O hydrogen bonding interactions to either O20 or O25 reveals only long intermolecular contacts between H18 and H30 to O20, at distances of 2·83 and 2·94 Å, respectively, and between H31 and H21 to O25, at distances of 2·92 and 3·18 Å. All of these distances are too long to be considered as significant interactions. Similarly, the intermolecular contacts to the two nitrogen atoms are well outside the range for any significant CH ... N interactions. The CH proton H32 is directed approximately towards the π face of the C14–C19 ring of an adjacent molecule, but the distance of 3·2 Å from the proton to the ring centroid is rather long for there to be any significant interaction. We must conclude therefore that in this instance the dominant intermolecular interactions must be van der Waal's in nature.

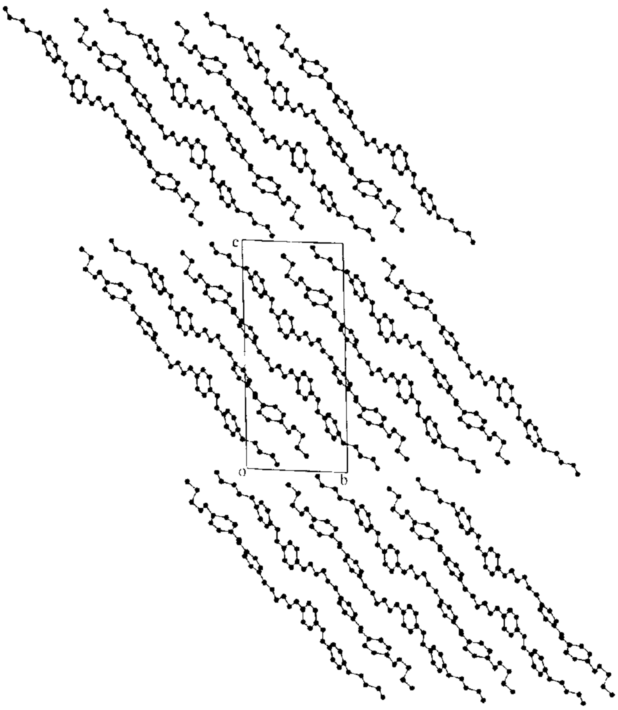

Figure 4. Parallel projection of the packing of 5.O4O.5 viewed down the crystallographic a direction, showing the tilted monolayer arrangement. Note that the chain axis does not lie in the bc plane but is also strongly tilted towards the a axis.

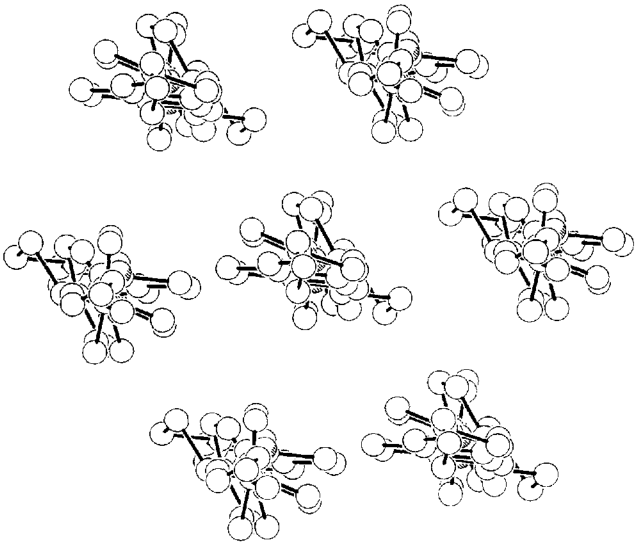

Figure 5. Pseudo-hexagonal close-packed arrangement of 5.O4O.5 viewed down the molecular long axis.

3.2. *5.O5O.5*

In contrast to 5.O4O.5, 5.O5O.5 crystallizes in the non-centrosymmetric polar space group $P2_1$, with two crystallographically independent molecules in the asymmetric unit. These independent molecules are virtually

Table 3. Atomic coordinates (× 10^4) and equivalent isotropic displacement factors (Å^2 × 10^3) for 5.O5O.5.

