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The Molecular and Crystal Structure of α,ω-bis [4-(4′-butyloxybenzylideneiminophenyl)] (40.8.04) and α,ω-bis [4-(4′-pentyloxybenzylideneiminophenyl (50.8.05)

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The Molecular and Crystal Structure of α,ω-bis [4-(4′-butyloxybenzylideneimino-phenyl)]octane (4O.8.O4) and α,ω-bis [4-(4′-pentyloxybenzylideneiminophenyl)]octane (5O.8.O5)

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The crystal and molecular structures of α,ω-bis[4-(4′-butyloxybenzylideneiminophenyl)]octane (4O.8.O4) and the homologue α,ω -bis[4-(4′-pentyloxybenzylideneiminophenyl)]octane (5O.8.O5) have been determined at room temperature, the starting model obtained by direct methods. These two dimesogenic compounds possess besides two crystalline phases (KI, KII) also SmG phases. The crystals KI of the compound 4O.8.O4 belong to the triclinic system with space group P −1, a = 5.484(3), b = 11.826(8), c = 28.03(3) Å, α = 95.77(5), β = 92.39(5), γ = 96.44(5)° with two molecules per unit cell. The compound 5O.8.O5 crystallizes in the monoclinic system with space group $P2_1/n$ (KI), a = 5.571(2), b = 7.460(2), c = 89.55(3) Å, β = 90.92(2)° with four molecules per unit cell. The structures were refined by full-matrix least-squares calculations to R = 0.069 for 6647/(3340 unique) observed reflections for 4O.8.O4 and to R = 0.106 for 3760/(3329 unique) reflections for 5O.8.O5.

The conformations of the two compounds differ considerably. Nevertheless, the molecules exhibit straight and S-shaped extended forms, respectively. 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.

Keywords: crystal structure; molecular packing; dimesogenic compounds

1. INTRODUCTION

The investigation of the crystal structure of mesogenic compounds seems to be suitable to obtain general information on the molecular arrangement in the LC

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state. Nevertheless, at the present it is an open question whether the knowledge of crystal structure enables to predict the type and properties of mesomorphic phases [1,2]. An extension of systematic investigations of a large number of liquid crystals of different types will certainly help to provide an answer.

The number of liquid crystalline compounds with crystal structures solved is rather small [3]. Most of them are carried out on crystal precursors of nematic or fluid smectic phases of monomesogenic compounds, although it seems more likely that highly ordered phases are most suitable for such investigations, since they resemble the crystalline state. Investigations on dimesogenic systems are rare as well [3].

In this paper structure determinations of the crystalline state of two dimesogenic compounds of the type nO.m.On are presented. The compounds investigated are two homologues of the α,ω-bis[4-(4′-alkyloxybenzylideneiminophenyl)]alkane, the dimeric analogues of the well known monomesogenic series N-(4-n-alkoxybenzylidene)-4′-alkylanilines (nO.m), some of them were also studied in our group [4–6]. Only one crystal structure of a homologous nO.m.On, 4O.2.O4, has been published so far [7]. Furthermore, structures of two other dimesogenic analogues of similar type m.OnO.m, 5.O4O.5 and 5.O5O.5, have been determined [8]. Several crystal structures of the monomesogenic compounds belonging to the type nO.m have been published: 1O.4 [9], 2O.4 [10,11], 4O.2 and 7O.6 [6], 4O.8 [1] and 8O.4 [2]; see also [3]; and the structure of the unsubstituted benzylideneaniline was presented in [12].

Besides information on conformation and packing of mesogenic compounds, the dimesogenic molecules offer the possibility to model thermotropic main chain polymers. The combination of rigid mesogens alternating with flexible spacers and flexible wing groups influences properties of mesogenic compounds such as the thermal range of stability or the distribution on nematic or smectic mesophases [13–17]. The two compounds investigated exhibit both smectic phases of the highly ordered type SmG, resembling the crystalline state, and nematic phases over a wide range of temperature (table I)[18,19].

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*
4O.8.O4	63.9[a] (17.5; 51.9)	121.3 (5.3; 13.5)	125.8 (21.6; 54.2)	182.3 (11.1; 24.3)
5O.8.O5	48.6[a] (16.8; 52.2)	105.0 (12.4; 32.7)	139.2 (12.5; 30.2)	171.8 (9.9; 22.3)

a. Broad signal.

2. EXPERIMENTAL – STRUCTURE SOLUTION AND REFINEMENT

The synthesis of the dimesogenic compounds has been described previously [18,20]. Crystals suitable for an X-ray determination were obtained by slow crystallization from toluene and ethyl acetate at room temperature. Data collection was performed with a CAD4 single crystal diffractometer with MoK_α radiation and data processing and refinement against F with the MolEN package of Enraf Nonius, Delft [21]. The hydrogen atoms were placed at respective 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 conformation and packing of the structures were produced with SCHAKAL 92 [22].

