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The Molecular and Crystal Structure of α,ω-bis [4-(4′-hexyloxybenzylidene-iminophenyl)]octane (60.8.06) and α,ω-bis [4-(4′-heptyloxybenzylidene-iminophenyl)]octane (70.8.07)

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The Molecular and Crystal Structure of α,ω-bis [4-(4′-hexyloxybenzylidene-iminophenyl)]octane (6O.8.O6) and α,ω-bis [4-(4′-heptyloxybenzylidene-iminophenyl)]octane (7O.8.O7)

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The crystal and molecular structures of α,ω-bis [4-(4′-hexyloxybenzylideneiminophenyl)]octane (6O.8.O6) and the homologue α,ω-bis [4-(4′-heptyloxybenzylideneiminophenyl)]octane (7O.8.O7) have been determined by direct methods at room temperature. The crystals of both compounds belong to the monoclinic system with space group P $2_1/a$ and two molecules per unit cell which are placed on centers of symmetry. For 6O.8.O6: a = 10.613(4), b = 8.7596(10), c = 22.149(7) Å, β = 100.02(2)°; for 7O.8.O7: a = 5.909(4), b = 7.412(3), c = 47.174(27) Å, β = 91.15(3)°. The structures were refined by full-matrix least-squares calculations against F to R = 0.078 for 4993/(3596 unique) collected reflections for 6O.8.O6 and to R = 0.077 for 1772/(1548 unique) reflections for 7O.8.O7.

Both molecules as a whole exhibit a rod-like form although the conformations in the spacer and wing groups differ considerably. For both compounds the molecular packing consists of layers parallel to the a,b-plane, piled up in c^*-direction with minimal interdigitation of the wing groups. In 6O.8.O6 the layers are strongly tilted by an angle of about 60 °, in 7O.8.O7 they are tilted by a smaller angle of about 25 ° towards the c^*-direction.

Keywords: Crystal Structure; Molecular Packing; Dimesogenic Compound

1. INTRODUCTION

The compounds reported in this paper belong to the family of dimesogenic α,ω-bis[4-(4′-alkoxybenzylideneiminophenyl)-alkanes, nO.m.On. They are the

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dimeric analogues of the monomesogenic compounds N-(4-n-alkoxybenzylidene)-4′-n-alkylanilines (nO.m) and may serve as important models for comparison between low molar mass and polymeric liquid crystals. Crystal structures of homologous nO.m.On already published are 4O.2.O4 [1], 4O.8.O4 and 5O.8.O5 [2,3]. Here the structure determination of two longer-chain compounds, 6O.8.O6 and 7O.8.O7, is presented.

Furthermore, structures of two similar dimesogenic analogues of type m.OnO.m, 5.O4O.5 and 5.O5O.5, have been determined [4]. In general investigations on dimesogenic systems are rare [5]. Studies on the monomesogenic nO.m's are more extensive, several crystal structures have been published: 1O.4 [6], 2O.4 [7,8], 4O.2 and 7O.6 [9,10], 4O.8 [11] and 8O.4 [12]; see also [5]. The crystal structures of 9O.4 and 5O.7 have been determined, too, and will be discussed elsewhere [13]. The structure of the unsubstituted benzylideneaniline was presented in [14].

The two compounds investigated exhibit both smectic phases of the highly ordered type SmG and at higher temperatures nematic phases over a wide range of temperature (table I) [3,15]. A precise study on transitions into these phases offers the possibility to obtain some general information about the molecular arrangement in the LC state, especially because highly ordered phases are most suitable for such investigations due to their similarity to the crystalline state.

TABLE I Phase transition temperatures (°C), enthalpies (first value in parentheses, kJ mol^{-1}) and entropies (second value in parentheses, J $mol^{-1}K^{-1}$) of the compounds investigated based on DSC cooling thermograms (cooling rate: 5 °C min^{-1})

compound	*KI – KII*	*KII – SmG*	*SmG – N*	*N – I*
6O.8.O6	51.2[a] (18.9; 58.2)	97.5 (12.7; 34.3)	144.5 (11.8; 28.3)	170.5 (11.4; 25.7)
7O.8.O7		76.1[b] (32.5; 93.1)	152.1 (15.5; 36.5)	162.9 (11.4; 26.2)

a. Broad signal.
b. KI-SmG transition.

