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Crystal Structures of Chiral Mesogenic 4-[(*S*)-2-Methylbutyl]phenyl and 4-[(*S*)-1-Methylheptyloxy]phenyl 4′-Octylbiphenyl-4-carboxylates

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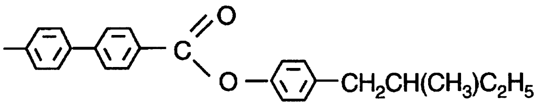
Single crystal X-ray analysis has been carried out for the title compounds with different chiral groups, which result in different phase sequences: crystal (cryst.)-smectic G(S_G)-S_J^*-S_F^*-S_I^*-S_C^*-S_A-cholesteric (chol.)-isotropic (iso.) for the 2-methylbutyl compound (**1**) and cryst.-S_B-S_A-iso. for the 1-methylheptyloxy compound (**2**). Each crystal has a smectic-like layer structure, in which the molecular tilt angle is 25° in **1** and 15° in **2**. Biphenyl moieties are almost coplanar and normal chains have all-trans conformations in both crystals. However, long chains of the chiral groups of **2** have twisted conformations and are arranged between layers. Relationships between the crystal structures and the mesophase behavior are discussed in terms of conjugation of the polar groups and overlapping of biphenyl moieties for the related compounds.

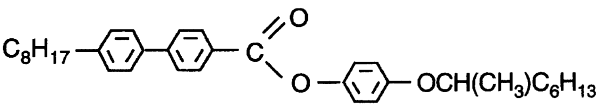
Chirality gives rise to marvelous effects on properties of matter. For example, it causes the symmetry change of liquid crystalline phases, often producing helical structures and/or ferroelectricity.[1] The title compounds, which are different only in the chiral groups, have remarkably different phase sequences, as follows:

4-[(*S*)-2-methylbutyl]phenyl 4′-octylbiphenyl-4-carboxylate (**1**)[2]



cryst.-S_G-S_J^*-S_F^*-S_I^*-S_C^*-S_A-chol.-iso.

4-[(*S*)-1-methylheptyloxy]phenyl 4′-octylbiphenyl-4-carboxylate (**2**)[3]



cryst.-S_B-S_A-iso.

The former has been studied extensively with an abbreviated name of 8SI or 8CE because of the richness of phases,[4—6] while the latter has only a simple phase sequence. We determined the crystal structures for the 4′-hexyl homologue of **1**,[7] which has a phase sequence of cryst.-S_A-chol.-iso. and also for two structural isomers of **2**,[8] which have phase sequences of cryst.-S_C^*-chol.-iso. and cryst.-S_C^*-S_A-chol.-iso. This paper describes the crystal structures of **1** and **2** and discusses the relationships between the crystal structures and the mesophase behavior in terms of conjugation of the polar groups and overlapping of biphenyl moieties for the related compounds.

Experimental

Compounds. **1** was purchased from BDH Chemicals Ltd. and **2** was donated by Chisso Petrochemical Corporation.

Apparatus. Powder X-ray diffraction patterns were obtained using a Rigaku RAD-RA diffractometer.

Crystal Structure Analysis. Single crystals appropriate to the structure determination were grown from an acetone–methanol solution and an ethyl acetate–methanol solution for **1** and **2**, respectively. Lattice parameter measurements and reflection data collection were done on a Rigaku AFC-7R four-circle diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54184$ Å) at room temperature. The 2θ–ω mode was applied up to $2\theta = 120°$ with the scan rate of 2 and 4° min^{-1} (in ω) for **1** and **2**, respectively. Three standard reflections were measured after every 150 reflections. No significant change was observed. All the data were corrected for Lorentz and polarization factors. Experimental details and crystal data are shown in Table 1.