TABLE II Summary of crystallographic data

	40.8.O4	*50.8.O5*
Molecular formula	$C_{42}H_{52}N_2O_2$	$C_{44}H_{56}N_2O_2$
Formula weight/g·mol^{-1}	616.89	644.95
Crystal system	triclinic	monoclinic
Space group	P −1 (No. 2)	P 2_1/n (No. 14)
a/Å	5.484(3)	5.571(2)
b/Å	11.826(8)	7.460(2)
c/Å	28.03(3)	89.55(3)
α/°	95.77(5)	90
β/°	92.39(5)	90.92(2)
γ/°	96.44(5)	90
V/Å^3	1794.5(24)	3721(2)
D_{cal}/g·cm^{-3}	1.14	1.15
Z	2	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	18	24
Scan range	8° < θ < 19°	9° < θ < 19°
F(000)	668	1400
Reflections collected	6647	3760
Unique data	3340	3329
Significant I's (> 3σ)	2222	1746
Data collection	1° ≤ θ ≤ 20°	1° ≤ θ ≤ 20°
Parameters refined	415	433
R	0.069	0.106
R_w	0.081	0.128
Highest peak/e·Å^{-3} in Δρ	0.35(8)	0.43(9)
Crystal color	colorless	colorless
Crystal size	parallelepiped	platelet

3. RESULTS AND DISCUSSION

3.1. Molecular geometry and conformation

3.1.1. Molecular geometry

Bond lengths and angles of the homologues 4O.8.O4 and 5O.8.O5 agree closely with literature data found for the monomeric analogues of the type nO.m e.g. 4O.2 and 7O.6 [6], 4O.8 [1], 8O.4 [2], 1O.4 [9] and 2O.4 [10,11] or the dimesogenic analogues 5.O4O.5 and 5.O5O.5 of the type m.OnO.m [8] and the homologue 4O.2.O4 [7]. Figures 1 and 2 represent the molecular structures and the numbering scheme of the non-hydrogen atoms for 4O.8.O4 and 5O.8.O5, respectively. In tables III and IV the fractional coordinates are listed.

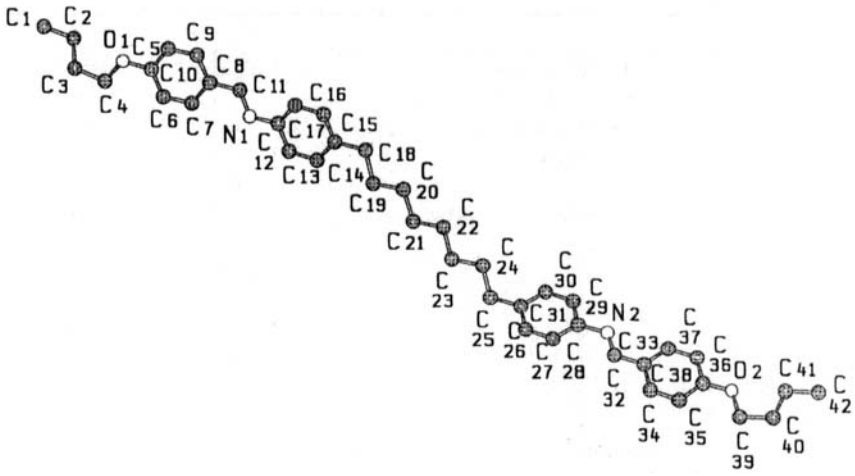

FIGURE 1 The molecular structure of 4O.8.O4 with the numbering scheme

TABLE III Atomic coordinates and equivalent isotropic displacement factors B_{eq} of 4O.8.O4 with their estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
O1	0.0854(5)	−0.7209(2)	−0.34279(8)	5.55(6)
O2	−0.6485(5)	1.4337(2)	0.41394(9)	5.88(6)
N1	0.0408(6)	−0.2995(2)	−0.1840(1)	5.23(8)
N2	−0.5658(6)	0.9993(2)	0.26489(9)	4.61(7)
C1	0.110(1)	−1.0493(3)	−0.4250(2)	9.2(2)
C2	0.1133(9)	−0.9547(3)	−0.3839(2)	7.2(1)
C3	−0.1129(9)	−0.8961(3)	−0.3842(2)	6.8(1)

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
C4	−0.1194(8)	−0.8071(3)	−0.3419(1)	5.7(1)
C5	0.1086(7)	−0.6295(2)	−0.3085(1)	4.27(8)
C6	−0.0654(7)	−0.6120(3)	−0.2744(1)	4.83(9)
C7	−0.0291(7)	−0.5155(3)	−0.2423(1)	4.87(9)
C8	0.1799(7)	−0.4369(3)	−0.2416(1)	4.43(9)
C9	0.3526(7)	−0.4584(3)	−0.2753(1)	4.71(9)
C10	0.3153(7)	−0.5537(3)	−0.3084(1)	4.86(9)
C11	0.2123(7)	−0.3326(3)	−0.2085(1)	4.74(9)
C12	0.0731(7)	−0.1943(3)	−0.1539(1)	4.56(9)
C13	−0.1040(7)	−0.1774(3)	−0.1216(1)	5.4(1)
C14	−0.0905(7)	−0.0788(3)	−0.0908(1)	5.4(1)
C15	0.1014(7)	0.0061(3)	−0.0905(1)	4.46(9)
C16	0.2777(8)	−0.0095(3)	−0.1233(1)	6.2(1)
C17	0.2630(8)	−0.1080(3)	−0.1551(1)	6.5(1)
C18	0.1323(8)	0.1142(3)	−0.0554(1)	5.4(1)
C19	−0.1012(7)	0.1493(3)	−0.0331(1)	5.1(1)
C20	−0.0558(8)	0.2636(3)	−0.0037(1)	5.4(1)
C21	−0.2755(8)	0.3009(3)	0.0215(1)	5.7(1)
C22	−0.2295(8)	0.4120(3)	0.0537(1)	5.6(1)
C23	−0.4530(8)	0.4526(3)	0.0753(1)	5.8(1)
C24	−0.4096(8)	0.5609(3)	0.1095(1)	5.4(1)
C25	−0.6405(8)	0.5976(3)	0.1304(1)	6.5(1)
C26	−0.6177(7)	0.7043(3)	0.1641(1)	4.71(9)
C27	−0.7859(7)	0.7818(3)	0.1624(1)	5.2(1)
C28	−0.7767(7)	0.8796(3)	0.1938(1)	5.2(1)
C29	−0.5915(7)	0.9035(3)	0.2303(1)	4.20(8)
C30	−0.4180(7)	0.8267(3)	0.2323(1)	5.03(9)
C31	−0.4295(7)	0.7293(3)	0.2004(1)	5.32(9)
C32	−0.7220(7)	1.0677(3)	0.2697(1)	4.63(9)
C33	−0.7060(7)	1.1636(2)	0.3059(1)	4.31(8)
C34	−0.8835(7)	1.2374(3)	0.3089(1)	5.3(1)
C35	−0.8747(7)	1.3290(3)	0.3438(1)	4.95(9)
C36	−0.6794(7)	1.3466(3)	0.3778(1)	4.54(9)
C37	−0.4991(7)	1.2738(3)	0.3757(1)	5.00(9)
C38	−0.5121(7)	1.1836(3)	0.3409(1)	4.83(9)
C39	−0.8226(8)	1.5124(3)	0.4191(1)	6.6(1)
C40	−0.7322(9)	1.6025(3)	0.4587(2)	6.8(1)
C41	−0.497(1)	1.6709(3)	0.4489(1)	7.5(1)
C42	−0.407(1)	1.7645(4)	0.4887(2)	10.6(2)

