Polymorphism and Crystal Structure of Chiral Smectogenic 4′-Heptyloxy-4-biphenylyl *p*-[(*S*)-2-Methylbutyl]benzoate

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Two crystal forms **1** and **2** were found for the title compound. DSC measurements showed that the two crystals transform to different mesophases (Sm* I and Sm* J). Crystal data. 4′-Heptyloxy-4-biphenylyl *p*-[(*S*)-2-methylbutyl]benzoate, **1**, M_r=458.61, $C_{31}H_{38}O_3$, monoclinic, $P2_1$, T=298 K, a=15.065(3), b=45.59(2), c=5.636(1) Å, β=95.51(2)°, V=4109(2) Å^3, Z=6, d_x=1.118 Mg m^{-3}, μ=0.475 mm^{-1}, $F(000)$=1488; **2**, triclinic, $P1$, a=13.37(2), b=22.96(2), c=10.213(5) Å, α=105.55(5), β=105.22(6), γ=102.31(9)°, V=2775(5) Å^3, Z=4, d_x=1.102 Mg m^{-3}. The crystal structure of **1** has been determined by single crystal X-ray analysis. Final R was 0.109. The crystal has a distinct layer structure similar to that of a smectic liquid crystal. Two of the three crystallographically independent molecules with extended paraffin chains have parallel arrangement, to which the third molecule with a twisted and highly disordered chain is antiparallel. The paraffin chains of the parallel molecules in a layer have close contacts with each other. Such contacts would enhance the intra-layer interaction which causes the transition to Sm* I.

In the preceding papers,[1,2] we discussed the relationships between mesophase behavior and crystal structures for the two series of chiral smectogenic biphenyl esters. The first series crystals (I-*n*), *p*-pentyloxyphenyl and *p*-heptyloxyphenyl 4′-[(*S*)-2-methylbutyl]biphenyl-4-carboxylates (I-5 and I-7, respectively), transform to a Sm*C followed by a cholesteric, while the second ones (II-*n*), *p*-[(*S*)-2-methylbutyl]phenyl 4′-heptyloxybiphenyl-4-carboxylate and 4′-octyloxybiphenyl-4-carboxylate, (II-7 and II-8, respectively), to a Sm*C and then to a Sm A phase. In the former crystals paraffin chains have close contacts between layers,[1] while in the latter whole molecules including paraffin chains contribute to the lateral molecular overlapping within a layer.[2] Different mesophase behavior related to the different phase sequences was successfully interpreted by the intermolecular interaction revealed in the crystal structures.

In contrast to these two series, the third one, 4′-alkoxy-4-biphenylyl *p*-[(*S*)-2-methylbutyl]benzoates (III-*n*), was reported to have phase sequences highly dependent on the chain length.[3] Since the preceding studies revealed that the different mesophase behavior is closely related to the difference in the packings of paraffin chains in the crystals, the crystal structure analyses of the third series were intended to elucidate the relationships between the mesophase behavior and the chain length. In the course of the crystal structure determination of these compounds, two crystal forms were found for III-7.

This paper describes the polymorphism of III-7 and one of the crystal structures.

Experimental

Compound. 4′-Heptyloxy-4-biphenylol was synthesized in an analogous way to that described previously.[4] 4-[(*S*)-2-Methylbutyl]benzoyl chloride was supplied by Dr. Shungo Sugawara. $[\alpha]_D^{20}$=13.8° (cf. $[\alpha]_D^{20}$=13.1° for the free acid[5]). Esterification and purification were done in the same way as described previously.[5]

Transition temperatures were measured using a Seiko SSC570 DSC and an Olympus POM polarizing microscope equipped with a Mettler FP82.

Crystal Structure Analysis. Transparent long parallelepiped or flat plate-like crystals were separately grown from a methanol-chloroform solution. The unit cell dimensions and space groups determined from oscillation and Weissenberg photographs revealed that they are polymorphs (III-7(**1**) and III-7(**2**), respectively). Accurate cell parameters of III-7(**1**) and III-7(**2**) were determined by a least squares fit for 15 and 20 reflections, respectively, within the range, $22°<2\theta<45°$, measured on a Rigaku AFC-4 diffractometer with Cu $K\alpha$ radiation (λ=1.54184 Å) monochromated by graphite.