The structures were solved by applying the programs SIR88[9] for **1** and MITHRIL90[10] for **2**. Refinements were done by full-matrix least-squares on F^2 for all the reflections using SHELXL93.[11] The benzene rings were constrained to have regular hexagonal geometry with the C–C distance of 1.39 Å and were refined as rigid groups. Several bonds in chains were also loosely constrained. Atomic scattering factors were taken from International Tables for Crystallography.[12] In the course of refinement of **2**, temperature factors for atoms of the long chains in the chiral groups became large. However, it was impossible to divide these

Table 1. Experimental Details, Crystal Data, and Final Results of Refinements

	1	**2**
Formula	$C_{32}H_{40}O_2$	$C_{35}H_{46}O_3$
FW	456.64	514.72
Crystal habit	Plate	Needle
Cryst. size/mm	0.30×0.15×0.01	0.48×0.12×0.06
l.s. for cell const.		
No. of refl.	17	18
2θ range/°	33—47	38—46
Space group	$P2_1$	$P2_1$
a/Å	29.162(10)	35.025(8)
b/Å	5.696(11)	5.534(2)
c/Å	17.508(15)	16.414(9)
β/°	106.39(5)	99.35(4)
V/Å^3	2790(6)	3139(2)
Z	4	4
D_x/g cm^{-3}	1.087	1.089
μ/cm^{-1}	5.03	5.21
$F(000)$	992	1120
No. of unique refl.	4017	5222
No. of obsd. refl. ($>2\sigma(I)$)	1540	2219
$R(F)$ ($>2\sigma(I)$)	0.101	0.091
$wR(F^2)^{a)}$ ($>2\sigma(I)$)	0.276	0.279
S	1.030	0.911

a) $w=[\sigma^2(F_o^2)+(0.2895P)^2]^{-1}$ for **1** and $w=[\sigma^2(F_o^2)+(0.1838P)^2]^{-1}$ for **2**, where $P=(F_o^2+2F_c^2)/3$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **1**