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

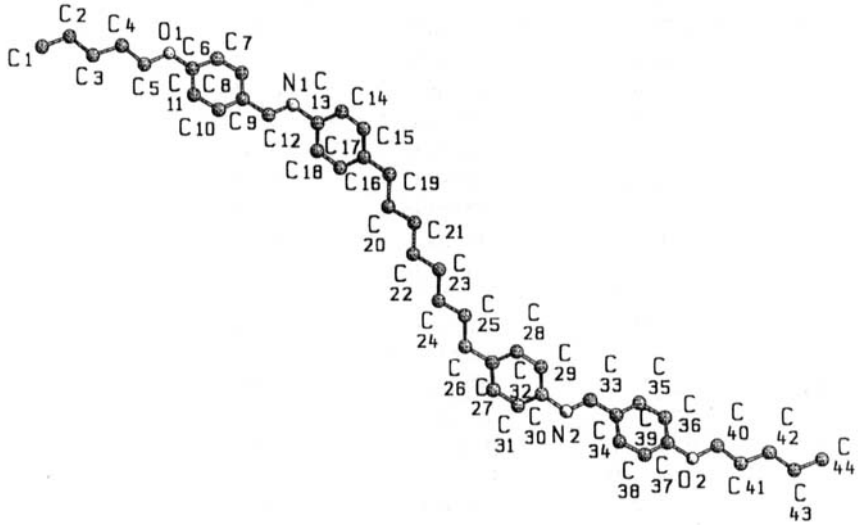

FIGURE 2 The molecular structure of 5O.8.O5 with the numbering scheme

TABLE IV Atomic coordinates and equivalent isotropic displacement factors B_{eq} of 5O.8.O5 with their estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
O1	0.624(1)	0.778(1)	0.08028(9)	4.2(2)
O2	0.413(1)	0.820(1)	0.43142(9)	4.9(2)
N1	0.886(2)	0.813(1)	0.1503(1)	3.3(3)
N2	0.116(2)	0.842(1)	0.3625(1)	3.1(2)
C1	0.022(3)	0.817(2)	0.0213(2)	7.8(5)
C2	0.237(3)	0.762(2)	0.0306(2)	6.6(5)
C3	0.220(2)	0.829(2)	0.0468(2)	4.7(4)
C4	0.435(2)	0.775(2)	0.0567(1)	4.5(4)
C5	0.414(2)	0.834(2)	0.0723(2)	4.3(4)
C6	0.633(2)	0.799(2)	0.0952(1)	3.1(3)
C7	0.831(2)	0.728(2)	0.1031(1)	3.4(3)
C8	0.853(2)	0.738(2)	0.1182(1)	3.3(3)
C9	0.674(2)	0.814(2)	0.1263(1)	2.8(3)
C10	0.474(2)	0.884(2)	0.1190(1)	3.4(3)
C11	0.453(2)	0.872(2)	0.1035(1)	3.5(3)
C12	0.694(2)	0.835(2)	0.1427(1)	3.2(3)
C13	0.880(2)	0.831(2)	0.1663(1)	2.4(3)
C14	1.076(2)	0.912(2)	0.1740(1)	2.0(3)
C15	1.068(2)	0.925(2)	0.1889(1)	2.8(3)
C16	0.881(2)	0.859(2)	0.1973(1)	2.8(3)
C17	0.695(2)	0.772(2)	0.1895(1)	2.9(3)