Intensity data of III-7(**1**) were collected on the diffractometer using a crystal of 0.2×0.18×0.15 mm up to 2θ=100°. A 2θ-ω scan mode and scan width of $\omega=(1.0+0.15\tan\theta)°$ were applied. Backgrounds were counted for 5 s at both ends of a scan. Three standard reflections were recorded after every 50 reflections. No significant intensity variations were observed. A total of 4286 reflections were collected at the rate of 4°(2θ) min^{-1}, of which 3378 were treated as significant ($|F_o|>3\sigma(|F_o|)$). The data were corrected for Lorentz and polarization factors but not for absorption. For the III-7(**2**) crystal, unfortunately, sufficient intensity data for the structure analysis have not been obtained probably due to poor crystallinity and large thermal motions.

The structure was determined by applying the program MULTAN78[6] and refined by block-matrix least-squares using SHELX76[7] and subsequently HBLS,[8] since the number of parameters exceeded the limit of SHELX76 at later stages. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$, where $w=(\sigma(F_o)^2+0.004|F_o|^2)^{-1}$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[9] In the course of the refinement, several additional peaks of 0.37—0.44 e Å^{-3} were found around the terminal moiety of the twisted paraffin chain, where the atoms had remarkably large temperature factors. These peaks were included as disordered atoms in further refinement. All the non-hydrogen atoms with occupation factors above 0.7 were refined anisotropically. Only 19 hydrogen

atoms found in the difference Fourier maps were included in the refinement, because the number of the reflections was limited due to the large thermal effect. Max. Δ/σ and max. $\Delta\rho$ in the final difference map were 0.46 and 0.30 e Å^{-3}, respectively. Final R and R_w were 0.109 and 0.130. The large R value is due to the large thermal motion and the highly disordered chain.

The final coordinates of non-hydrogen atoms are given in Table 1.[10] Computations were carried out on a HITAC M-680H computer at the Computer Center of the University of Tokyo.

Results and Discussion

Polymorphism. In order to find a relationship

Table 1. Final Atomic Coordinates with Their Estimated Standard Deviations of 4′-Heptyloxy-4-biphenylyl *p*-[(*S*)-2-Methylbutyl]benzoate (III-7(**1**))