Atom	*x*	*y*	*z*	*U*(eq)†
C(1)	11999 (53)	4499 (24)	1577 (7)	218 (14)
C(2)	9996 (59)	4291 (25)	1821 (8)	221 (15)
C(3)	10981 (49)	4572 (22)	2141 (6)	162 (11)
C(4)	9097 (45)	4362 (21)	2411 (6)	151 (11)
C(5)	9821 (37)	4663 (17)	2753 (5)	104 (7)
C(6)	8527 (33)	4452 (15)	3058 (4)	67 (6)
C(7)	6366 (36)	4063 (15)	3032 (5)	93 (7)
C(8)	5222 (32)	3910 (14)	3330 (4)	72 (6)
C(9)	6001 (33)	4189 (14)	3646 (5)	69 (6)
C(10)	8151 (32)	4569 (15)	3668 (5)	73 (6)
C(11)	9281 (34)	4722 (15)	3384 (4)	77 (6)
N(12)	4654 (25)	4032 (12)	3909 (4)	62 (6)
C(13)	4994 (33)	4435 (15)	4188 (4)	71 (6)
C(14)	3637 (32)	4342 (15)	4489 (4)	65 (6)
C(15)	1663 (28)	3836 (13)	4446 (4)	58 (5)
C(16)	293 (30)	3719 (14)	4717 (4)	65 (5)
C(17)	860 (32)	4110 (15)	5019 (5)	64 (6)
C(18)	2835 (31)	4585 (15)	5082 (5)	69 (6)
C(19)	4107 (32)	4685 (14)	4811 (4)	68 (6)
O(20)	−631 (20)	3961	5274 (3)	69 (5)
C(21)	−97 (28)	4290 (14)	5608 (4)	58 (5)
C(22)	−2186 (28)	4106 (15)	5799 (4)	69 (6)
C(23)	−2079 (30)	4455 (15)	6168 (4)	74 (6)
C(24)	−4096 (30)	4253 (15)	6365 (4)	74 (6)
C(25)	−3991 (32)	4533 (15)	6733 (4)	75 (6)
O(26)	−6111 (19)	4325 (11)	6861 (3)	74 (5)
C(27)	−6266 (35)	4421 (15)	7197 (5)	66 (6)
C(28)	−8258 (30)	4147 (13)	7344 (4)	60 (5)
C(29)	−8644 (35)	4238 (14)	7684 (4)	75 (6)
C(30)	−6850 (36)	4536 (16)	7905 (5)	81 (6)
C(31)	−4940 (37)	4818 (14)	7769 (5)	81 (6)
C(32)	−4611 (32)	4769 (14)	7424 (4)	66 (5)
C(33)	−7112 (42)	4621 (17)	8277 (6)	96 (8)
N(34)	−9073 (32)	4421 (14)	8407 (4)	90 (8)
C(35)	−9029 (38)	4526 (16)	8763 (5)	83 (6)
C(36)	−10934 (40)	4837 (16)	8907 (5)	107 (8)
C(37)	−11143 (40)	4959 (14)	9254 (5)	95 (7)
C(38)	−9445 (42)	4630 (18)	9477 (6)	103 (7)
C(39)	−7538 (37)	4307 (15)	9337 (5)	96 (7)
C(40)	−7274 (35)	4216 (15)	8990 (5)	85 (6)
C(41)	−9622 (52)	4806 (21)	9864 (7)	165 (12)
C(42)	−11474 (46)	4500 (21)	10008 (6)	154 (10)
C(43)	−11372 (51)	4639 (22)	10418 (7)	166 (11)
C(44)	−13353 (68)	4374 (27)	10549 (9)	240 (18)
C(45)	−13474 (53)	4535 (22)	10920 (7)	202 (14)
C(1′)	−16680 (53)	1972 (24)	8317 (7)	211 (14)
C(2′)	−14806 (52)	2066 (22)	8056 (7)	184 (13)
C(3′)	−15582 (41)	1839 (19)	7719 (6)	129 (9)
C(4′)	−13936 (37)	1992 (17)	7448 (5)	114 (8)
C(5′)	−14679 (35)	1654 (16)	7127 (5)	102 (7)
C(6′)	−13205 (34)	1748 (16)	6825 (5)	77 (6)
C(7′)	−11203 (32)	2192 (14)	6829 (5)	70 (6)
C(8′)	−9958 (33)	2256 (14)	6555 (4)	71 (6)
C(9′)	−10761 (35)	1938 (16)	6227 (5)	68 (6)
C(10′)	−12884 (30)	1545 (14)	6229 (4)	67 (5)
C(11′)	−14083 (31)	1480 (14)	6517 (4)	62 (5)
N(12′)	−9326 (24)	2067 (12)	5954 (4)	71 (7)
C(13′)	−9674 (34)	1678 (16)	5675 (5)	74 (6)
C(14′)	−8198 (30)	1789 (14)	5412 (4)	56 (5)
C(15′)	−6176 (32)	2266 (15)	5434 (4)	74 (6)
C(16′)	−4795 (30)	2332 (14)	5161 (4)	65 (5)
C(17′)	−5481 (32)	1930 (14)	4844 (4)	56 (5)
C(18′)	−7435 (28)	1514 (14)	4814 (4)	58 (5)
C(19′)	−8736 (30)	1416 (14)	5091 (4)	61 (5)
O(20′)	−3881 (21)	2067 (10)	4614 (3)	83 (6)
C(21′)	−4423 (29)	1763 (15)	4270 (4)	68 (5)
C(22′)	−2475 (30)	1971 (15)	4068 (4)	73 (6)
C(23′)	−2628 (28)	1705 (14)	3694 (4)	64 (5)
C(24′)	−535 (30)	1935 (15)	3523 (4)	70 (6)
C(25′)	−732 (31)	1689 (16)	3140 (4)	79 (6)
O(26′)	1309 (23)	1903 (13)	2991 (3)	95 (7)
C(27′)	1348 (34)	1850 (15)	2648 (5)	71 (6)
C(28′)	3282 (35)	2168 (14)	2515 (5)	79 (6)
C(29′)	3606 (33)	2169 (13)	2179 (4)	74 (6)
C(30′)	1959 (33)	1892 (15)	1943 (5)	72 (6)
C(31′)	−27 (30)	1620 (13)	2080 (4)	62 (5)
C(32′)	−399 (31)	1599 (13)	2433 (4)	58 (5)
C(33′)	2276 (35)	1885 (14)	1591 (5)	70 (6)
N(34′)	4005 (26)	2044 (14)	1441 (4)	84 (7)
C(35′)	4056 (38)	2041 (16)	1090 (5)	88 (7)
C(36′)	5954 (39)	1701 (16)	947 (5)	94 (7)
C(37′)	6004 (37)	1668 (16)	598 (5)	100 (7)
C(38′)	4342 (43)	2025 (18)	390 (6)	115 (8)
C(39′)	2511 (40)	2392 (17)	533 (6)	116 (8)
C(40′)	2483 (39)	2397 (16)	881 (5)	112 (8)
C(41′)	4344 (42)	2020 (19)	−3 (6)	145 (10)
C(42′)	6245 (51)	2101 (22)	−156 (6)	167 (11)
C(43′)	6340 (43)	2068 (19)	−548 (6)	142 (9)
C(44′)	8428 (59)	2008 (26)	−682 (8)	209 (15)
C(45′)	8762 (54)	2051 (22)	−1040 (7)	220 (15)

† Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

enantiomeric, with an rms deviation from the best fit of one molecule to the enantiomer of the other of 0·25 Å, and a maximum deviation of 0·49 Å for one of the terminal methyl groups. As with 5.O4O.5, the molecules adopt an essentially linear extended chain conformation (see figure 6), the distance between the terminal methyl hydrogen atoms being 42 Å, giving an effective molecular length of *c.* 44 Å when allowance for the van der Waal's radius of the two hydrogens is made.

Within each independent molecule, the conformations of the two mesogenic units differ markedly. The phenyl rings C6–C11 and C14–C19 are rotated (see table 4) by 10° (6° for the independent molecule) with respect to each other, whereas rings C27–C32 and C35–C40 are rotated by 46° (48°) with respect to each other.

In contrast to the non-planar geometry observed for the spacer linking the two mesogenic groups in 5.O4O.5, in 5.O5O.5 this chain, which contains an additional methylene group, is essentially planar and adopts an all-*anti*-conformation which extends from C17 to C27. Indeed the planarity observed within this portion of the molecule is seen to extend in one direction to C1, and in the other to N34 (maximum deviation from planarity 0·33 Å for C33, with an rms deviation of 0·17 Å). This extended planarity is then broken by the significant torsional twist that occurs

Table 4. Selected torsion angles (°) for the two crystallographically independent molecules *A* and *B* of 5.O5O.5, with the e.s.d.'s in parentheses.