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
C18	0.693(2)	0.752(2)	0.1743(1)	2.7(3)
C19	0.889(2)	0.885(2)	0.2138(1)	3.5(3)
C20	0.662(2)	0.839(2)	0.2227(1)	2.8(3)
C21	0.676(2)	0.887(2)	0.2389(1)	3.3(3)
C22	0.452(2)	0.840(2)	0.2476(1)	3.8(3)
C23	0.470(2)	0.890(2)	0.2640(1)	3.0(3)
C24	0.250(2)	0.841(2)	0.2731(1)	3.3(3)
C25	0.275(2)	0.881(2)	0.2893(1)	3.5(3)
C26	0.062(2)	0.831(2)	0.2986(1)	2.4(3)
C27	0.083(2)	0.838(2)	0.3152(1)	2.4(3)
C28	0.273(2)	0.920(2)	0.3229(2)	3.2(3)
C29	0.288(2)	0.919(2)	0.3384(1)	3.4(3)
C30	0.109(2)	0.843(2)	0.3467(1)	2.2(3)
C31	–0.082(2)	0.770(2)	0.3391(1)	3.2(3)
C32	–0.097(2)	0.765(2)	0.3237(1)	2.7(3)
C33	0.312(2)	0.802(2)	0.3695(1)	3.2(3)
C34	0.337(2)	0.806(2)	0.3853(1)	2.8(3)
C35	0.543(2)	0.734(2)	0.3918(1)	3.9(3)
C36	0.571(2)	0.727(2)	0.4075(1)	3.1(3)
C37	0.405(2)	0.808(2)	0.4160(1)	3.6(3)
C38	0.200(2)	0.883(2)	0.4097(1)	3.2(3)
C39	0.165(2)	0.883(2)	0.3945(1)	3.2(3)
C40	0.631(2)	0.767(2)	0.4387(2)	4.9(4)
C41	0.619(3)	0.818(2)	0.4546(2)	6.0(4)
C42	0.841(2)	0.765(2)	0.4636(2)	5.1(4)
C43	0.836(2)	0.815(2)	0.4797(2)	6.1(4)
C44	1.052(3)	0.760(3)	0.4888(2)	8.6(6)

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(cosγ) B(1,2) + ac(cos β) B(1,3) + bc(cos α) B(2,3)].

The mean values of the bond lengths and angles of the aromatic rings are as follows: 4O.8.O4: ring A (C5 to C10) 1.382(5) Å, ring B (C12 to C17) 1.376(5) Å ring C (C26 to C31) 1.387(5) Å and ring D (C33 to C38) 1.382(5) Å with 120.0(3)°; 5O.8.O5: ring A (C6 to C11) 1.38(2) Å, ring B (C13 to C18) 1.39(2) Å, ring C (C27 to C32) 1.38(2) Å and ring D (C34 to C39) 1.38(2) Å with 120(1)° for all aromatic carbon atoms.

The C=N and C-N distances in the azomethine group within the mesogens are 1.262(5) Å and 1.420(4) Å between ring A and B and 1.244(5) Å and 1.406(4) Å between ring C and D for 4O.8.O4 and 1.27(1) Å, 1.44(1) Å and 1.29(1) Å and 1.42(1) Å for 5O.8.O5, respectively. The average bond lengths and angles in the alkyl and alkoxy chains are determined to 1.506(6) Å and 114.0(4)° for 4O.8.O4 and 1.51(2) Å and 114(1)° for 5O.8.O5.

The average values for the bond lengths of the C-C single bond are relatively short compared with the actual empirically established CCDC values (1.531 Å for CH_2-CH_2). But they are comparable with the values determined for other C-C single bonds of similar compounds: the alkyl spacer in α,ω-bis(4-cyanobiphenyl-4′-oxy)heptane [17] or the alkoxy and alkyl chains in bis-(4′-n-butoxybenzal)-2-chloro-1,4-phenylinediamine [23] or the monomeric 4O.8 and 8O.4 [1,2] for example. This seems to be a result of high thermal motion in the wing groups [1]. The temperature factors of the atoms at the chain end (Cl to C4 and C39 to C42 for 4O.8.O4 or C1 to C5 and C40 to C44 for 5O.8.O5) are relatively high, but not for the spacer atoms (tables III and IV).

3.1.2. Molecular conformation

The molecular conformations of 4O.8.O4 and 5O.8.O5 differ considerably from each other. In 4O.8.O4, all bonds in the alkoxy and alkyl groups have nearly trans conformation except one gauche conformation near the oxygen in each wing group with torsion angles τ(C2-C3-C4-O1) = 60.7(0.4)° and τ(O2-C39-C40-C41) = 62.7(0.4)° (table V). Despite of these gauche conformations the molecule exhibits an almost extended shape as entity with a molecular length of 43.5 Å as compared with 45.7 Å calculated for an all-trans conformation [24]. This shape agrees well with that of the dimeric compound 5.O4O.5 where the alkoxy spacer is not planar but shows one bond in gauche conformation near the oxygen [8]. In contrast to 4O.8.O4, in 5O.8.O5 the alkyl and alkoxy chains exist in the trans conformation as in the similar compound 5.O5O.5 [8] or in α,ω-bis(4-cyanobiphenyl-4′-oxy)heptane [17]. Nevertheless, the molecule is not completely straight extended because the wing groups including the mesogens are not connected to the spacer in a trans conformation (the corresponding torsion angles are τ(C25-C26-C27-C32) = −169.4(1.1)° and τ(C40-O2-C37-C36) = 10.1(1.8)° or τ(C15-C16-C19-C20) = 170.2(1.1)° and τ(C5-O1-C6-C11) = 0.0(1.7)°, cf. figure 2). The result is an S-shaped form (figure 2) with a molecular length of 45.3 Å which differs from the value calculated for the all-trans form (48.2 Å [24]; the molecular length and the overall molecular axis are defined as the distance or the line between the terminal carbon atoms). In both compounds the mesogenic long axes of the rings A and B are nearly colinear to those of the rings C and D with angles of 177.9° (4O.8.O4) and 175.2° (5O.8.O5) between the mesogenic axes (the mesogenic long axis is defined as the line between the carbon atoms at the end of the mesogenic unit, e.g. between C5 and C15 (ring A and B) for compound 4O.8.O4).