Atom	x	y	z	B_{eq}/Å$^{2a)}$	Atom	x	y	z	B_{eq}/Å$^{2a)}$
O(1A)	1.1384(6)	0.9129	1.288(2)	11.7	C(13B)	0.4798(7)	1.0593(3)	0.032(2)	5.2
O(2A)	1.1896(5)	0.9367(2)	0.993(1)	6.4	C(14B)	0.4261(7)	1.0840(3)	0.064(2)	5.3
O(3A)	0.7533(5)	1.0880(2)	0.794(2)	7.5	C(15B)	0.3662(9)	1.0931(3)	−0.124(3)	7.3
C(1A)	0.8100(7)	1.0649(3)	0.819(2)	5.8	C(16B)	0.3130(8)	1.1158(3)	−0.101(2)	6.7
C(2A)	0.8146(7)	1.0440(3)	0.642(2)	6.1	C(17B)	0.3181(8)	1.1323(3)	0.101(2)	6.6
C(3A)	0.8746(8)	1.0218(3)	0.679(2)	6.4	C(18B)	0.3770(8)	1.1250(3)	0.293(2)	7.1
C(4A)	0.9287(7)	1.0216(3)	0.878(2)	4.9	C(19B)	0.4297(8)	1.1005(3)	0.271(2)	6.3
C(5A)	0.9205(7)	1.0430(3)	1.052(2)	6.6	C(21B)	0.2630(9)	1.1574(3)	0.134(3)	7.9
C(6A)	0.8624(7)	1.0646(4)	1.021(2)	7.1	C(22B)	0.3040(13)	1.1853(4)	0.100(4)	12.1
C(7A)	0.9969(6)	0.9985(3)	0.910(2)	4.6	C(23B)	0.2357(18)	1.2110(6)	0.142(5)	17.7
C(8A)	1.0034(8)	0.9776(3)	0.739(2)	6.9	C(24B)	0.2758(20)	1.2399(7)	0.200(7)	20.5
C(9A)	1.0704(9)	0.9562(4)	0.765(2)	7.9	C(25B)	0.3333(17)	1.1887(6)	−0.138(4)	16.2
C(10A)	1.1212(7)	0.9558(3)	0.968(2)	5.7	C(31B)	0.9621(8)	0.8807(3)	0.682(3)	7.1
C(11A)	1.1158(8)	0.9772(3)	1.139(2)	7.1	C(32B)	1.0463(8)	0.8644(3)	0.690(3)	7.7
C(12A)	1.0540(8)	0.9972(3)	1.116(2)	6.7	C(33B)	1.0539(9)	0.8443(3)	0.905(3)	7.8
C(13A)	1.1912(8)	0.9157(3)	1.156(2)	6.5	C(34B)	1.1334(9)	0.8256(4)	0.926(3)	8.2
C(14A)	1.2645(7)	0.8957(3)	1.156(2)	6.0	C(35B)	1.1442(10)	0.8058(4)	1.137(3)	9.4
C(15A)	1.2806(9)	0.8753(4)	1.329(3)	8.5	C(36B)	1.2139(13)	0.7845(5)	1.114(4)	13.5
C(16A)	1.3495(9)	0.8564(4)	1.339(3)	8.2	C(37B)	1.2335(15)	0.7661(6)	1.356(5)	16.8
C(17A)	1.4029(8)	0.8582(3)	1.162(3)	7.4	O(1C)	0.3500(5)	1.0239(2)	−0.669(2)	7.3
C(18A)	1.3893(8)	0.8792(3)	0.989(3)	7.4	O(2C)	0.2922(5)	0.9997(2)	−0.369(2)	6.2
C(19A)	1.3177(8)	0.8973(3)	0.973(2)	6.5	O(3C)	0.7392(5)	0.8521(2)	−0.112(2)	7.7
C(21A)	1.4816(9)	0.8394(4)	1.179(3)	9.1	C(1C)	0.6836(7)	0.8737(3)	−0.135(2)	6.4
C(22A)	1.4643(11)	0.8071(4)	1.117(3)	10.2	C(2C)	0.6337(8)	0.8734(4)	−0.343(3)	8.2
C(23A)	1.5493(14)	0.7914(5)	1.135(5)	13.5	C(3C)	0.5703(7)	0.8948(4)	−0.384(2)	7.4
C(24A)[c)]	1.5905(20)	0.7883(7)	1.370(6)	13.1	C(4C)	0.5589(7)	0.9178(3)	−0.219(2)	5.0
C(24A′)[c)]	1.5621(58)	0.7697(21)	1.266(17)	16.7(27)[b)]	C(5C)	0.6109(8)	0.9170(3)	−0.016(2)	7.2