2. EXPERIMENTAL – STRUCTURE SOLUTION AND REFINEMENT

The synthesis of the dimesogenic compounds has been described previously [3,16]. Single crystals suitable for X-ray determination were obtained by slow crystallization from toluene and ethyl acetate at room temperature. Data collection was performed on a CAD4 single crystal diffractometer with MoK_α radiation and the MolEN package of Enraf Nonius, Delft [17], was used for data processing and refinement against F. The hydrogen atoms were placed at respec-

tive sites and not refined as well as their isotropic B values. Table II represents the basic crystallographic data. The mostly imperfect, small crystals do not allow a better resolution. The figures representing the conformation and packing of the structures were produced with SCHAKAL 92 [18].

TABLE II Summary of crystallographic data

	6O.8.O6	*7O.8.O7*
Formula unit (asymmetric unit)	$C_{23}H_{30}NO$	$C_{24}H_{32}NO$
Formula weight/g·mol^{-1}	336.50	350.53
Crystal system	monoclinic	monoclinic
Space group	P 2_1/a (No. 14)	P 2_1/a (No. 14)
a/Å	10.613(4)	5.909(4)
b/Å	8.7596(10)	7.412(3)
c/Å	22.149(7)	47.174(27)
α/°	90	90
ß/°	100.02(2)	91.15(3)
γ/°	90	90
V/Å^3	2027.7(10)	2066(2)
D_{cal}/g·cm^{-3}	1.10	1.13
Z (asymmetric units)	4	4
μ(MoK_α)/cm^{-1}	0.6	0.6
λ(MoK_α)/Å	0.71073	0.71073
Number of reflections used for lattice parameter refinement	25	23
Scan range	$10° < \theta < 21°$	$8° < \theta < 11°$
F(000)	732	764
Reflections collected	4993	1772
Unique data	3596	1548
Significant I's (> 3σ)	2104	972
Data collection	$1° \leq \theta \leq 25°$	$1° \leq \theta \leq 20°$
Parameters refined	226	235
R	0.078	0.077
R_w	0.112	0.107
Highest peak/e·Å^{-3} in Δρ	0.38(5)	0.27(6)
Crystal color	colorless	colorless
Crystal size	platelet	platelet

3. RESULTS AND DISCUSSION

3.1. Molecular geometry and conformation

3.1.1. Molecular geometry

Bond lengths and angles of 6O.8.O6 and 7O.8.O7 closely agree with the data found for the homologous 4O.2.O4 [1], 4O.8.O4 and 5O.8.O5 [2], for the dimesogenic analogues 5.O4O.5 and 5.O5O.5 of the type m.OnO.m [4] and for the monomeric analogues of the type nO.m [6–13].

Figures 1 (a-b) represent the molecular structures and the numbering scheme of the non-hydrogen atoms for 6O.8.O6 and 7O.8.O7, respectively. In tables III and IV the fractional coordinates are listed. For both compounds half a molecule serves as asymmetric unit to describe the content of the unit cell with a total of two molecules because each of the individuals is located on a crystallographic inversion center and therefore, a center of symmetry exists in each of the molecules.