TABLE V Selected torsion angles (°) for non-hydrogen atoms in 4O.8.O4 and 5O.8.O5 with their estimated standard deviations in parentheses

4O.8.O4		*5O.8.O5*	
(C9-C8-C11-N1)	166.1(0.3)	(C10-C9-C12-N1)	−163.8(1.2)
(C8-C11-N1-C12)	−176.6(0.3)	(C9-C12-N1-C13)	−177.7(1.1)
(C11-N1-C12-C13)	−167.0(0.3)	(C12-N1-C13-C14)	−142.4(1.2)
(C30-C29-N2-C32)	−172.7(0.3)	(C31-C30-N2-C33)	137.3(1.2)
(C29-N2-C32-C33)	177.3(0.3)	(C30-N2-C33-C34)	177.5(1.1)
(N2-C32-C33-C34)	179.0(0.3)	(N2-C33-C34-C35)	170.2(1.2)
(C2-C3-C4-O1)	60.7(0.4)	(C3-C4-C5-O1)	−179.4(1.1)
(O2-C39-C40-C41)	62.7(0.4)	(O2-C40-C41-C42)	179.2(1.2)

TABLE VI Dihedral angles (°) between various planes of 4O.8.O4 and 5O.8.O5

4O.8.O4			*5O.8.O5*		
plane	*plane*	*angle*	*plane*	*plane*	*angle*
A	B	5.6	A	B	56.1
A	C	63.4	A	C	123.9
A	D	59.5	A	D	1.6
B	C	66.2	B	C	175.0
B	D	62.8	B	D	57.4
C	D	5.7	C	D	122.8

4O.8.O4: A (C5 to C10), B (C12 to C17), C (C26 to C31) and D (C33 to C38)
5O.8.O5: A (C6 to C11), B (C13 to C18), C (C27 to C32) and D (C34 to C39)

The planes of the two phenyl rings in one mesogenic unit are nearly coplanar for 4O.8.O4, the planes of different mesogens are twisted by approximately 63° (table VI). For the homologue 4O.2.O4 the results are comparable: the two planes in one mesogenic unit show a high degree of coplanarity, but the planes between the two mesogens separated by the spacer are twisted by 63.5° [7]. In 5O.8.O5, the planes of the phenyl rings in each mesogen are rotated by an angle of about 56° and −57°, respectively. These differences in the conformation of 4O.8.O4 and 5O.8.O5 are reflected in the corresponding torsion angles (cf. table V).

Comparing the mutual orientation of the phenyl rings, the compounds 5.O4O.5 and 5.O5O.5 significantly differ from those reported here: the two rings in the first mesogenic unit are nearly coplanar (15° for 5.O4O.5 and 10° for 5.O5O.5 (6° for the second independent molecule)), but the rings of the second mesogenic unit are twisted to a higher degree (33° for 5.O4O.5, 46° and 48° for 5.O5O.5) [8].

3.2. Molecular packing

3.2.1. Packing of 4O.8.O4

Figures 3 (a-c) represent the crystal structure in projection along the three crystallographic directions [1 0 0], [0 1 0] and [0 0 1] of 4O.8.O4. The molecular long axes don't follow one of these basic directions and is confirmed by the size of the cell dimensions listed in table II of which none comes close to the expected molecular length of 45.7 Å for an all-trans conformation [24]. The projections on two strongly scattering lattice planes (0 2 –6) and (1 1 –2) are depicted in figures 4 (a-b). The direction [1 –3 –1] represents the direction of the molecular long axis. The view down this molecular long axis shows a pseudo-hexagonal arrangement of the molecules (figure 5).

The molecular packing consists of layers parallel to the a,b-plane, piled up in c^*-direction with a layer spacing near the c-dimension and minimal interdigitation of the wing groups (figure 6). Within the layers the molecules form a pseudo-hexagonal packing with four adjacent molecules pointing in opposite direction and two in the same direction (figure 5).

Because of the twisting of the planes of the two mesogens in one molecule, the dipole moments of the C=N-C and C-O-C bonds are placed in quite different directions. A compensation of the dipole moments is realized through the symmetry of the space group P –1 by the stacking of different sheets parallel the a,c-plane or b,c-plane (figures 3 (a-b)).

On the one hand the twisted conformation of the mesogenic planes might hinder the shifting of the molecules along the molecular long axis at the transition into the liquid crystalline phases. On the other hand it gives rise to an efficient packing of the molecules [27]. At this point it should be emphasized that a second crystalline phase (KII), whose structure is not yet determined, occurs between the crystalline phase reported here (KI) and the SmG phase at higher temperature (table I) [18,19]. The KII phase shows a powder diffraction pattern with the longest spacing of about 75 % of the expected molecular length (KI: 62 %). This indicates that the molecular long axis also does not follow one of the basic crystallographic directions as in the KI phase [18].

