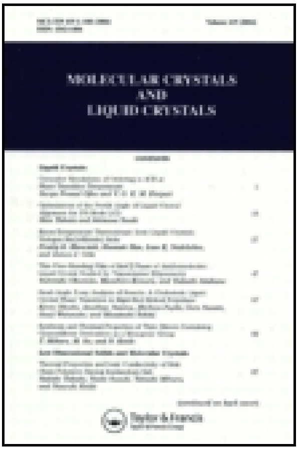

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The Molecular and Crystal Structure of N-(4-n-Pentyloxybenzylidene)-4′-Heptylaniline (5O.7) and N-(4-n-Nonyloxybenzylidene)-4′-Butylaniline (9O.4)

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The Molecular and Crystal Structure of N-(4-n-Pentyloxybenzylidene)-4′-Heptylaniline (5O.7) and N-(4-n-Nonyloxybenzylidene)-4′-Butylaniline (9O.4)

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The crystal and molecular structures of the homologous mesogenic compounds N-(4-n-pentyloxybenzylidene)-4′-heptylaniline (5O.7) and N-(4-n-nonyloxybenzylidene)-4′-butylaniline (9O.4) have been determined at room temperature, the starting model obtained by direct methods. The crystals of both compounds belong to the triclinic system with space group P –1: a = 5.645(3), b = 18.92(1), c = 21.85(1) Å, α = 80.07(4), β = 85.95(4), γ = 84.63(4)° with four molecules per unit cell for 5O.7 and a = 5.570(2), b = 8.227(4), c = 26.614(12) Å, α = 88.40(3), β = 87.84(3), γ = 74.66(4) ° with two molecules per unit cell for 9O.4. The structures were refined by full-matrix least-squares calculations to R = 0.061 for 1792 unique observed reflections for 5O.7 and to R = 0.074 for 983 unique reflections for 9O.4. The conformations of 5O.7 and 9O.4 differ considerably from each other. In the two crystallographically independent molecules of 5O.7 the phenyl rings of one mesogenic group are twisted by 58.0° and 56.1°, respectively. In contrast to these conformations, in 9O.4 they are nearly coplanar. The molecular packing in 9O.4 and 5O.7 differs as well. 9O.4 shows a tilted smectic-like layer structure. The structure of 5O.7 consists of blocks, in which the mesogenic units overlap almost completely. These blocks are arranged in a stepwise shifted fashion. But both compounds transform to a smectic G phase at higher temperature.

Keywords: Monomesogenic Benzylideneanilines of Type nO.m; Crystal Structure; Molecular Packing

1. INTRODUCTION

In this paper the crystal structures are presented of two monomesogenic benzylideneanilines of the type N-(4-n-alkoxybenzylidene)-4′-n-alkylaniline (nO.m),

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50.7 and 90.4. Such compounds are well-known for some time as liquid crystalline compounds with rich smectic polymorphism (see e.g. [1–4]) and are of great importance as reference materials. Crystal structures of further compounds of the type nO.m have been published for 10.4 [5], 20.4 [6, 7], 40.2 and 70.6 [8], 40.8 [9] and 80.4 [10]; see also [11]. The structure of the unsubstituted benzylideneaniline was presented in [12]. The knowledge of the crystal structure of mesomorphic compounds seems to lead to a better understanding of the molecular arrangement in the liquid crystalline state. Both compounds discussed here are crystal precursors of the highly ordered SmG phase. This is most suitable for a comparison of crystalline and liquid crystalline structures because of the similarity of both phases. The phase sequence of 50.7 and 90.4 are as follows [13]:

50.7: Cryst 29.5 SmG 33.9 SmB 51.0 SmC 53.1 SmA 62.8 N 78 °C I
90.4: Cryst 50.5 SmG 67.5 SmF 70.0 SmA 82.5 °C I

2. EXPERIMENTAL, STRUCTURE SOLUTION AND REFINEMENT

The compounds have been synthesized according to standard procedures and recrystallized several times for purification (e.g. [14]). Imperfect single crystals suitable for an X-ray determination were obtained by slow crystallization from ethanol at a temperature of 10°C. Data collection was performed on a CAD4 single crystal diffractometer with MoK$_\alpha$ radiation and data processing and refinement against F with the MolEN package of Enraf Nonius, Delft [15]. The starting model was produced with SIR97 [16]. The hydrogen atoms were placed at respective sites and not refined as well as their isotropic B values. Table I represents the basic crystallographic data. The figures representing conformation and molecular packing were produced with SCHAKAL 92 [17].