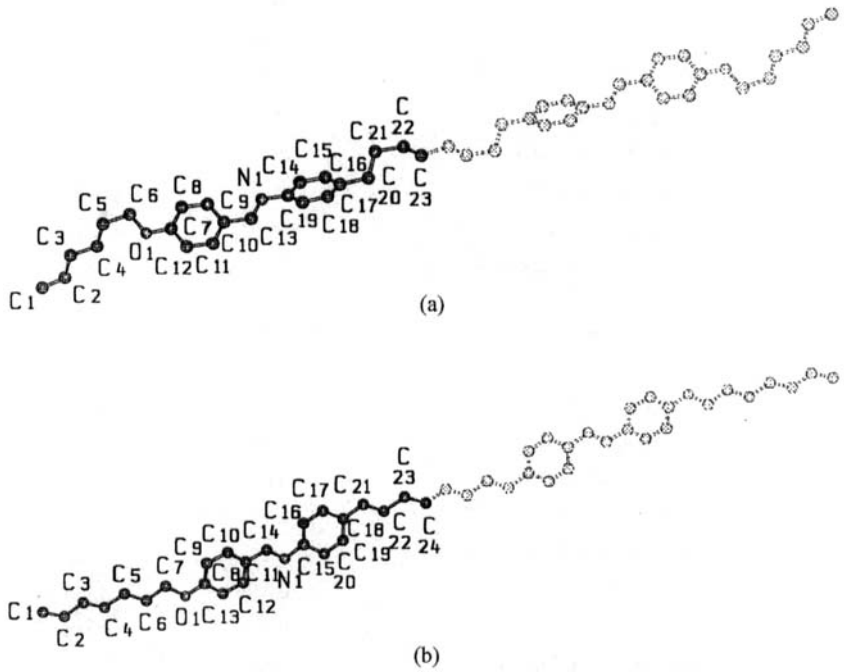

FIGURE 1 The molecular structure of (a) 6O.8.O6 and (b) 7O.8.O7 with the numbering schemes

TABLE III Atomic coordinates and equivalent isotropic displacement factors B_{eq} of 6O.8.O6 with their estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
O1	0.0448(2)	–0.0057(3)	0.1700(1)	5.77(6)
N1	0.6294(2)	0.0170(3)	0.3048(1)	5.30(7)
C1	–0.4532(7)	0.270(1)	–0.0214(4)	16.8(3)
C2	–0.3397(5)	0.259(1)	0.0139(3)	14.7(2)
C3	–0.3241(4)	0.1610(7)	0.0741(2)	9.9(1)
C4	–0.1890(4)	0.1609(5)	0.1083(2)	7.3(1)
C5	–0.1701(3)	0.0740(5)	0.1675(2)	6.24(9)
C6	–0.0362(3)	0.0811(5)	0.2028(2)	5.93(9)
C7	0.1721(3)	–0.0115(4)	0.1935(2)	4.90(8)
C8	0.2295(3)	0.0663(4)	0.2459(2)	5.45(8)
C9	0.3591(3)	0.0525(4)	0.2657(2)	5.49(8)
C10	0.4361(3)	–0.0362(4)	0.2349(2)	4.89(7)
C11	0.3769(3)	–0.1143(4)	0.1828(2)	5.73(8)
C12	0.2471(3)	–0.1030(4)	0.1624(2)	5.80(9)
C13	0.5733(3)	–0.0531(4)	0.2574(2)	5.13(8)
C14	0.7603(3)	–0.0100(4)	0.3276(1)	4.76(8)
C15	0.8291(3)	0.1103(4)	0.3587(2)	5.73(8)
C16	0.9564(3)	0.0931(5)	0.3833(2)	6.5(1)
C17	1.0193(3)	–0.0454(5)	0.3801(2)	6.43(9)
C18	0.9477(3)	–0.1653(4)	0.3508(2)	6.43(9)
C19	0.8217(3)	–0.1482(4)	0.3245(2)	5.87(9)
C20	1.1614(4)	–0.0607(7)	0.4086(2)	9.4(1)
C21	1.1944(4)	–0.0387(7)	0.4727(3)	10.6(2)
C22	1.3324(4)	–0.0763(8)	0.4987(3)	11.1(2)
C23	1.4330(4)	0.0180(6)	0.4825(3)	10.3(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3) $[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\gamma) B(1,2) + ac(\cos ß) B(1,3) + bc(\cos \alpha) B(2,3)]$.

TABLE IV Atomic coordinates and equivalent isotropic displacement factors B_{eq} of 7O.8.O7 with their estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
O1	0.9267(7)	–0.0251(8)	–0.32077(8)	5.8(1)
N1	0.5424(8)	–0.0261(9)	–0.1952(1)	4.7(1)
C1	1.774(2)	0.036(2)	–0.4698(2)	9.1(3)
C2	1.589(1)	–0.041(2)	–0.4527(1)	8.0(3)
C3	1.572(1)	0.036(1)	–0.4233(1)	6.4(2)
C4	1.383(1)	–0.038(1)	–0.4062(1)	6.4(2)
C5	1.360(1)	0.038(1)	–0.3766(1)	6.5(2)