C(25A)	1.4198(12)	0.8037(4)	0.858(3)	10.8	C(6C)	0.6779(8)	0.8955(3)	0.037(2)	7.0
C(31A)	0.6981(8)	1.0898(3)	0.579(3)	6.9	C(7C)	0.4896(6)	0.9390(2)	−0.277(2)	4.3
C(32A)	0.6487(12)	1.1197(5)	0.594(4)	11.7	C(8C)	0.4346(8)	0.9399(3)	−0.480(2)	6.3
C(33A)	0.6060(13)	1.1219(5)	0.798(4)	12.3	C(9C)	0.3720(7)	0.9595(3)	−0.516(3)	6.4
C(34A)	0.5715(22)	1.1519(7)	0.834(6)	20.0	C(10C)	0.3601(7)	0.9801(3)	−0.337(2)	5.7
C(35A)[c)]	0.6150(43)	1.1721(15)	1.071(13)	21.6(24)[b)]	C(11C)	0.4147(8)	0.9809(3)	−0.130(2)	5.9
C(35A′)[c)]	0.6142(38)	1.1757(14)	0.856(10)	18.6(19)[b)]	C(12C)	0.4755(7)	0.9608(3)	−0.099(2)	6.0
C(36A)[c)]	0.5746(41)	1.1957(14)	0.966(11)	19.6(22)[b)]	C(13C)	0.2943(7)	1.0210(3)	−0.532(2)	5.8
C(36A′)[c)]	0.6642(45)	1.1796(16)	1.011(12)	21.9(24)[b)]	C(14C)	0.2230(7)	1.0414(2)	−0.518(2)	4.6
C(37A)[c)]	0.5951(43)	1.2110(15)	1.188(13)	21.5(24)[b)]	C(15C)	0.1683(7)	1.0393(3)	−0.344(2)	5.5
C(37A′)[c)]	0.7032(40)	1.2052(14)	1.186(12)	20.1(22)[b)]	C(16C)	0.1023(7)	1.0592(3)	−0.347(2)	5.9
O(1B)	0.4813(6)	1.0455(3)	−0.156(2)	8.4	C(17C)	0.0852(7)	1.0800(3)	−0.521(2)	5.5
O(2B)	0.5280(5)	1.0531(2)	0.232(1)	6.0	C(18C)	0.1428(7)	1.0827(3)	−0.705(2)	6.0
O(3B)	0.9543(4)	0.8967(2)	0.465(1)	6.5	C(19C)	0.2131(8)	1.0635(3)	−0.693(2)	6.3
C(1B)	0.8946(7)	0.9171(3)	0.437(2)	5.3	C(21C)	0.0090(8)	1.0996(3)	−0.535(3)	7.2
C(2B)	0.8929(7)	0.9352(3)	0.241(2)	5.2	C(22C)	0.0129(9)	1.1241(3)	−0.358(3)	7.8
C(3B)	0.8340(7)	0.9569(3)	0.194(2)	5.3	C(23C)	−0.0757(10)	1.1378(4)	−0.380(4)	10.2
C(4B)	0.7678(7)	0.9598(3)	0.344(2)	5.0	C(24C)	−0.0767(17)	1.1606(6)	−0.190(5)	17.9
C(5B)	0.7697(7)	0.9429(3)	0.544(2)	5.5	C(25C)	0.0811(11)	1.1475(4)	−0.437(4)	10.8
C(6B)	0.8302(7)	0.9204(3)	0.591(2)	5.5	C(31C)	0.7856(9)	0.8467(3)	0.110(3)	7.9
C(7B)	0.7011(7)	0.9836(3)	0.298(2)	4.7	C(32C)	0.8208(9)	0.8156(4)	0.107(3)	8.4
C(8B)	0.7030(7)	1.0044(3)	0.123(2)	6.0	C(33C)	0.8676(11)	0.8092(4)	0.352(3)	9.7
C(9B)	0.6447(8)	1.0274(3)	0.082(2)	6.2	C(34C)	0.9033(12)	0.7772(4)	0.341(4)	10.8
C(10B)	0.5843(7)	1.0290(3)	0.239(2)	5.4	C(35C)	0.9540(10)	0.7680(4)	0.563(3)	9.8
C(11B)	0.5784(7)	1.0095(3)	0.419(2)	5.6	C(36C)	0.9822(13)	0.7360(4)	0.542(4)	11.9
C(12B)	0.6393(8)	0.9871(3)	0.454(2)	6.1	C(37C)	1.0371(15)	0.7267(5)	0.771(5)	15.4