TABLE I Summary of crystallographic data of 5O.7 and 9O.4

	5O.7	*9O.4*
Molecular formula	$C_{25}H_{35}NO$	$C_{26}H_{37}NO$
Formula weight/g·mol^{-1}	365.56	379.59
Crystal system	triclinic	triclinic
Space group	P –1 (No. 2)	P –1 (No. 2)
a/Å	5.645(3)	5.570(2)
b/Å	18.92(1)	8.227(4)
c/Å	21.85(1)	26.614(12)
α/°	80.07(4)	88.40(3)
β/°	85.95(4)	87.84(2)

	50.7	*90.4*
$\gamma/°$	84.63(4)	74.66(4)
$V/Å^3$	2285(2)	1175(1)
$D_{cal}/g{\cdot}cm^{-3}$	1.06	1.07
Z	4	2
$\mu(MoK_\alpha)/cm^{-1}$	0.6	0.6
$\lambda(MoK_\alpha)/Å$	0.71073	0.71073
Number of reflections used for lattice parameter refinement	25	25
Scan range	$7° < \theta < 18°$	$8° < \theta < 17°$
F(000)	800	416
Reflections collected	3593	1881
Unique data	3117	1634
Significant I's ($> 3\sigma$)	1792	983
Data collection	$1° < \theta < 18°$	$1° < \theta < 18°$
Parameters refined	487	253
R	0.061	0.074
R_w	0.092	0.095
Highest peak/$e{\cdot}Å^{-3}$ in $\Delta\rho$	0.16(3)	0.18(5)
Crystal color	turbid	colorless
Crystal size	parallelepiped	parallelepiped

3. RESULTS AND DISCUSSION

3.1. Molecular geometry and conformation

3.1.1. Molecular geometry

Figures 1 and 2 represent the molecular structures and the numbering schemes of the non-hydrogen atoms for 50.7 and 90.4, respectively. The fractional coordinates are listed in tables II and III.

The data for bond lengths and angles agree closely with those found for other compounds of the type nO.m [5–10].

The mean values of the bond lengths and angles of the aromatic rings are as follows: 50.7: ring A (C101 to C106) 1.39(1) Å, ring B (C108 to C113) 1.38(1) Å with 120.0(8)° for the first independent molecule and ring C (C201 to C206) 1.39(1) Å and ring D (C208 to C213) 1.39(1) Å with 120.0(8)° for the second molecule; 90.4: ring A (C1 to C6) 1.39(1) Å and ring B (C8 to C13) 1.39(1) Å with 120.0(10)° for all aromatic carbon atoms.