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
C6	1.155(1)	−0.032(1)	−0.3613(1)	6.2(2)
C7	1.140(1)	0.038(1)	−0.3313(1)	5.5(2)
C8	0.893(1)	−0.007(1)	−0.2922(1)	4.3(2)
C9	1.042(1)	0.071(1)	−0.2732(1)	4.6(2)
C10	0.984(1)	0.070(1)	−0.2447(1)	5.2(2)
C11	0.787(1)	0.000(1)	−0.2351(1)	4.5(2)
C12	0.639(1)	−0.075(1)	−0.2549(1)	5.0(2)
C13	0.691(1)	−0.082(1)	−0.2832(1)	4.7(2)
C14	0.735(1)	0.010(1)	−0.2050(1)	4.4(2)
C15	0.524(1)	−0.015(1)	−0.1650(1)	4.3(2)
C16	0.680(1)	−0.085(1)	−0.1462(1)	4.8(2)
C17	0.646(1)	−0.067(1)	−0.1177(1)	4.9(2)
C18	0.458(1)	0.021(1)	−0.1065(1)	4.5(2)
C19	0.302(1)	0.084(1)	−0.1258(1)	4.9(2)
C20	0.325(1)	0.064(1)	−0.1549(1)	4.9(2)
C21	0.433(1)	0.057(1)	−0.0754(1)	5.6(2)
C22	0.234(1)	−0.028(1)	−0.0609(1)	5.1(2)
C23	0.210(1)	0.037(1)	−0.0306(1)	5.4(2)
C24	0.014(1)	−0.036(1)	−0.0149(1)	4.9(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3) $[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\gamma) B(1,2) + ac(\cos \beta) B(1,3) + bc(\cos \alpha) B(2,3)]$.

The two phenyl rings A (C7 to C12) and B (C14 to C19) in 6O.8.O6 have C-C bond distances averaging 1.387(5) and 1.384(6) Å, respectively, with a mean value of 120.0(4)° for the aromatic bond angles. The mean bond lengths for 7O.8.O7 are as follows: ring A (C8 to C13) 1.379(9) Å, ring B (C15 to C20) 1.383(9) Å with mean bond angles of 120.0(6)° for all aromatic carbon atoms.

The C=N and C-N distances in the azomethine group within the mesogens are determined to 1.270(4) and 1.414(7) Å for 6O.8.O6 and 1.265(8) and 1.433(7) Å for 7O.8.O7. The average values of all the C-C bond lengths and angles in the alkyl and alkoxy chains except the terminal ones are 1.492(7) Å and 114.7(5)° for 6O.8.O6 and 1.51(1) Å and 114.4(7)° for 7O.8.O7, respectively. In 6O.8.O6 two bond lengths at the end of the chain (C1-C2 with 1.321(8) Å and C2-C3 with 1.570(9) Å) differ significantly from the mean value as well as two bond angles, one at the chain end (C1-C2-C3 with 119.6 (6) °) and one in the middle of the spacer (C21-C22-C23 with 119.2(5) °) due to high thermal motions.

Compared with the actual empirically established CCDC values (1.531 Å for CH_2-CH_2) the average values for the bond lengths of the C-C single bonds are relatively short, certainly as a result of the high thermal motion. The temperature factors of the atoms at the chain end C1 to C4 and the spacer atoms C20 to C23

for 6O.8.O6 and the atoms at the chain end C1 and C6 for 7O.8.O7 are relatively high (tables III and IV).

3.1.2. Molecular conformation

Both molecules, 6O.8.O6 and 7O.8.O7, as a whole exhibit a rod-like form (figure 1), although the molecular conformations differ considerably in detail. In 6O.8.O6, there are two gauche conformations in the asymmetric unit: one near the oxygen in the wing group with an torsion angle τ(C4-C5-C6-O1) = –69.8(0.4)° and one near the middle of the spacer with τ(C20-C21-C22-C23) = 67.4(0.8)° (table V). For this reason the molecule appears not in its most extended form. The molecular length, i.e. the length between the two end groups, of 47.2 Å is somewhat shorter than the value of 50.7 Å calculated for an all-trans conformation [19]. On the other hand a rod-like form is produced by the gauche conformations. 7O.8.O7 exhibits an essentially linear extended chain with all-trans conformations in the alkyl and alkoxy chains and a molecular length of 52.5 Å compared to 53.3 Å as the calculated value for the all-trans conformation [19]. In both compounds the spacer is linked with the mesogenic unit in gauche conformation. The torsion angles τ(C16-C17-C20-C21) for 6O.8.O6 and τ(C19-C18-C21-C22) for 7O.8.O7 are determined to 62.1(0.6) and 65.8(1.0) °, respectively (table V), as compared to the corresponding angles of the homologous compounds 4O.8.O4 and 5O.8.O5 of – 23.0(0.5) and –43.5 (0.5) ° (4O.8.O4) and –9.5(1.8) and 12.4(1.7) ° (5O.8.O5) [2], which are somewhat smaller. Because of the center of symmetry occurring in both molecules, the long axes of the two mesogenic groups in one molecule are collinear, and the compensation of the dipole moments of the C=N-C and C-O-C occurs within one molecule.