Atoms	Molecule *A*.	Molecule *B*
C8–C9–N12–C13	− 164 (2)	167 (2)
C10–C9–N12–C13	19 (3)	− 13 (4)
C9–N12–C13–C14	179 (2)	− 178 (2)
N12–C13–C14–C15	− 7 (3)	5 (3)
N12–C13–C14–C19	172 (2)	− 174 (2)
C16–C17–O20–C21	176 (2)	− 175 (2)
C18–C17–O20–C21	− 1 (3)	4 (3)
C17–O20–C21–C22	173 (2)	− 180 (2)
O20–C21–C22–C23	− 177 (2)	180 (2)
C21–C22–C23–C24	− 178 (2)	− 179 (2)
C22–C23–C24–C25	176 (2)	− 178 (2)
C23–C24–C25–O26	177 (2)	− 179 (2)
C24–C25–O26–C27	172 (2)	− 171 (2)
C25–O26–C27–C28	− 174 (2)	173 (2)
C25–O26–C27–C32	5 (3)	− 1 (3)
C29–C30–C31–N34	− 1 (4)	6 (4)
C31–C30–C33–N34	174 (2)	− 174 (2)
C30–C33–N34–C35	179 (2)	− 178 (2)
C33–N34–C35–C36	144 (2)	− 142 (2)
C33–N34–C35–C40	− 45 (3)	43 (4)

about the N34–C35 bond within the C27–C40 mesogenic unit. There is a further rotation of 49° (28°) of the near-planar terminal C41–C45 pentyl chain out of the plane of the C35–C40 ring. A search [15] for structures containing the Ph–O–(CH$_2$)$_5$–O–Ph unit revealed only one other comparable example—pentamidine isethionate trihydrate [18]—which in the crystalline state also adopts a near planar geometry with an all-*anti*-conformation for the central O–(CH$_2$)$_5$–O unit. The linearity of the 5.O5O.5 molecule as a whole may be appreciated by considering the angle subtended by a pair of vectors linking C6 to C23, and C23 to C38, which has a value of 171°. Within the central core, the angle subtended by the vectors C13 ... O20 and O26 ... C33 is 33° from collinear for both of the independent molecules. The long axes of the two independent molecules are almost exactly parallel to each other (179·8°), as defined by the angle between the vectors linking C6 and C38 in each of the two molecules.

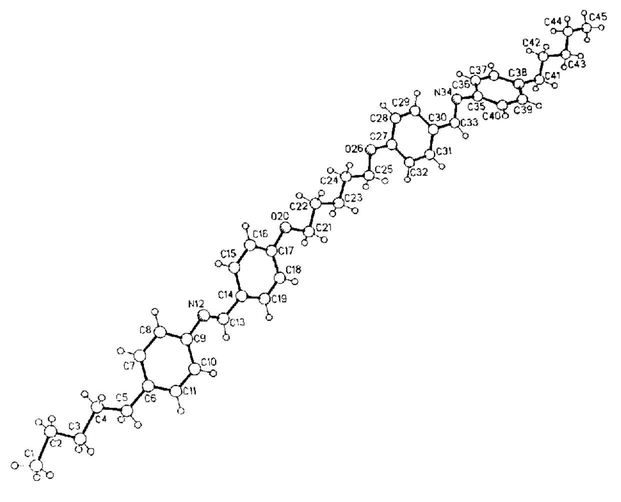

Figure 6. Perspective view of 5.O5O.5 showing the atomic numbering scheme.