a)$B_{eq}=(4/3)\sum_{ij}\beta_{ij}(a_i\cdot a_j)$. b) Isotropic temperature factors. c) Occupation factors are fixed to be 0.7 for C(24A), 0.3 for C(24A′), and 0.5 for (35A) to C(37A′).

Table 2. Enthalpies of Transitions (ΔH/kJ mol^{-1})

Transition	III-7a	III-7b
Crystal-mesophase	16.3±0.7	16.8±0.7
Sm*I-Sm*C	2.4±0.2	2.4±0.2
Sm*C-cholesteric	4.7±0.2	4.6±0.1
Cholesteric-isotropic[a)]	1.1±0.1	1.4±0.2

a) Via a blue phase.

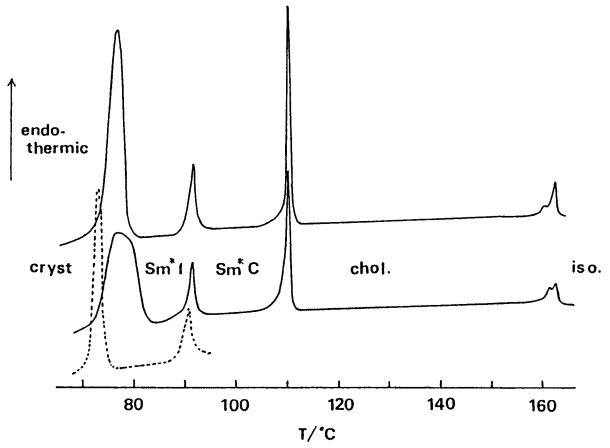

Fig. 1. DSC peaks for the two polymorphs of 4′-heptyloxy-4-biphenylyl *p*-[(*S*)-2-methylbutyl]-benzoate: III-7(**1**) (upper) and III-7(**2**) (lower). A broken line denotes a curve for the solid obtained from a melt. Scan speed was 2° min^{-1}.

between the two polymorphs, DSC measurements were carried out. ΔH values are summarized in Table 2. Transition temperatures of Sm*I-Sm*C and Sm*C-cholesteric were in good agreement with the reported values,[3)] while the cholesteric-isotropic transition temperature was higher (ca.161 °C) than the reported one (154 °C) and a blue phase was observed during the transition.

As shown in Fig. 1, the shapes of the crystal-mesophase transition peaks are remarkably different: a sharp peak for III-7(**1**) and a broad one for III-7(**2**). The former peak is as sharp as the crystal-Sm*C transition peaks of the series I and II and the profile is independent of the heating rate, while the latter has a truncated profile, which is slightly dependent on heating rate. These facts indicate that the former peak corresponds to a single step of transition while the latter is composed of two (or more) steps. Goodby and Leslie reported that the phase sequence of III-7 was crystal-Sm*J-Sm*I-Sm*C-cholesteric-isotropic.[3)] Refering to this, it is interpreted that the sharp peak of III-7(**1**) corresponds to a direct transition to Sm*I, while the broad one of III-7(**2**) to successive transitions, Sm*J-Sm*I-Sm*C, because the Sm*I-Sm*C transition temperature is in good agreement with the reported one. On re-heating, the peak of III-7(**2**) also becomes sharp and ΔH is about 60—70% of the first run, showing that the solid obtained from a melt is much more disordered than the crystalline state obtained from a solution.

Molecular Conformations in the Crystal. All the bond lengths and angles are almost compatible with those found in the mesogens studied previously,[1,2)] as shown in Table 3. All the phenyl rings are planar within the experimental error. Table 4 shows torsion angles. The molecule A has two disordered conformations in the largely twisted chain and the other two molecules B and C have straightly extended paraffin chains. The C(24) atom in the molecule A is also slightly disordered. The molecules B and C have approximately the same structure. Figure 2 shows ORTEP drawings of the molecules A and B with the numbering scheme.

Biphenyl moieties were nearly coplanar in all the molecules. The ester moieties composed of C(10), C(13), C(14), O(1), and O(2) atoms, which are planar within the experimental error, are approximately coplanar with the phenyl rings of C(14)—(19), as is easily expected by considering the conjugation of the double bonds. In the cases of the I and II crystals, they are coplanar with one of the biphenyl rings.