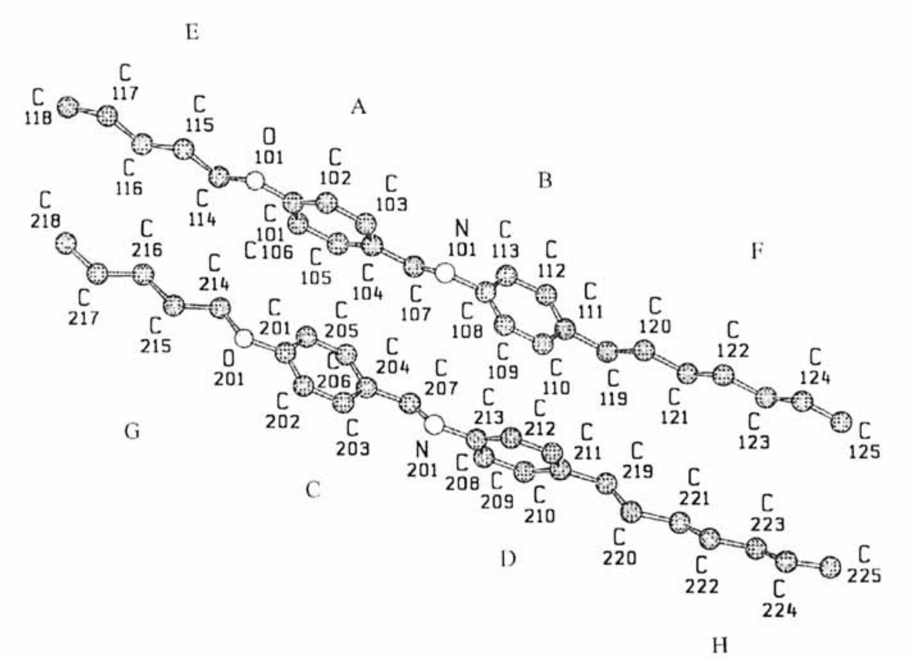

FIGURE 1 The molecular structure of 5O.7 with the numbering scheme

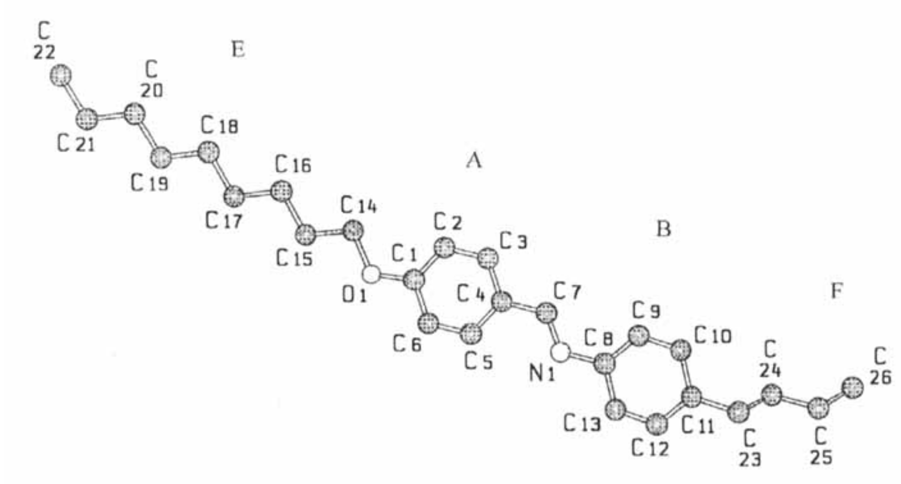

FIGURE 2 The molecular structure of 9O.4 with the numbering scheme

TABLE II Atomic coordinates and equivalent isotropic displacement factors B_{eq} of 5O.7 with their estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
O101	0.2978(8)	0.4542(3)	−0.0512(2)	6.7(1)
O201	−0.1537(8)	0.2781(3)	−0.1438(2)	6.6(1)
N101	0.032(1)	0.2035(3)	0.1708(3)	6.2(2)
N201	−0.390(1)	0.0294(3)	0.0811(3)	5.8(2)
C101	0.294(1)	0.3934(4)	−0.0061(3)	5.9(2)
C102	0.083(1)	0.3900(4)	0.0315(3)	6.2(2)
C103	0.061(1)	0.3318(4)	0.0780(3)	5.5(2)
C104	0.245(1)	0.2762(4)	0.0885(3)	5.5(2)
C105	0.453(1)	0.2823(4)	0.0506(3)	5.6(2)
C106	0.479(1)	0.3391(4)	0.0025(3)	5.7(2)
C107	0.222(1)	0.2162(4)	0.1385(3)	5.0(2)
C108	0.028(1)	0.1450(4)	0.2202(3)	5.1(2)
C109	−0.146(1)	0.0996(4)	0.2270(3)	5.8(2)
C110	−0.158(1)	0.0432(4)	0.2737(3)	6.3(2)
C111	0.013(1)	0.0298(4)	0.3187(3)	6.7(2)
C112	0.188(1)	0.0772(4)	0.3125(3)	7.3(2)
C113	0.202(1)	0.1341(4)	0.2645(3)	6.3(2)
C114	0.512(1)	0.4645(4)	−0.0908(3)	6.4(2)
C115	0.472(1)	0.5366(4)	−0.1321(3)	6.1(2)
C116	0.685(1)	0.5523(4)	−0.1781(4)	7.6(3)
C117	0.656(1)	0.6243(4)	−0.2195(4)	7.4(2)
C118	0.876(2)	0.6430(5)	−0.2608(4)	10.7(3)
C119	0.012(2)	−0.0354(6)	0.3690(4)	10.4(3)
C120	−0.199(2)	−0.0391(5)	0.4112(4)	9.0(3)
C121	−0.202(2)	−0.1060(5)	0.4632(4)	10.4(3)
C122	−0.425(2)	−0.1120(5)	0.5025(5)	12.2(4)
C123	−0.434(2)	−0.1769(5)	0.5533(4)	10.0(3)
C124	−0.653(2)	−0.1860(6)	0.5912(5)	14.9(4)
C125	−0.670(2)	−0.2450(6)	0.6374(5)	14.0(4)
C201	−0.149(1)	0.2251(4)	−0.0912(3)	5.5(2)
C202	−0.337(1)	0.1816(4)	−0.0863(3)	5.6(2)
C203	−0.353(1)	0.1274(4)	−0.0365(3)	5.5(2)
C204	−0.183(1)	0.1144(4)	0.0095(3)	5.7(2)
C205	0.009(1)	0.1586(4)	0.0017(3)	5.7(2)
C206	0.023(1)	0.2142(4)	−0.0471(3)	6.0(2)
C207	−0.197(1)	0.0591(4)	0.0641(3)	5.2(2)