The planes of the two phenyl rings A and B, forming one mesogenic unit, are not parallel oriented in both compounds. In 6O.8.O6 they are twisted by approximately 35 °, in 7O.8.O7 by 55 °. The differences in the twisting angle are reflected in the torsion angles near the C=N bonds (cf. table V).

TABLE V Selected torsion angles τ (°) for non-hydrogen atoms in 6O.8.O6 and 7O.8.O7 with their estimated standard deviations in parentheses

6O.8.O		*7O.8.O7*	
τ(C11-C10-C13-N1)	179.9(0.3)	τ(C10-C11-C14-N1)	168.6(0.8)
τ(C10-C13-N1-C14)	175.7(0.3)	τ(C11-C14-N1-C15)	177.9(0.7)
τ(C13-N1-C14-C15)	151.2(0.3)	τ(C14-N1-C15-C20)	138.8(0.7)
τ(C4-C5-C6-O1)	–69.8(0.4)	τ(C5-C6-C7-O1)	174.5(0.6)
τ(C16-C17-C20-C21)	62.1(0.6)	τ(C19-C18-C21-C22))	65.8(1.0)
τ(C20-C21-C22-C23)	67.4(0.8)		

3.2. Molecular packing

3.2.1. Packing of 6O.8.O6

The crystal structure of 6O.8.O6 in projections along the crystallographic directions [0 1 0] and [1 0 0] is depicted in figures 2 (a-b). The molecular long axes defined as the line between the terminal carbon atoms don't follow one of the basic directions. The unit cell dimensions listed in table II also point to this fact. Figure 2a represents the projection on the strongly scattering lattice plane (0 2 0). The directions [4 0 1] approximately correspond to the molecular long axis and [5 0 1] to the direction of the spacer including the mesogenic units which is defined as the line between the oxygen bonded carbon atoms of the two mesogenic units. Figures 3 (a-b) show the pseudo-hexagonal arrangement of the molecules viewed down the directions [4 0 1] and [5 0 1].

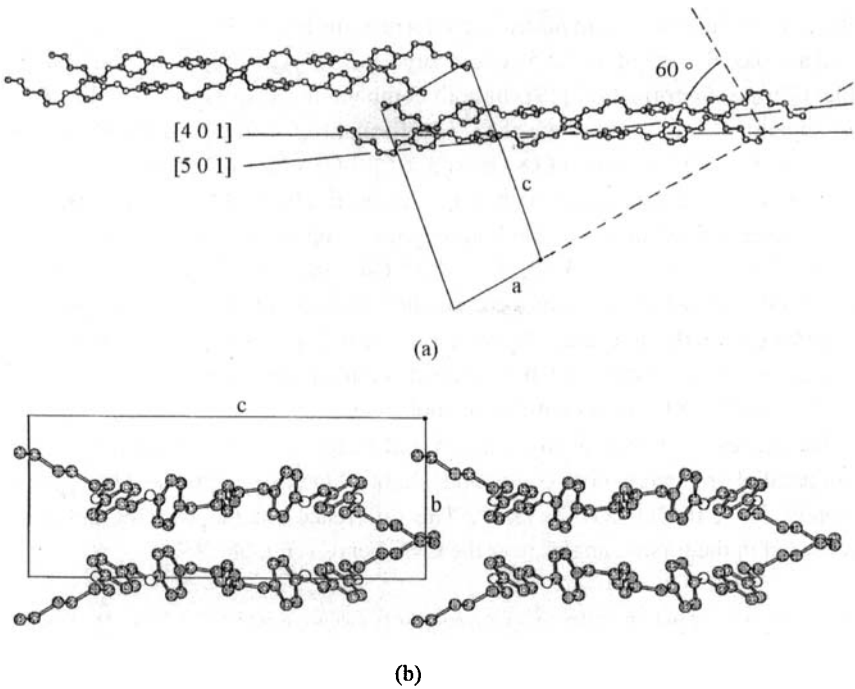

FIGURE 2 Schematic representation along the crystallographic directions (a) [0 1 0] and (b) [1 0 0] of 6O.8.O6 without hydrogen atoms. (a) represents the projection on one of the strongest scattering lattice plane (0 2 0); the direction [4 0 1] approximately indicates the molecular long axis and [5 0 1] the spacer long axis including the mesogenic units