3.2.1. Packing of 5O.8.O5

Figures 7 (a-c) represent the crystal structure in projection along the three crystallographic directions [1 0 0], [0 1 0] and [0 0 1] of 5O.8.O5. In contrast to 4O.8.O4 the molecular long axis approximately follows the c-axis of the cell: two molecules lie nearly along the [0 0 1]-direction one succeeding the other (figures 7 (a-b)) resulting in a very long c dimension of 89.55(3) Å, c twice the molecular

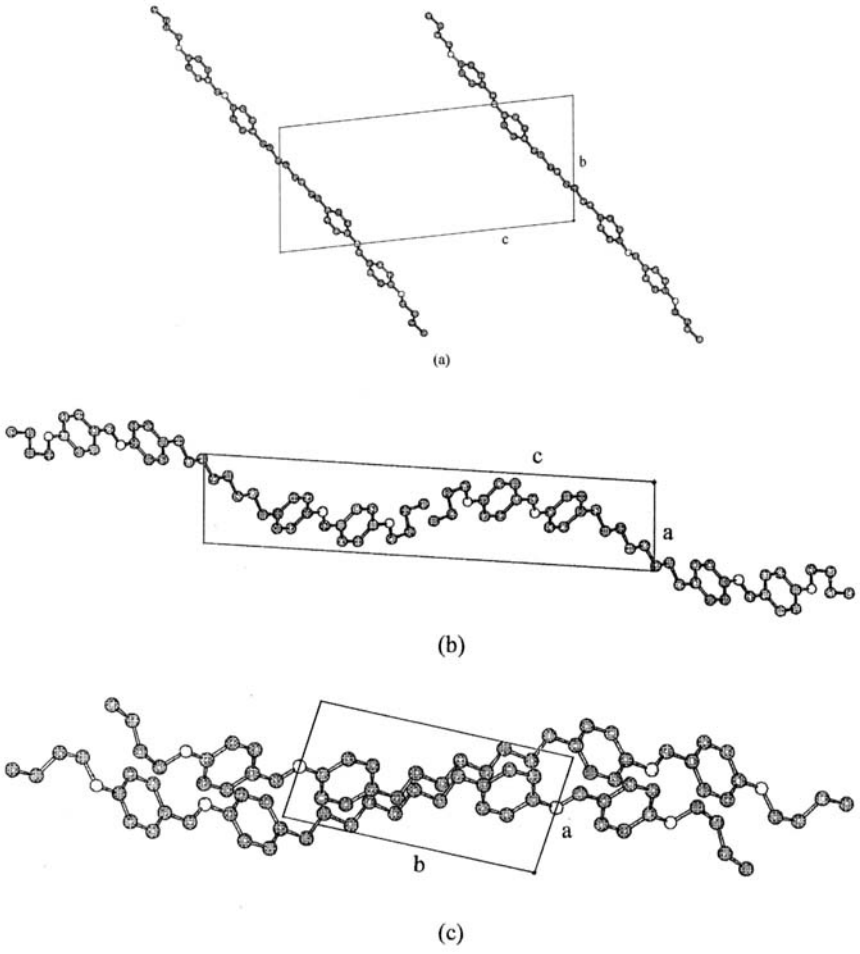

FIGURE 3 Schematic representation of 4O.8.O4 without hydrogen atoms along the three crystallographic directions (a) [1 0 0], (b) [0 1 0] and (c) [0 0 1]

length and four molecules per unit cell (table II). Figure 7 (b) also shows the projection on the strongest scattering lattice plane (0 2 0) indicating the direction [3 0 1] as the mesogenic and molecular long axis, [7 0 1] the directions of the wing groups inclusive the mesogenic units, [7 0 −1] and [9 0 1] the direction of the spacer long axis and the wing groups, respectively. The view down the mesogenic long axis with the traces of the strongly scattering lattice planes (0 2 0), (1 1 −3) and (-1 1 3) is depicted in figure 8 (a). Figure 8 (b) shows the projection along the spacer long axis.

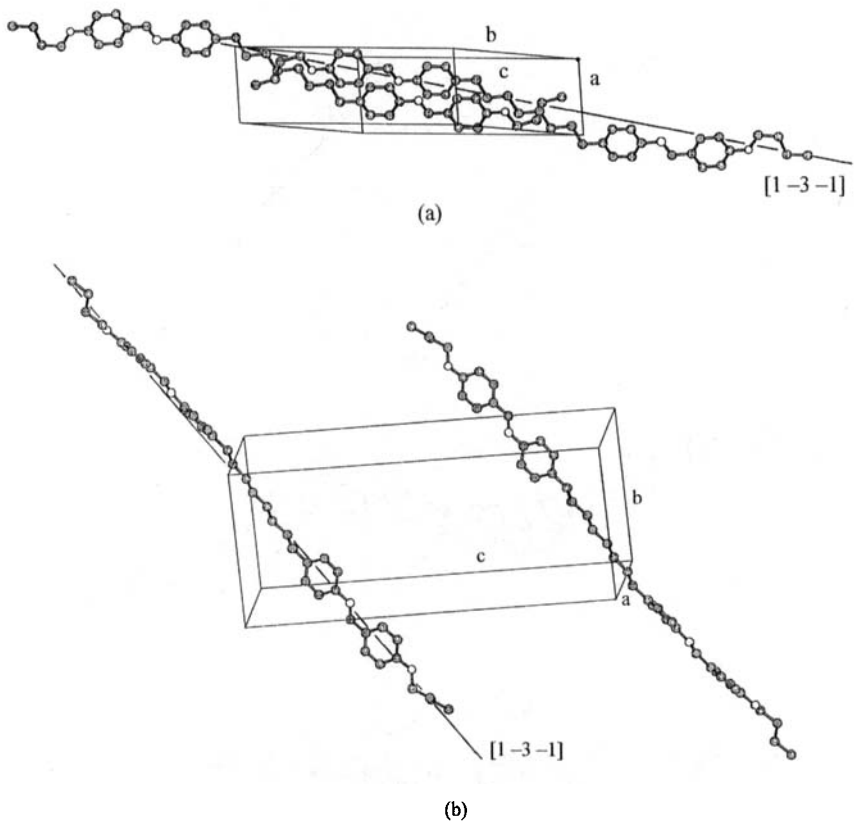

FIGURE 4 Projection on the strongly scattering lattice planes (a) (0 2 –6) and (b) (1 1 –2) with the direction [1 –3 –1] (molecular long axis) of 4O.8.O4 without hydrogen atoms