Crystal Packing. Figure 3 shows the crystal structure. In a distinct layer structure parallel to the (010) plane, molecules have two opposite tilt (±45°) alternately from layer to layer.

Molecular arrangement within a layer is quite different from those of the series I and II. The latter two series have antiparallel arrangements of molecular long axes related by a pseudo-inversion (I) or a 2-fold screw axis (II). On the other hand, in the III-7(**1**) crystal the two molecules with the extended paraffin chains have parallel arrangement, to which the third molecule with the twisted chain is antiparallel.

The phenyl rings of adjacent molecules have non-

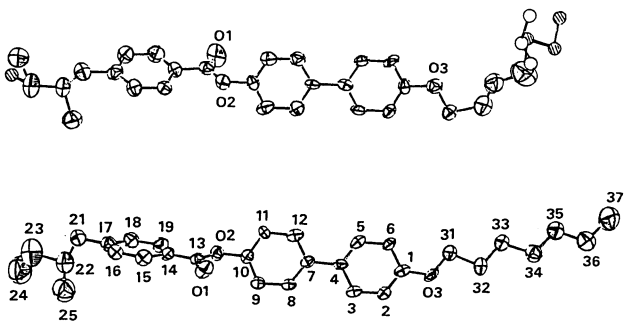

Fig. 2. ORTEP views of the molecules A (upper) and B (lower) in III-7(**1**) with 50% probability thermal ellipsoids. The molecule C has almost the same conformation as the molecule B. The isotropically refined atoms are shown by spheres with an arbitrary diameter. Shadowed atoms indicates the other conformer. All the molecules are numbered in the same way.

Table 3. Bond Lengths (l/Å) and Angles (ϕ/°) of III-7(**1**)[a)]