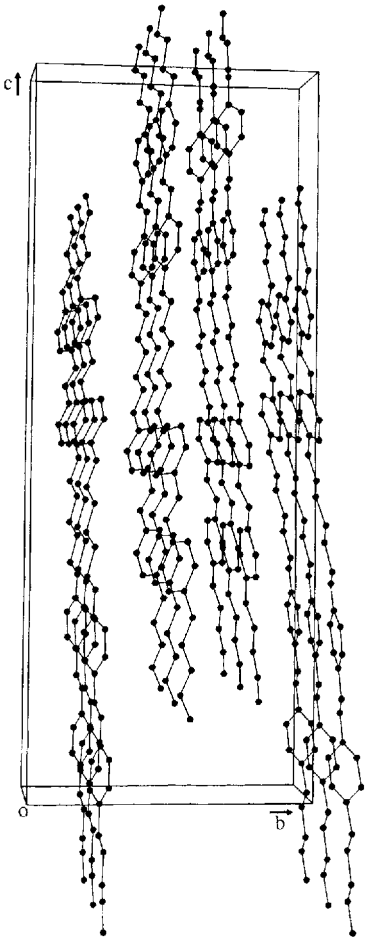

Figure 7. Perspective view of the packing of 5.O5O.5 viewed down the crystallographic *a* direction, showing the layering of the molecules.

The packing of the molecules is markedly different from that observed for 5.O4O.5. The molecules again stack to form sheets which extend along the crystallographic *a* direction (see figure 7). However, alternate pairs of sheets are displaced along the *c* direction, producing an interdigitated arrangement of the layers (see figure 8), in contrast to the simple lamellar arrangement observed for 5.O4O.5 (see figure 4). The molecules are aligned with their principal plane parallel to the crystallographic *ac* plane, and with their chain axis (C41–C45) inclined by 22° to the *c* axis and 65° to the *a* axis directions.

A view of the molecules down the chain axis reveals a pseudo close-packed hexagonal arrangement which is

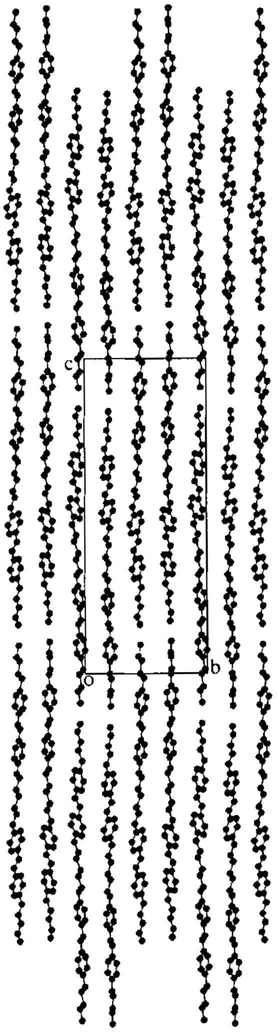

Figure 8. Parallel projection of the packing of 5.O5O.5 viewed down the crystallographic *a* direction, showing the partial interdigitation of the layers.

significantly flattened (see figure 9) in comparison to that observed for 5.O4O.5 (see figure 5). As in the case of 5.O4O.5, there again seems to be a distinct lack of any π–π interactions. Indeed, as can be seen in figure 8, there is a marked tendency for the aromatic regions of one molecule to lie adjacent to either the aliphatic terminal chains, or to the O–$(CH_2)_5$–O spacer units, of its neighbours. There is only one marginal CH … O contact (2·61 Å) between the proton attached to C16 and O20′ of a non-symmetry-related adjacent molecule. This is at the upper limit for consideration as a possible hydrogen bonding interaction. We must again conclude that the principal packing force between the molecules is van der Waal's in nature.

A notable feature of the chain conformation of both 5.O4O.5 and 5.O5O.5 is a retention of coplanarity of the phenoxy methylene carbons with their adjacent phenyl rings. This geometry is consistent with the theoretically predicted geometries for methoxyphenyl units, and is stabilized by interaction between the lone pair electrons on the ether oxygen and the π electrons of the phenyl ring [19]. Indeed this conjugation between the $2p_\pi$ orbitals on the oxygen with those on the phenyl ring is believed to stablize the nematic phase of nematogens with terminal alkoxy chains relative to those with alkyl chains, through the higher anisotropy in the molecular polarizability (see for example, [20]; note, however, that the difference in geometry between ether and methylene linkages also results in a stabilization of the nematic phase for alkoxy linked mesogens [21]). This coplanarity is clearly a contributory factor to the nearly linear chain conformations observed for both molecules. For 5.O5O.5 the all-*anti*-conformation is then compatible with a linear molecule; however, this is not true for 5.O4O.5, where a distinct bend would be introduced. For the latter molecule a *gauche* bond is introduced at C21–C22, breaking the molecular symmetry, but increasing the linearity, and hence presumably enhancing the packing.