The molecular packing consists of layers parallel to the a,b-plane, piled up in c^*-direction. Neighboring molecules are not shifted against each other in one layer and minimal interdigitation of layers only occurs. An almost complete compensation of the dipole moments in direction and size of the C=N-C and C-O-C bonds already occurs within a molecule, in contrast to 4O.8.O4, because the same two dipoles are pointing in opposite directions in a sheet parallel the a,c-plane (figure 7 (b)).

At higher temperatures another crystalline phase KII follows (table I) with the first diffraction peak at 29.7 Å [18] which is about 62 % of the expected molecular length. A comparable value about 62 % is obtained for the KI structure of 4O.8.O4 and suggests similar unit cell dimensions of the KII phase of 5O.8.O5 and the KI phase of 4O.8.O4. Therefore, a shortening of the long cell dimension

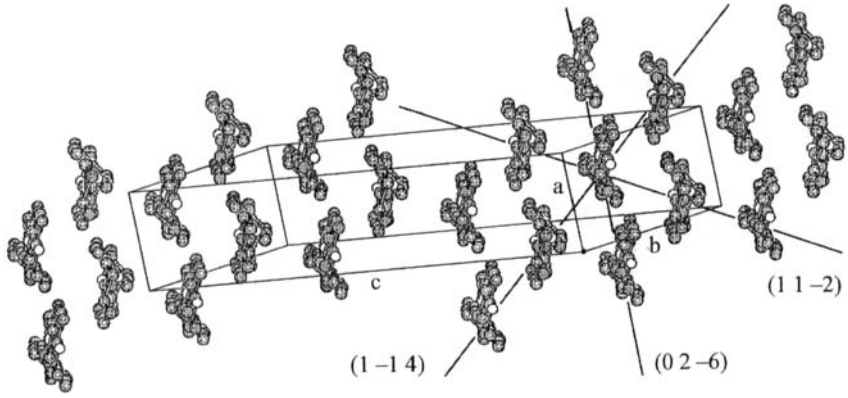

FIGURE 5 Pseudo-hexagonal close-packed molecular arrangement of 4O.8.O4 without hydrogen atoms. Projection along [1 –3 –1] with the traces of the strongly scattering lattices planes (0 2 –6), (1 –1 4) and (1 1 –2). The direction [1 –3 –1] is the view down the molecular long axis

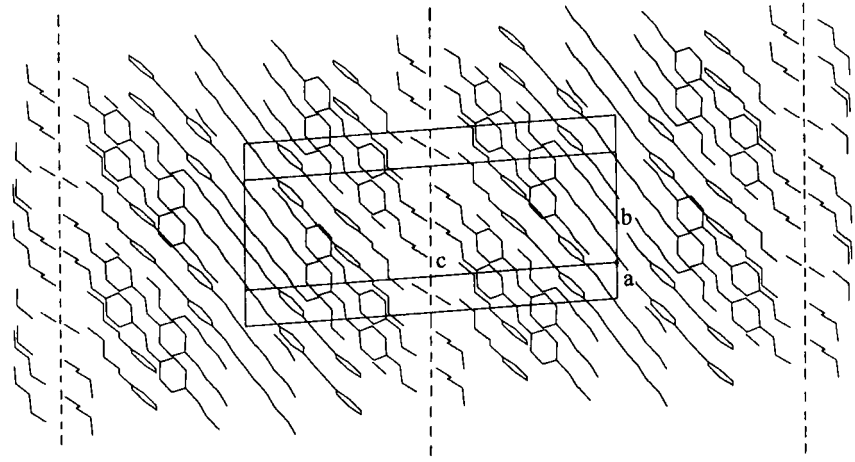

FIGURE 6 Molecular packing with layers parallel to the a,b-plane, piled up in c*-direction of 4O.8.O4

of 5O.8.O5 from the KI to KII phase must result in a different orientation of the c-axis in respect to the molecular long axis. The fundamental packing of the molecules may be kept the same.

At further heating the second crystalline phase KII transforms into the highly ordered SmG phase (table I) [18]. In the C-centered monoclinic cell of the SmG