Atoms	mol. A	mol. B	mol. C	Atoms	mol.A	mol. B	mol. C
Bond length (l/Å)				C(2)-C(1)-C(6)	122(1)	118(1)	122(1)
O(1)-C(13)	1.19(2)	1.24(2)	1.24(2)	C(1)-C(2)-C(3)	118(1)	123(1)	116(1)
O(2)-C(10)	1.40(2)	1.42(2)	1.41(2)	C(2)-C(3)-C(4)	120(1)	119(1)	125(1)
O(2)-C(13)	1.33(2)	1.33(2)	1.34(2)	C(3)-C(4)-C(5)	119(1)	119(1)	115(1)
O(3)-C(1)	1.39(2)	1.34(2)	1.33(2)	C(3)-C(4)-C(7)	120(1)	121(1)	126(1)
O(3)-C(31)	1.43(2)	1.42(2)	1.42(2)	C(5)-C(4)-C(7)	121(1)	120(1)	119(1)
C(1)-C(2)	1.39(2)	1.38(2)	1.40(2)	C(4)-C(5)-C(6)	122(1)	122(1)	123(2)
C(1)-C(6)	1.35(2)	1.42(2)	1.36(2)	C(1)-C(6)-C(5)	119(2)	119(1)	120(2)
C(2)-C(3)	1.40(2)	1.38(2)	1.47(2)	C(4)-C(7)-C(8)	120(1)	120(1)	127(1)
C(3)-C(4)	1.36(2)	1.43(2)	1.36(2)	C(4)-C(7)-C(12)	122(1)	123(1)	118(1)
C(4)-C(5)	1.40(2)	1.37(2)	1.42(2)	C(8)-C(7)-C(12)	118(1)	116(1)	115(1)
C(4)-C(7)	1.52(2)	1.53(2)	1.49(2)	C(7)-C(8)-C(9)	120(1)	121(1)	124(1)
C(5)-C(6)	1.35(2)	1.42(2)	1.41(2)	C(8-C(9)-C(10)	119(2)	119(1)	119(1)
C(7)-C(8)	1.37(2)	1.39(2)	1.38(2)	O(2)-C(10)-C(9)	120(1)	116(1)	120(1)
C(7)-C(12)	1.41(2)	1.37(2)	1.44(2)	O(2)-C(10)-C(11)	118(1)	120(1)	120(1)
C(8)-C(9)	1.45(2)	1.42(2)	1.34(2)	C(9)-C(10)-C(11)	121(1)	123(1)	120(1)
C(9)-C(10)	1.34(2)	1.36(2)	1.40(2)	C(10)-C(11)-C(12)	120(1)	115(1)	119(1)
C(10)-C(11)	1.38(2)	1.38(2)	1.40(2)	C(7)-C(12)-C(11)	122(1)	125(1)	123(1)
C(11)-C(12)	1.35(2)	1.41(2)	1.34(2)	O(1)-C(13)-O(2)	123(1)	124(1)	125(1)
C(13)-C(14)	1.49(2)	1.44(2)	1.48(2)	O(1)-C(13)-C(14)	123(1)	124(1)	125(1)
C(14)-C(15)	1.36(2)	1.42(2)	1.38(2)	O(2)-C(13)-C(14)	114(1)	112(1)	110(1)
C(14)-C(19)	1.40(2)	1.39(2)	1.41(2)	C(13)-C(14)-C(15)	121(1)	121(1)	123(1)
C(15)-C(16)	1.40(2)	1.36(2)	1.39(2)	C(13)-C(14)-C(19)	121(1)	123(1)	117(1)
C(16)-C(17)	1.38(2)	1.36(2)	1.38(2)	C(15)-C(14)-C(19)	118(1)	116(1)	121(1)
C(17)-G(18)	1.37(2)	1.41(2)	1.45(2)	C(14)-C(15)-C(16)	123(2)	123(1)	119(1)
C(17)-C(21)	1.52(2)	1.47(2)	1.51(2)	C(15)-C(16)-C(17)	119(2)	121(1)	124(1)
C(18)-C(19)	1.41(2)	1.41(2)	1.43(2)	C(16)-C(17)-C(18)	119(1)	120(1)	118(1)
C(21)-C(22)	1.54(3)	1.46(3)	1.50(2)	C(16)-C(17)-C(21)	119(1)	123(1)	123(1)
C(22)-G(23)	1.54(3)	1.64(4)	1.55(3)	C(18)-C(17)-C(21)	121(1)	117(1)	119(1)
C(22)-C(25)	1.57(3)	1.47(4)	1.62(3)	C(17)-C(18)-C(19)	122(1)	119(1)	118(1)
C(23)-C(24)	1.43(4)	1.49(5)	1.49(4)	C(14)-C(19)-C(18)	118(1)	122(1)	120(1)
C(31)-C(32)	1.58(3)	1.54(2)	1.52(2)	C(17)-C(21)-C(22)	113(1)	112(1)	115(1)
C(32)-C(33)	1.40(3)	1.52(2)	1.54(2)	C(21)-C(22)-C(23)	107(2)	107(2)	106(1)
C(33)-C(34)	1.50(4)	1.53(2)	1.57(3)	C(21)-C(22)-C(25)	112(2)	114(2)	107(1)
C(34)-C(35)	1.72(8)	1.49(2)	1.49(3)	C(23)-C(22)-C(25)	110(2)	110(2)	111(1)
C(35)-C(36)	1.37(10)	1.50(3)	1.54(3)	C(22)-C(23)-C(24)	116(2)	113(3)	107(2)
C(36)-C(37)	1.44(10)	1.60(4)	1.55(4)	O(3)-C(31)-C(32)	106(1)	106(1)	109(1)
				C(31)-C(32)-C(33)	113(2)	109(1)	108(1)
Bond angle (ϕ/°)				C(32)-C(33)-C(34)	113(2)	114(1)	107(1)
C(10)-O(2)-C(13)	119(1)	120(1)	118(1)	C(33)-C(34)-C(35)	118(3)	116(1)	114(2)
C(1)-O-(3)-C(31)	119(1)	117(1)	121(1)	C(34)-C(35)-C(36)	87(5)	111(2)	110(2)
O(3)-C(1)-C(2)	122(1)	118(1)	123(1)	C(35)-C(36)-C(37)	87(6)	111(2)	110(2)
O(3)-C(1)-C(6)	116(1)	124(1)	115(1)				

a) The bond lengths and angles including the disordered atoms are shown for one of the conformers.