It is interesting to compare this conformational behaviour with that of the α,ω-bis(4-cyanobiphenyl-4′-yloxy)alkanes (CBO*n*OCB), where the members with *n* even are believed to have an extended conformation (although kinked), whereas those with *n* odd should be bent, this latter feature being confirmed in the crystalline state [4]. For the *m*.O*n*O.*m* compounds, the odd–even

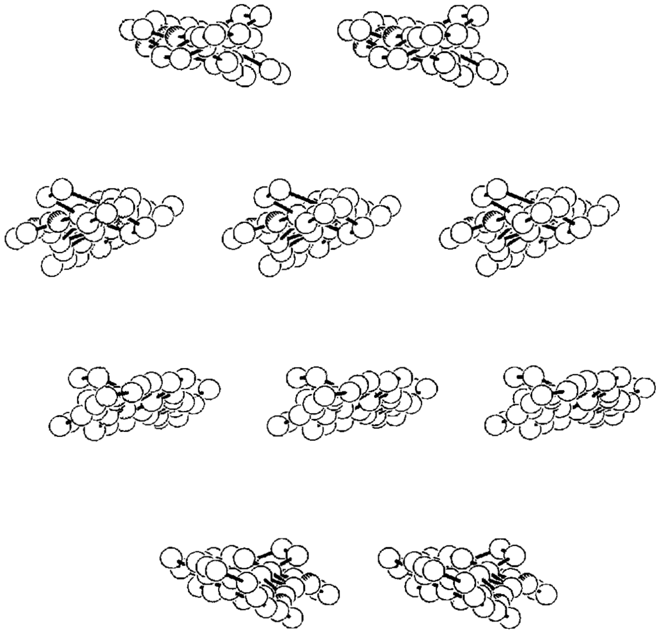

Figure 9. Close-packed arrangement of 5.O5O.5 viewed down the molecular long axis.

effect is similar to that of the CBO*n*OCBs, even though the crystal structures presented here indicate that if anything the odd member should be more linear than the even one, in the fully extended state. It is clear that the packing forces in the crystal are stronger than those in the liquid crystalline phases, and thus the preferred conformational states of the dimers need not be the same in both states. However, our results do suggest that the explanation of the odd–even effect as arising from the different shapes of the fully extended odd and even spacer dimer molecules is over simplistic, and that more subtle effects must be involved.

A recent molecular dynamics simulation study of dimers, modelled by two spherocylinders connected by a flexible alkyl chain containing 4, 5, 6 or 7 methylene groups, has found striking odd–even effects in the nematic order parameters and the stability of the liquid crystal phase [22]. Furthermore, differences are seen in the conformation of the spacer for odd- and even-parity dimers. With increasing density, it is found that for the even-parity dimers, the odd-numbered torsions in the spacer become predominantly *anti*, whereas the even-numbered torsions become predominantly *gauche*, thereby maximizing the collinearity of the spherocylinders and the spacer. This result can be compared with the spacer conformation we have found for the even-parity Schiff's base dimer 5.O4O.5 in the crystal phase. As seen in figure 1, we observe a similar effect, but with only a single *gauche* link being introduced at the second bond from one end of the alkyl chain spacer. In the simulation study, the alternation between *anti* and *gauche* conformations along the spacer for odd-parity dimers is less pronounced. Similarly, in the crystal of 5.O5O.5, the spacer is found to be all-*anti* (see figure 6).

For 5.O4O.5, the S_A layer spacing increases from 41·2 Å to 41·6 Å on cooling from the transition to the isotropic phase (218°C) to the transition to the S_B phase (162°C) [8]. It then jumps to a value of 42·6 Å on entering the more ordered S_B phase. These layer spacings are close to the value of 41 Å we have estimated for the molecular length within the crystal phase (*vide ut supra*). Thus all three phases have a monolayer packing, although in the crystal the molecules are tilted to the layer normal, whereas in the two smectic phases they are not. For 5.O5O.5, the S_A layer spacing is 40·5 Å at 134°C [8], which is significantly less than the estimated molecular length of 44 Å in the crystal. This suggests that there are significant differences in the way that 5.O4O.5 and 5.O5O.5 pack in the smectic layers in the S_A phase, although whether this may be attributed to the odd-spacer dimer adopting a more bent conformation than the even-spacer dimer is unclear.

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