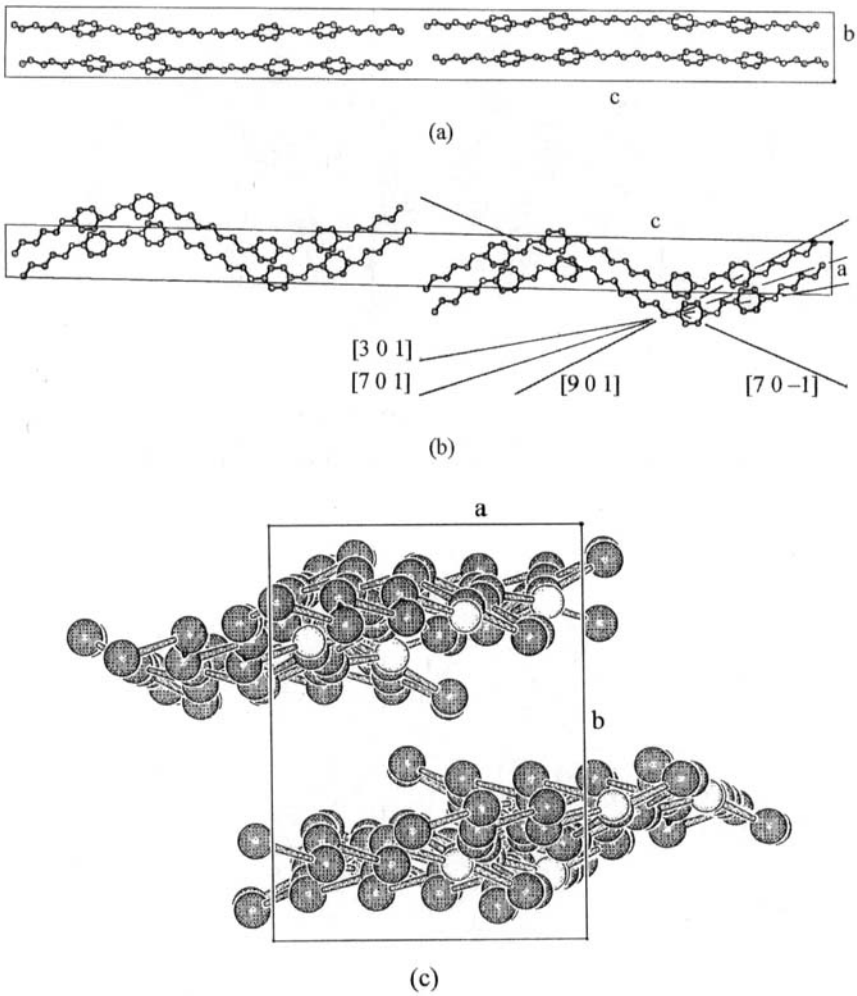

FIGURE 7 Schematic representation along the three crystallographic directions (a) [1 0 0], (b) [0 1 0] and (c) [0 0 1] of 5O.8.O5 without hydrogen atoms. (b) is the projection on the strongest scattering lattice (0 2 0); the direction [3 0 1] indicates the mesogenic and molecular long axis, [7 0 1] the direction of the wing group inclusive the mesogenic unit, [7 0 –1] and [9 0 1] the direction of the spacer long axis and the wing group, respectively

phase, the molecular long axes lie along the c-direction and form a nearly hexagonal packing, which has been encountered in the structurally determined crystalline phase of KI. In the case considered here, it was possible to solve the difficult problem of the determination of the unit cell dimensions of the SmG phase. This

evaluation will be dealt with in a further paper [19]. The c dimension of the monoclinic SmG phase was established to 41.6 Å [18] which is close to the layer spacing in KI with c/2 = 44.8 Å, and it was confirmed that only an insignificant shift of the molecules along c of KI leads to the SmG phase.

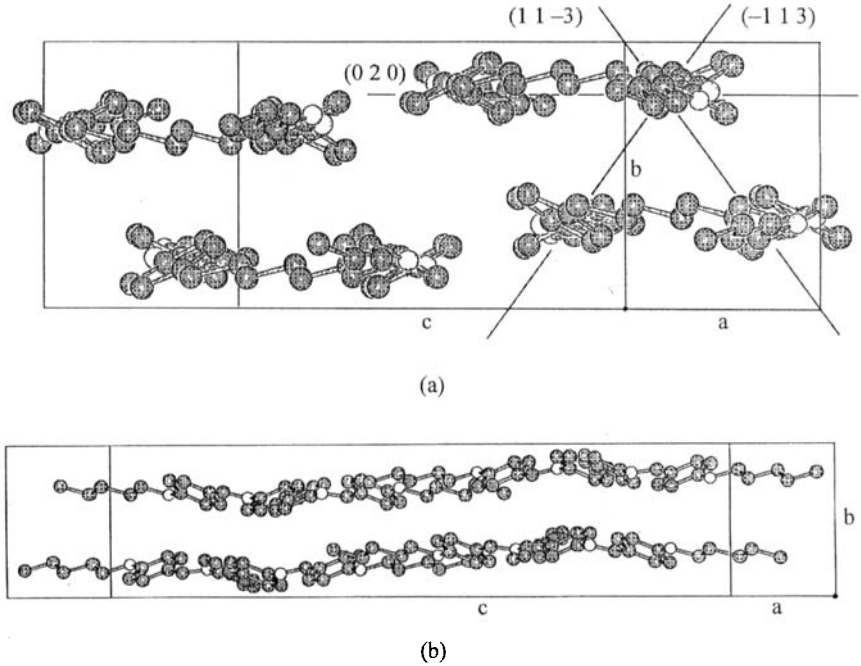

FIGURE 8 Projection (a) along [3 0 1] (mesogenic long axis) with the traces of the strongly scattering lattices (0 2 0), (1 1 –3) and (-1 1 3) and (b) along [7 0 –1] (spacer long axis) of 5O.8.O5 without hydrogen atoms

4. CONCLUSION

In this paper the crystal structures of two crystal precursors of highly ordered smectic phases are presented. In spite of the differently extended molecular shape of 4O.8.O4 and 5O.8.O5 – 4O.8.O4 exhibits an straight extended shape, 5O.8.O5 an S-shaped form - both compounds transform to a SmG phase at higher temperature. At the present it seems difficult to correlate the crystalline structure with the type and properties of the mesomorphic phases without some knowledge of the second crystalline form, not yet determined, before the smectic phases are obtained.

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