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
C208	−0.390(1)	−0.0244(4)	0.1345(3)	4.8(2)
C209	−0.200(1)	−0.0769(4)	0.1479(3)	5.6(2)
C210	−0.216(1)	−0.1282(4)	0.1994(3)	6.2(2)
C211	−0.414(1)	−0.1307(4)	0.2412(3)	5.9(2)
C212	−0.607(1)	−0.0796(4)	0.2262(3)	6.5(2)
C213	−0.591(1)	−0.0276(4)	0.1749(3)	5.5(2)
C214	0.048(1)	0.3206(4)	−0.1575(4)	7.0(2)
C215	0.022(1)	0.3618(4)	−0.2222(4)	6.8(2)
C216	0.228(1)	0.4090(4)	−0.2440(4)	8.1(3)
C217	0.215(2)	0.4466(5)	−0.3095(4)	10.1(3)
C218	0.420(2)	0.4919(6)	−0.3320(5)	12.4(4)
C219	−0.421(2)	−0.1854(5)	0.2999(5)	10.4(3)
C220	−0.629(2)	−0.2234(5)	0.3152(5)	11.9(3)
C221	−0.637(2)	−0.2748(6)	0.3787(5)	14.1(4)
C222	−0.853(2)	−0.2984(6)	0.4055(5)	13.9(4)
C223	−0.853(2)	−0.3476(7)	0.4664(5)	14.8(4)
C224	−1.082(3)	−0.3645(9)	0.4926(6)	22.2(7)
C225	−1.091(3)	−0.4049(8)	0.5511(6)	18.9(6)

Anisotropically refined displacement parameters are given in the form of their isotropic equivalents defined as (4/3) [a^2B(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)].

TABLE III Atomic coordinates and equivalent isotropic displacement factors B_{eq} of 9O.4 with their estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
O1	−0.2025(7)	0.3245(5)	−0.0209(2)	6.7(1)
N1	0.2432(9)	0.0582(6)	0.1900(2)	6.3(2)
C1	−0.151(1)	0.2429(8)	0.0235(3)	5.5(2)
C2	−0.259(1)	0.1245(7)	0.0449(3)	6.2(2)
C3	−0.189(1)	0.0551(8)	0.0912(3)	6.5(2)
C4	−0.004(1)	0.0972(7)	0.1173(3)	5.6(2)
C5	0.104(1)	0.2192(8)	0.0955(3)	5.7(2)
C6	0.033(1)	0.2902(8)	0.0500(3)	6.1(2)
C7	0.072(1)	0.0240(8)	0.1654(3)	5.9(2)
C8	0.313(1)	−0.0115(8)	0.2374(3)	5.5(2)
C9	0.229(1)	−0.1338(8)	0.2635(3)	6.5(2)
C10	0.310(1)	−0.1928(8)	0.3100(3)	7.2(2)
C11	0.489(1)	−0.1278(9)	0.3345(3)	6.9(2)
C12	0.570(1)	−0.0064(9)	0.3070(3)	7.1(2)

Atom	*x*	*y*	*z*	$B_{eq}/\text{Å}^2$
C13	0.490(1)	0.0520(8)	0.2615(3)	7.0(2)
C14	−0.389(1)	0.2875(8)	−0.0515(3)	6.2(2)
C15	−0.405(1)	0.3952(8)	−0.0976(3)	5.8(2)
C16	−0.599(1)	0.3737(8)	−0.1341(3)	5.8(2)
C17	−0.614(1)	0.4863(8)	−0.1798(3)	5.9(2)
C18	−0.807(1)	0.4688(8)	−0.2171(3)	6.2(2)
C19	−0.820(1)	0.5805(8)	−0.2629(3)	6.5(2)
C20	−0.997(1)	0.5532(8)	−0.3017(3)	6.1(2)
C21	−1.005(1)	0.6607(9)	−0.3487(3)	6.9(2)
C22	−1.179(1)	0.630(1)	−0.3876(4)	9.5(3)
C23	0.571(1)	−0.193(1)	0.3865(3)	9.0(3)
C24	0.377(1)	−0.160(1)	0.4268(4)	9.1(3)
C25	0.463(2)	−0.238(1)	0.4765(4)	11.3(3)
C26	0.277(2)	−0.230(2)	0.5148(4)	15.1(5)

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

The C=N and C-N distances of the azomethine group within the mesogens are 1.259(8) and 1.408(8) Å between ring A and B and 1.276(9) and 1.411(8) Å between ring C and D for 50.7 and 1.272(9) and 1.396(9) Å for 90.4. The average C-C bond lengths and C-C-C angles in the alkyl and alkoxy chains are determined to 1.49(2) Å and 115.5(8)° for the first molecule of 50.7, 1.47(2) Å and 116.2(9)° for the second molecule of 50.7 and 1.50(1) Å and 114.2(3)° for 90.4.