The molecules are arranged in strongly tilted layers similar to that in smectic liquid crystalline phases. The layers lie parallel to the a,b-plane, piled up in c^*-direction with minimal interdigitation of the wing groups. The angle of inclination of these tilted layers of about 60 ° corresponds approximately with the angle between the [4 0 1]- and the c^*-direction (figure 2a).

The transition into the highly ordered SmG phase at higher temperature via a second crystalline phase KII (table I, [3,15]) will possibly be caused by a slight shifting along the molecular long axes since the twisting angle between the phenyl rings is small and the molecules exhibit rod-like shapes. In general the tilted layer-like structure in the KI phase resembles the tilted smectic SmG phase. For the compounds reported here it was possible to determine the unit cell dimensions of the SmG phase [3]. The evaluation of this problem with only a few reflections available will be dealt with elsewhere [15]. The c-dimension of the monoclinic SmG phase of 6O.8.O6 was determined to 43.9 Å [3] and approximately corresponds to the periodicity along [4 0 1] in the KI phase with 44.3 Å. This fact leads to the conclusion that the c-axes point in different directions in the KI and SmG phase, in which the molecular long axes lie along the c-dimension.

3.2.2. Packing of 7O.8.O7

Figures 4 (a-b) represent the crystal structure along the crystallographic directions [0 1 0] and [1 0 0] of 7O.8.O7. In contrast to 6O.8.O6 the molecular long axis roughly lies in the direction of the c-axis of the unit cell as expected by a comparison of the molecular length (53.3 Å for an all-trans conformation [19]) with the cell dimensions listed in table 2 (c = 47.17 Å).

Figure 4a shows the projection on the strongest scattering lattice plane (0 2 0). In this figure several important directions are indicated: the direction [3 0 −1] along the molecules excluding the wing groups, [4 0 −1] the direction of the molecular long axis and [5 0 −1] of the spacer (line between the terminal carbon atoms of the spacer) and wing group long axes (line between the terminal carbon atom and the oxygen of the wing group). Figures 5 (a-b) depict the pseudo-hexagonal closed-packed arrangement of the molecules viewed down [3 0 −1] and [4 0 −1] with the traces drawn of the strongly scattering lattice planes (0 2 0), (1 1 3) and (1 −1 3) or (0 2 0), (1 1 4) and (1 −1 4), respectively.

The molecular smectic-like layers are placed parallel to the a,b-plane and piled up in c^*-direction. The molecular long axes are tilted by a smaller angle of about 25 ° towards the c^*-direction (figure 4a) as compared to 60 ° for 6O.8.O6 (figure 2a). Neighboring molecules overlap almost completely in a projection onto a sheet along the molecular axes with minimal interdigitation of the wing groups proceeding to the next layer (figure 4a).