Table 4. Tortion Angles (ϕ/°) of III-7(**1**)

	mol. A	mol. B	mol. C
Phenyl groups			
ring(C1—C6)-ring(C7—12)	3	6	4
ring(C7—C12)-ring(C14—C19)	61	59	61
Phenyl and ester groups			
ring(C7—C12)-ester	68	54	67
ring(C14—C19)-ester	7	5	6
Alkyl chains			
O(3)-C(31)-C(32)-C(33)	57	174	177
C(31)-C(32)-C(33)-C(34)	190	183	180
C(32)-C(33)-C(34)-C(35)	112, 59	181	183
C(33)-C(34)-C(35)-C(36)	192, 63	191	189
C(34)-C(35)-C(36)-C(37)	194, 144	188	182

parallel contacts as found in the former two series. The angles between the mean planes are 60°, on average. The molecular overlapping within a layer is relatively large from an end to the other, as in the case of the series II crystals, although the tilt angle is larger than that in the series II crystals (30°). On the other hand, the packing of the paraffin chains within a layer is different. In the series II crystals paraffin chains have rather loose contacts, while those of the parallel molecules in the III-7(**1**) crystal form sheets composed of close contacts along the c axis, as shown in Fig. 4. This seems to enhance the molecular interaction within a layer, leading to the transition to Sm*I, an intermediately highly ordered smectic with a pseudo-hexagonal arrangement in a layer.[12)]

Intermolecular interaction due to the close contacts

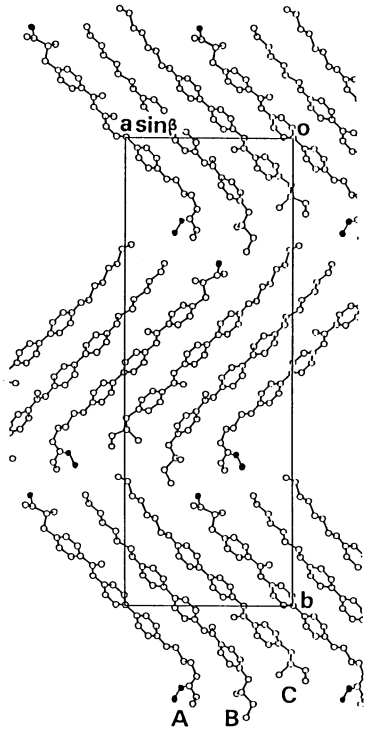

Fig. 3. Crystal structure of III-7(**1**) viewed along the c axis. Filled circles denote disordered atoms.

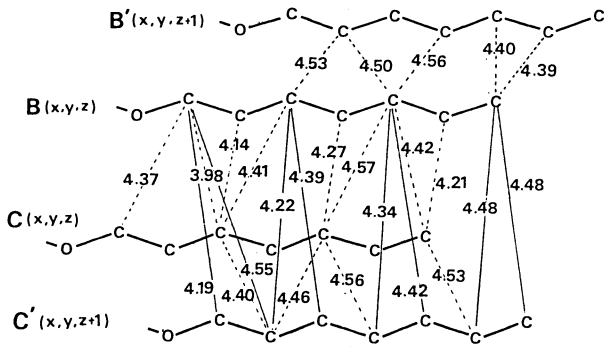

Fig. 4. Inter-chain distances (Å) of III-7(**1**). Only distances less than 4.6 Å are shown. Symmetry codes are shown in parentheses.

between the paraffin chains would largely depend on the chain length. This may be responsible for the different phase sequences depending on the chain length in this series.

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