3.1.2. Molecular conformation

In some respects the molecular conformations of 50.7 and 90.4 are comparable, in others they differ considerably from each other. In 50.7 the alkyl and alkoxy chains are approximately in trans conformation, but in both independent molecules the heptyl group is linked to the phenyl ring nearly in a gauche conformation (τ(C110-C111-C119-C120) = −62.3(1.1)° and τ(C210-C211-C219-C220) = 46.7(1.2)°, table IV), leading to a twist angle of the heptyl group (C119 to C125 and C219 to C225) from the plane of the phenyl ring B and ring D (C108 to C113 and C208 to C213) in one molecule of 57.7 (ring B) and 41.0° (ring D), respectively (table V). The alkyl and alkoxy chains of 50.7 and 90.4 exhibit all-trans conformation and the butyl group of 90.4 is linked to the phenyl ring in a gauche conformation (τ(C10-C11-C23-C24) = −63.2(1.0)°, table IV) as in one of the independent molecule of 50.7. This leads to a twist angle of the plane of the alkyl carbon atoms of 61.8° from the plane of the phenyl ring B, C8 to C13 (table V).

Some similarities of the shape of 90.4 occur to that of the homologues of 70.6 [8], 40.8 [9] and 80.4 [10]. The corresponding twist angles between the carbon atoms of the alkyl groups and the plane of ring B had been determined to 111.1° for 70.6, to –116.4° for 80.4 and to –61.4 and 64.9° for the two independent molecules of 40.8.

50.7 exhibits a rod-like form as a whole with a molecular length of 29.7 Å for the first and 29.5 Å for the second molecule. These values correspond to the expected molecular length of the all-trans conformation [18]. The angles between the long axes of the alkyl and mesogenic group or the alkoxy and mesogenic group amount to about 163°. These long axes of the alkyl or alkoxy group are defined as the lines between the terminal carbon atom and the adjacent aromatic atom of the phenyl ring (C125 to C111 and C225 to C211 or C118 to C101 and C218 to C201), the mesogenic long axes as the lines between the carbon atoms at the end of the mesogenic unit, C101 to C111 or C201 to C211, respectively.

In 90.4 the long axis of the nonyloxy group is in line with the mesogenic long axis with a small deviation of 7° from 180°. In contrast the butyl group sticks out. The appropriate angle is determined to about 145° and comparable with 70.6 [8] – the corresponding angle amounts here to about 140°. The molecular length of 90.4 is calculated to 30.3 A, close to the expected length of the all-trans conformation [18].

The twist of the phenyl rings of the mesogenic unit differs for 50.7 and 90.4 considerably. The rings of both molecules in the crystal structure of 50.7 are twisted by 58.0° (ring A and B) for the first and 56.1° (ring C and D) for the second independent molecule (table V), comparable to 40.2 (-61.2 [8]). Ring A and D of the two molecules are nearly coplanar as well as ring B and C. In contrast the phenyl rings of 90.4 are nearly coplanar (3.1°, table V), comparable with 70.6 (4.6° [8]) and 80.4 (2.2° [10]) or 40.8 (13.6 and 29.2° [9]). These differences in the conformation of 50.7 and 90.4 are reflected in the corresponding torsion angles near the C=N bonds (cf table III). Despite the different placement of the phenyl rings with regard to each other, the dipole moments of the C=N-C and C-O-C bonds approximately point in the same direction in both compounds (figure 1 and 2), because the twist between the phenyl rings in 50.7 is mainly caused by the torsion angle τ(C107-N101-C108-C109) or τ(C207-N201-C208-C209), respectively, which have approximately the same size in value.

TABLE IV Selected torsion angles τ(°) for non-hydrogen atoms in 5O.7 and 9O.4 with their estimated standard deviations in parentheses

5O.7	τ	*9O.4*	τ
(C103-C104-C107-N101)	−172.9(7)	(C3-C4-C7-N1)	179.0(6)
(C203-C204-C207-N201)	163.3(7)		
(C108-N101-C107-C104)	−177.7(6)	(C8-N1-C7-C4)	178.7(6)
(C208-N201-C207-C204)	179.5(6)		
(C107-N101-C108-C109)	−133.1(7)	(C7-N1-C8-C13)	−174.3(6)
(C207-N201-C208-C209)	142.0(7)		
(C110-C111-C119-C120)	−62.3(11)	(C10-C11-C23-C24)	−63.2(10)
(C210-C211-C219-C220)	46.7(12)		