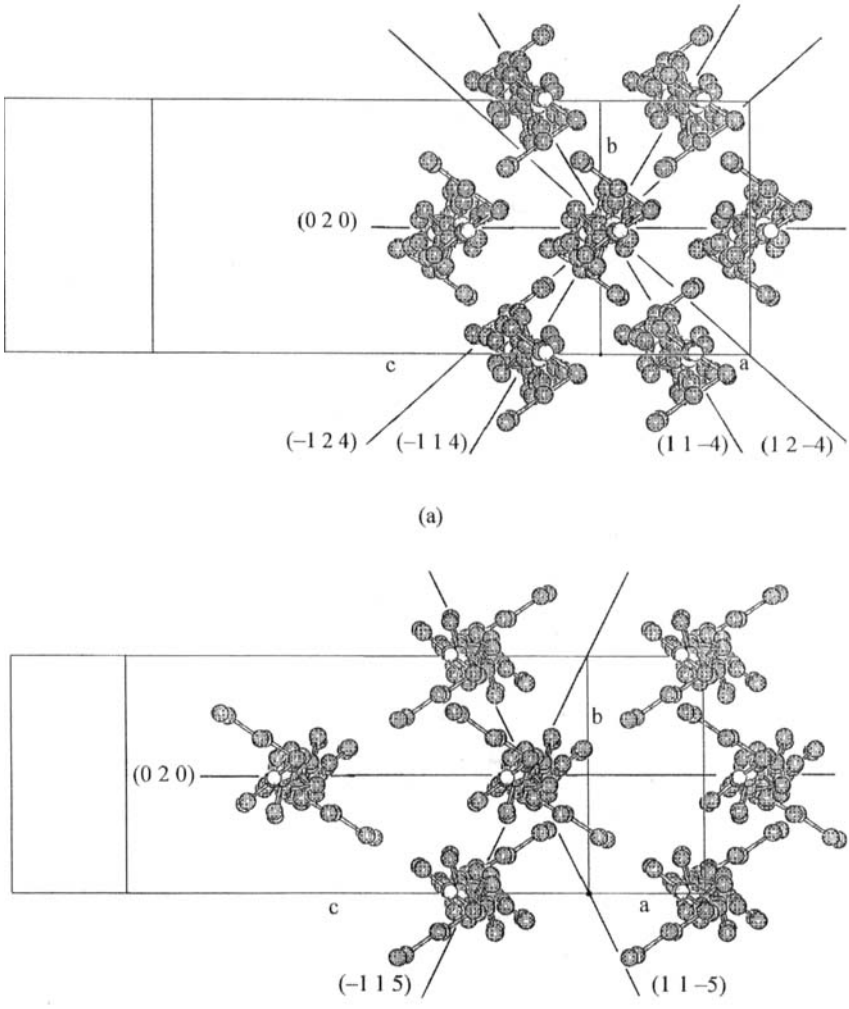

FIGURE 3 Pseudo-hexagonal close-packed arrangement of 6O.8.O6 without hydrogen atoms. Projection (a) along [4 0 1] (molecular long axis) with the traces of the strongly scattering lattice planes (0 2 0), (-1 2 4), (1 2 −4), (-1 1 4) and (1 1 −4) and (b) along [5 0 1] (spacer long axis including the mesogenic units) with the traces of (0 2 0), (-1 1 5) and (1 1 −5). (b) shows clearly that the wing groups fall out of the direction [5 0 1]

At higher temperature an SmG phase appears (table I) [3,15]. DSC measurements indicate that a second crystalline phase KIa occurs in the heating cycle between the

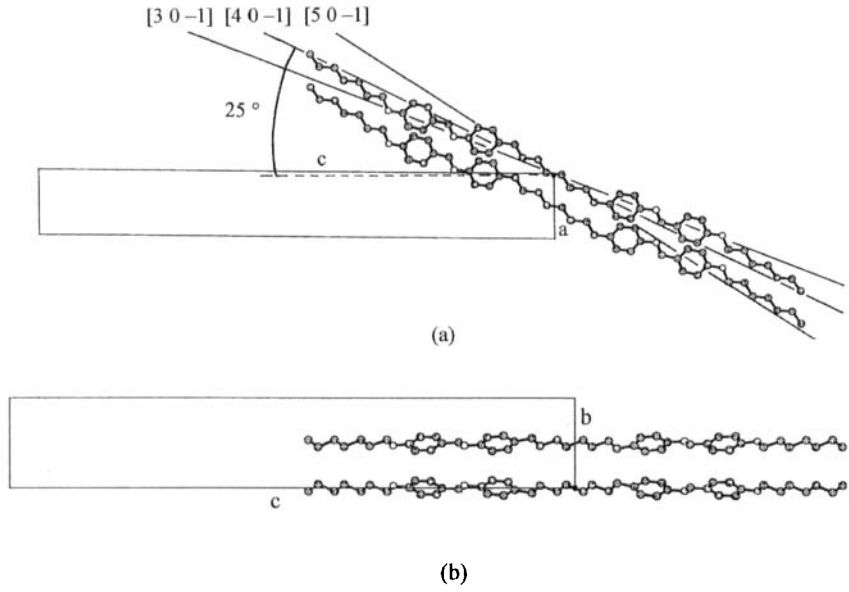

FIGURE 4 Schematic representation along the crystallographic directions (a) [0 1 0] and (b) [1 0 0] of 7O.8.O7 without hydrogen atoms. (a) is the projection on the strongest scattering lattice plane (0 2 0); [3 0 –1] indicates the direction of the molecules excluding the wing groups, [4 0 –1] the direction of the molecular long axis and [5 0 –1] the direction of the spacer and wing group axes