Atom	x	y	z	$U_{\rm eq}^{\rm a)}$/Å^2
O(1A)	0.3193(4)	−0.116(2)	0.4928(7)	0.140(5)
O(2A)	0.2990(5)	0.193(3)	0.4114(7)	0.131(4)
C(1A)	0.5966(3)	−0.010(2)	0.3374(6)	0.106(5)
C(2A)	0.5642(4)	0.170(2)	0.3083(6)	0.137(7)
C(3A)	0.5201(4)	0.171(2)	0.3239(6)	0.130(6)
C(4A)	0.5083(3)	−0.008(2)	0.3687(6)	0.096(4)
C(5A)	0.5407(4)	−0.189(2)	0.3979(5)	0.132(6)
C(6A)	0.5848(4)	−0.189(2)	0.3822(6)	0.141(7)
C(7A)	0.4602(3)	−0.002(2)	0.3863(6)	0.105(5)
C(8A)	0.4276(4)	0.1765(19)	0.3554(6)	0.133(6)
C(9A)	0.3842(4)	0.184(2)	0.3734(6)	0.144(7)
C(10A)	0.3733(3)	0.013(3)	0.4222(6)	0.111(5)
C(11A)	0.4058(4)	−0.165(2)	0.4530(6)	0.127(6)
C(12A)	0.4493(4)	−0.1724(18)	0.4351(6)	0.116(5)
C(13A)	0.3289(6)	0.020(4)	0.4485(10)	0.111(5)
C(14A)	0.2555(4)	0.215(3)	0.4269(7)	0.112(5)
C(15A)	0.2470(5)	0.420(2)	0.4636(7)	0.135(6)
C(16A)	0.2028(6)	0.456(2)	0.4771(6)	0.142(7)
C(17A)	0.1672(4)	0.287(4)	0.4539(7)	0.134(7)
C(18A)	0.1758(5)	0.082(3)	0.4172(7)	0.135(6)
C(19A)	0.2199(6)	0.046(2)	0.4037(6)	0.140(7)
C(21A)	0.1182(7)	0.329(5)	0.4666(11)	0.159(8)
C(22A)	0.0833(7)	0.483(5)	0.4063(15)	0.164(8)
C(23A)	0.0398(8)	0.524(7)	0.4334(14)	0.222(14)
C(24A)	0.0066(11)	0.691(7)	0.3827(18)	0.277(16)
C(25A)	0.0711(8)	0.367(8)	0.3242(12)	0.243(16)
C(31A)	0.6447(6)	−0.003(3)	0.3202(10)	0.122(6)
C(32A)	0.6729(5)	−0.231(4)	0.3347(11)	0.138(7)
C(33A)	0.7194(6)	−0.217(3)	0.3169(9)	0.127(6)
C(34A)	0.7490(6)	−0.444(4)	0.3291(11)	0.145(7)
C(35A)	0.7976(7)	−0.434(4)	0.3145(12)	0.147(7)
C(36A)	0.8247(8)	−0.659(4)	0.3277(12)	0.167(8)
C(37A)	0.8740(9)	−0.634(5)	0.3136(17)	0.205(11)
C(38A)	0.8988(9)	−0.863(6)	0.3212(16)	0.221(13)
O(1B)	0.3146(5)	0.392(3)	0.1133(8)	0.158(5)
O(2B)	0.3396(5)	0.683(3)	0.2017(9)	0.162(5)
C(1B)	0.6258(4)	0.444(3)	0.0830(8)	0.132(7)
C(2B)	0.6145(5)	0.631(2)	0.1255(7)	0.166(8)
C(3B)	0.5699(6)	0.640(2)	0.1393(6)	0.144(8)
C(4B)	0.5366(4)	0.464(3)	0.1105(7)	0.118(6)
C(5B)	0.5480(5)	0.277(2)	0.0680(8)	0.163(9)
C(6B)	0.5926(6)	0.268(2)	0.0543(7)	0.159(9)
C(7B)	0.4887(4)	0.469(2)	0.1283(7)	0.118(6)
C(8B)	0.4775(5)	0.6536(18)	0.1714(6)	0.129(6)
C(9B)	0.4319(6)	0.670(2)	0.1813(6)	0.125(6)
C(10B)	0.3977(4)	0.501(3)	0.1480(7)	0.116(5)
C(11B)	0.4090(5)	0.316(2)	0.1048(6)	0.134(6)
C(12B)	0.4545(5)	0.2998(17)	0.0950(5)	0.127(6)
C(13B)	0.3467(8)	0.510(3)	0.1547(11)	0.129(7)
C(14B)	0.2932(5)	0.717(3)	0.2031(9)	0.139(8)
C(15B)	0.2698(8)	0.916(3)	0.1651(7)	0.149(7)
C(16B)	0.2232(8)	0.963(3)	0.1659(8)	0.163(9)
C(17B)	0.1999(5)	0.811(4)	0.2047(10)	0.164(9)
C(18B)	0.2233(8)	0.612(4)	0.2427(8)	0.157(8)
C(19B)	0.2699(8)	0.566(2)	0.2419(8)	0.170(8)
C(21B)	0.1507(9)	0.864(5)	0.2085(13)	0.177(9)
C(22B)	0.1100(11)	0.837(6)	0.1308(18)	0.196(12)
C(23B)	0.0628(11)	0.904(7)	0.1483(15)	0.236(14)

atoms into precise disordered structures, because there were no significant peaks around them. Therefore, we concluded that these atoms distribute continuously around the average positions and the temperature factors ($U_{\rm iso}$) were fixed to be 0.33. Except for these atoms with fixed temperature factors, all other non-hydrogen atoms were refined anisotropically. Hydrogen atom positions calculated geometrically (C–H distances; 0.96 for primary, 0.97 for secondary, 0.98 for tertiary, and 0.93 Å for aromatic) only for the C atoms which were refined anisotropically were included in structure factor calculations, but not refined. Final results of the refinements are shown in Table 1. The large values of esd for the lattice parameters and the large R value of **1** are due to the small size of crystal used, in spite of the repeated attempts at crystallization. The final atomic coordinates of non-hydrogen atoms are given in Tables 2 and 3.[13]