TABLE V Dihedral angles (°) between various planes of 5O.7 and 9O.4

5O.7 (first molecule)			*5O.7 (second molecule)*			*9O.4*		
plane	*plane*	*angle*	*plane*	*plane*	*angle*	*plane*	*plane*	*angle*
A	B	58.0	C	D	56.1	A	B	3.1
A			C		56.8			
A				D	7.8			
	B		C		2.9			
	B			D	57.7			
A	E	4.1	C	G	12.7	A	E	2.7
A	F	0.4	C	H	20.7	A	F	59.0
B	E	56.6	D	G	54.9	B	E	1.9
B	F	57.7	D	H	41.0	B	F	61.8
E	F	3.8	G	H	14.1	E	F	61.6

A (C1 to C6) or (C101 to C106)
B: (C8 to C13) or (C108 to C113)
C: (C201 to C206)
D: (C208 to C213)
cf figures 1 and 2
E: (C14 to C22) or (C114 to C118)
F: (C23 to C26) or (C119 to C125)
G: (C214 to C218)
H: (C219 to C225)

3.2. Molecular packing

3.2.1. Packing of 5O.7

In figure 3 (a, b) the crystal structures of 5O.7 are shown in projections along the two crystallographic directions [1 0 0] and [0 1 0], respectively. Four molecules, the content of the unit cell, are representing a domain or block in figure 3a. The molecules don't lie parallel to the b^*,c^*-plane, but nearly along the direction [1 1 −1] as depicted in figure 4. Within one block of four molecules, which is repro-

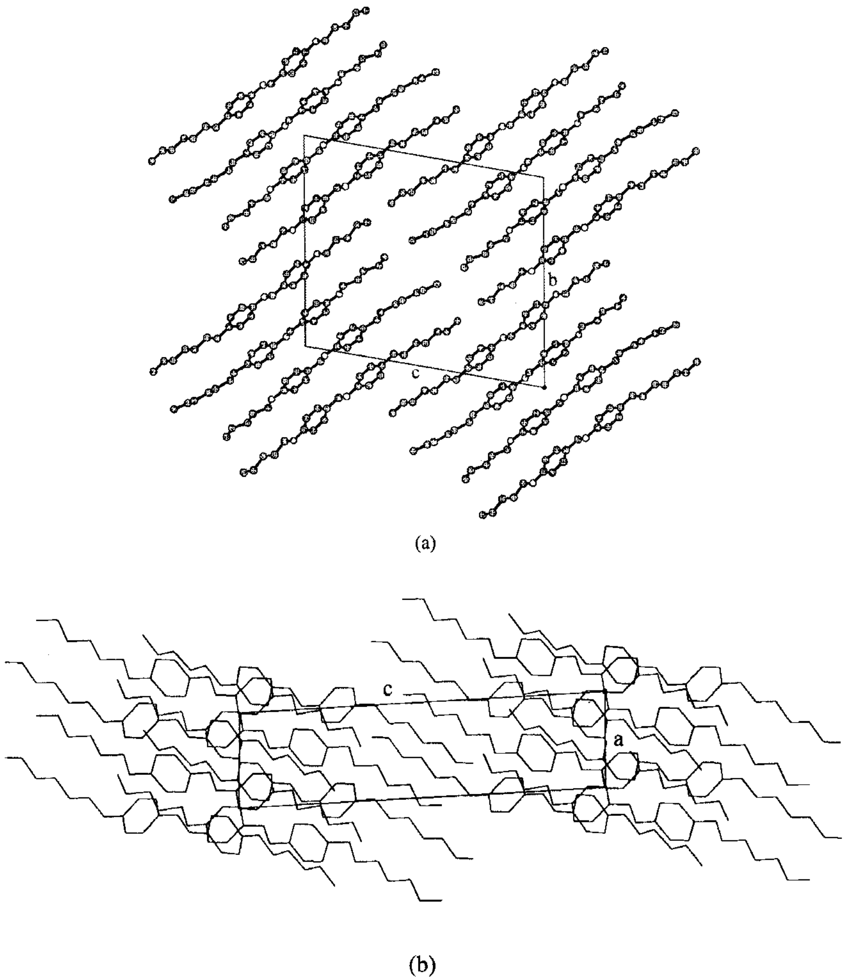

FIGURE 3 Schematic representation of the crystal structure of 5O.7 without hydrogen atoms along the two crystallographic directions (a) [1 0 0] and (b) [0 1 0]