KI and SmG phase which is omitted by cooling [3]. Without consideration of this second crystalline phase the transition of KI into SmG presumably involves a change in direction of the molecular axis along c by about 25 °. The c-dimension of the SmG phase was established to 45.2 Å [3,15]. Since this value is somewhat shorter than the molecular length of 52.5 Å in the KI phase, a change in conformation has to be assumed which is not surprising, because of the most extended shape of the molecules in the KI phase.

The angle between the molecular long axis – the expected c-dimension in the SmG phase – and the a,b-plane in the KI phase corresponds to the angle ß of the monoclinic unit cell of the SmG phase [3,15]. Therefore, only an slight parallel shift of the molecules is expected (figure 4a).

4. CONCLUSION

The crystal structures of two precursors of highly ordered smectic phases are presented. They transform as the two homologues 4O.8.O4 and 5O.8.O5 [2] with

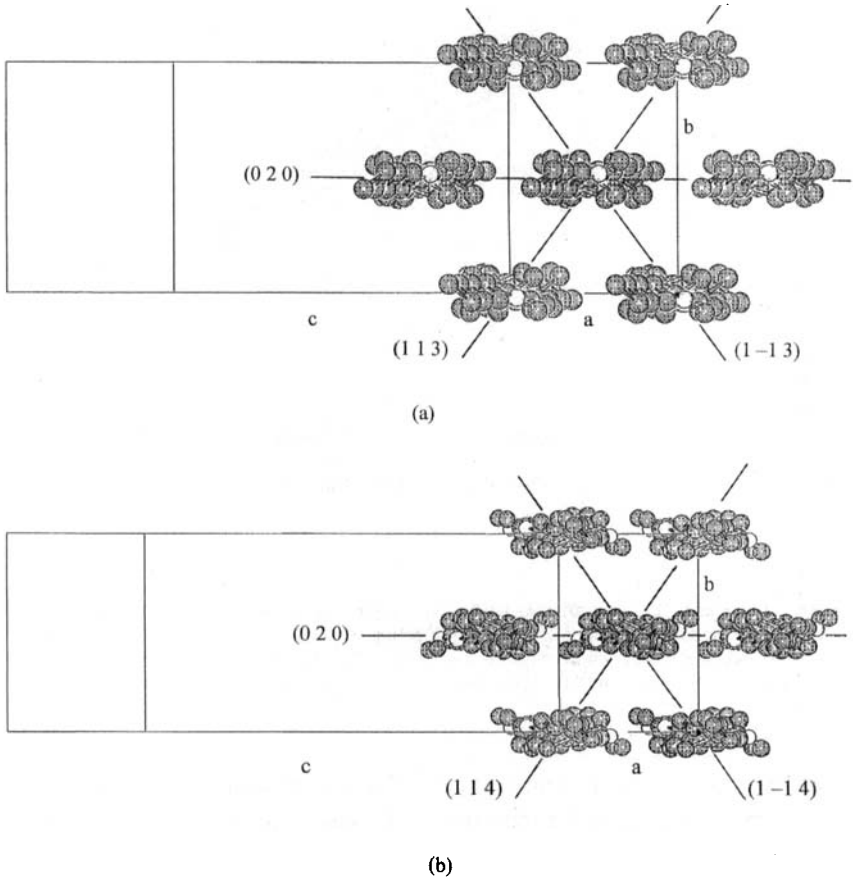

FIGURE 5 Pseudo-hexagonal close-packed arrangement of 7O.8.O7 without hydrogen atoms. Projection (a) along [3 0 −1] (direction of the spacer and mesogenic units) with the traces of the strongly scattering lattice planes (0 2 0), (113) and (1 −1 3) and (b) along [4 0 −1] (molecular long axis) with the traces of (0 2 0), (114) and (1 −1 4)

shorter wing groups to an SmG phase at higher temperature regardless of the actual detailed molecular shape of the individual compounds. Although the packing of the crystalline structure and the SmG phase are quite different as discussed in 3.2.1. and 3.2.2., with the knowledge available at the present, it seems at least possible to predict the general packing arrangements to some extent.

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