duced in a-direction to strings, the mesogenic cores overlap almost completely. In the direction along [0 1 1] the blocks or strings, respectively, are shifted to such an extent that the mesogenic units of one block overlap again only with those two blocks back. The alkyl and alkoxy chains of the neighboring strings are found in between. Viewed along [0 1 0] (figure 3b) strips only containing the heptyl chains of the strongly to the b,c*-plane tilted molecules exist in addition to regions of a mixture of mesogenic units and pentyloxy chains. A pseudo-hexagonal arrangement is depicted in figure 4. A center molecule is surrounded by three pairs of equally projected molecules, two in the same manner as the center one, two antiparallel oriented molecules and two of the crystallographically independent molecules, pointing in the direction of the center molecule. The molecules at the edges of the block are adjacent to two matching molecules, two of the crystallographically independent molecules and the corresponding portions of altogether four molecules shifted along [1 1 −1] and pointing in the opposite direction.

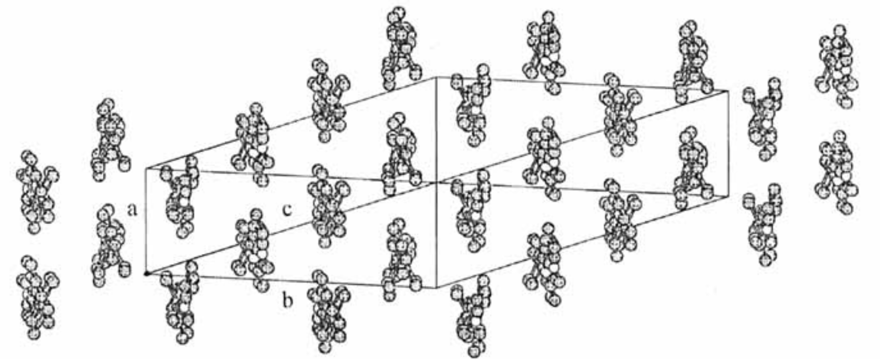

FIGURE 4 Pseudo-hexagonal close-packed molecular arrangement of 5O.7 without hydrogen atoms. Projection along [1 1 −1], the direction of the molecular long axis

In the crystalline phase 50.7 shows no simple layer-like structure although 50.7 is a precursor of a smectic phase. Drastic changes at the transition into the SmG phase have to occur by shifting the molecules along [1 1 −1] to break off the block structure leading to smectic layers (figure 3a). The structural parameters of the SmG phase have been determined from an unoriented powder diffraction diagram of the molten and not recrystallized phase at room temperature to a = 9.9, b = 5.1, c = 28.7 Å, β = 119.0° [21], which well compare to a = 9.54, b = 5.02, c = 27.9 Å, β = 114.8° at T = 33°C [22]. It is difficult to visualize from the pseudo-hexagonal arrangement of the crystalline phase (figure 3a and 4) without further drastic rearrangements that locally a C-centered cell exists in SmG. This nearest neighbor arrangement is different in 50.7 and 90.4 (cf following chapter).

3.2.2. Packing of 90.4

Figures 5 (a, b) represent the crystal structures of 90.4 in projections along the two crystallographic directions [1 0 0] and [0 1 0]. The molecules are placed in smectic-like layers parallel to the a,b-plane and piled up in c^*-direction (figure 5

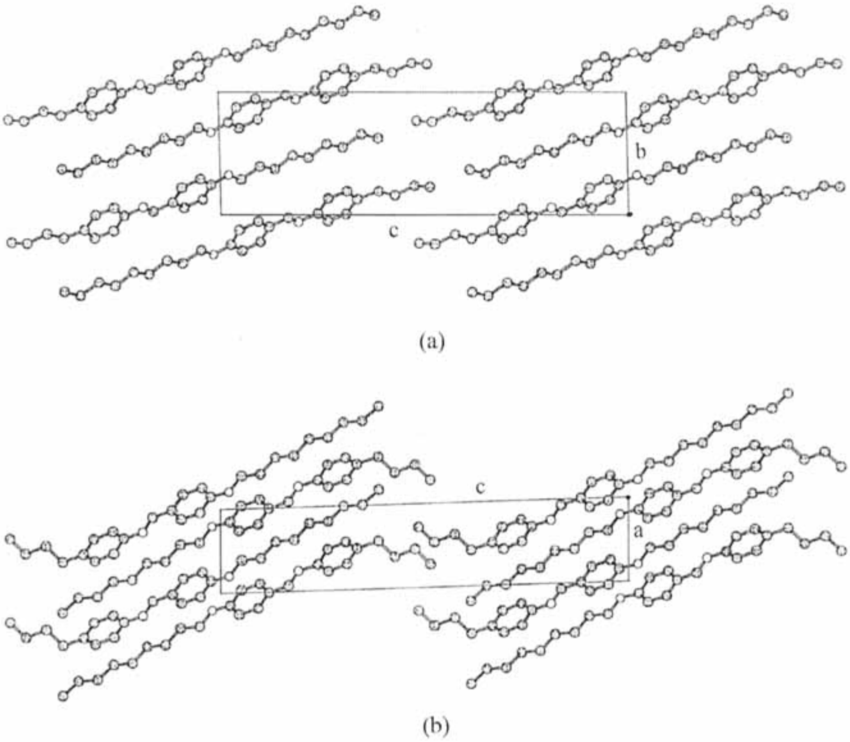

FIGURE 5 Schematic representation of 9O.4 without hydrogen atoms along the two crystallographic directions (a) [1 0 0] and (b) [0 1 0]

(a, b)). Within a layer the molecules form an antiparallel pseudo-hexagonal arrangement with four molecules in the opposite direction and two in the same direction (figure 6). The mesogenic cores of parallel oriented molecules in the layer overlap with the nonyloxy chains of the antiparallel oriented neighboring molecules producing sheets of oxygens parallel to the a,b-plane, as in 7O.6 [8] and 8O.4 [10]. The result is a protrusion of the butyl chains on both sides of the layer and a slight interdigitation of the layers (figure 5 (a,b)). In 4O.2 the mesogenic cores of neighboring molecules in one layer overlap almost completely [8], whereas in 4O.8 they are shifted somewhat against each other so that only half the mesogenic cores overlap [9].

At higher temperature 9O.4 exhibits an SmG phase with structural parameters of a = 9.4, b = 5.1, c = 29.2 Å, β = 112° at T = 59 °C, which are comparable with those in the literature (a = 9.41, b = 5.11, c = 29.6 Å, β = 109° at T = 64°C [22]). In contrast to 5O.7 only an slight shift of the molecules in the crystalline phase

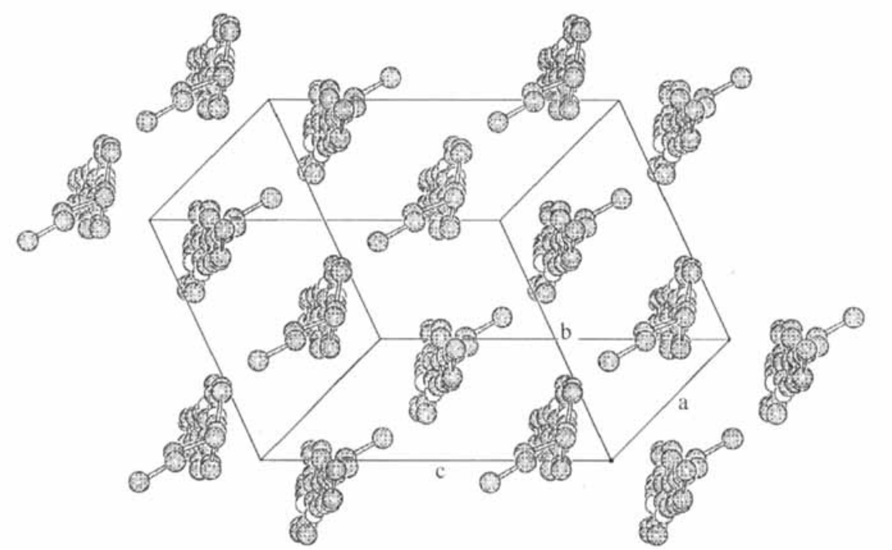

FIGURE 6 Pseudo-hexagonal close-packed molecular arrangement of 9O.4 without hydrogen atoms. Projection along [2 −1 1]. The picture shows clearly that the butyl group stacks out of the direction of the remaining molecule

along [2 −1 1] is expected to transform to an SmG phase, since a smectic-like structure already exists in the crystalline phase. Locally the cell is not C-centered, since one molecule is surrounded by two molecules pointing in the same direction and four molecules having an opposite sense.

4. CONCLUSION

The crystal structures of two monomesogenic compounds are presented of the type nO.m, 5O.7 and 9O.4. While 9O.4 exhibits a smectic-like layer structure from which the molecular packing of the SmG phase, appearing at higher temperature, can easily be derived, 5O.7 forms a more complex structure, although it transforms into a SmG phase too. Here, more drastic changes are needed to obtain the layered SmG structure. The correlation of the crystal structure and mesophase structure is not understood at the present and it seems difficult to predict the type of the mesophase to follow. For example, for 5O.7 an orthogonal smectic phase would be also plausible since an almost complete overlap of the mesogenic cores occurs.

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