Results and Discussion

Molecular Conformations. All the bond lengths and angles are normal within experimental errors. There are two crystallographically independent molecules, A and B, in both crystals. Molecular structures with numbering schemes are shown in Fig. 1. The molecules have nearly planar biphenyl moieties, whose dihedral angles are 3.5(10)° (A) and 3.9(9)° (B) in crystal **1**, and 1.6(8)° (A) and 1.6(8)° (B) in crystal **2**. The normal chains in both crystals have almost all-trans conformation, while the long chains of the chiral groups in **2** have twisted conformations, as shown in Table 4. The chiral 2-methylbutyl groups of both molecules in **1**

Table 2. (Continued)

Atom	x	y	z	$U_{eq}^{a)}/\text{Å}^2$
C(24B)	0.0281(11)	0.984(9)	0.083(2)	0.33(2)
C(25B)	0.1092(11)	0.588(6)	0.0999(16)	0.253(15)
C(31B)	0.6730(7)	0.426(4)	0.0637(10)	0.137(7)
C(32B)	0.7023(7)	0.205(4)	0.0895(11)	0.158(8)
C(33B)	0.7484(7)	0.195(5)	0.0685(13)	0.167(8)
C(34B)	0.7768(9)	−0.025(5)	0.0929(12)	0.174(8)
C(35B)	0.8220(10)	−0.037(5)	0.0750(16)	0.207(12)
C(36B)	0.8498(11)	−0.264(6)	0.0969(19)	0.236(13)
C(37B)	0.8977(11)	−0.266(7)	0.097(2)	0.250(16)
C(38B)	0.9261(12)	−0.478(6)	0.126(2)	0.263(16)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

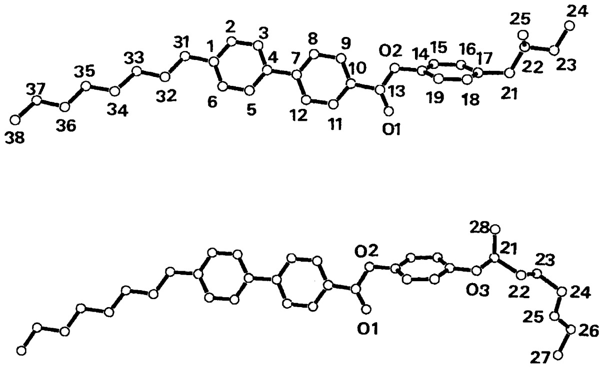


Fig. 1. Molecular structures with numbering schemes; the molecules A of **1** (upper) and **2** (lower). The molecules B have similar conformations with the corresponding A molecules and are numbered in the same way.

have well-defined structures, in contrast to many other cases, where the round group was found to be more or less disordered.[6,14—16)]

Crystal Packing. Figures 2 and 3 show the crystal structures of **1** and **2**, respectively, viewed along the *b* and *c* axes. Both crystals have similar features, as follows. First, each crystal has a smectic-like layer structure. The layer plane is parallel to the *bc* plane. Second, the crystallographically independent molecules, A and B, form a parallel pair, and the pairs are arranged in an antiparallel manner by the 2-fold screw axis, within a layer. Third, both the core moiety and normal paraffin chain contribute to the lateral overlapping of molecules within a layer, leading to the small tilt angle of molecular long axes, 25° (**1**) and 15° (**2**). Fourth, extended paraffin chains deviate from the molecular long axes, as viewed along the *c* axis. As for the core moiety, the lateral packing modes are very similar, as shown in Fig. 4(a) and (b). Both crystals, **1** and **2**, have pseudo-hexagonal array with almost the same size and shape. On the other hand, a difference is observed between the chiral groups. The short 2-methylbutyl groups are accomodated in a layer, while the long chains of the 1-methylheptyloxy groups face each other with twisted conformations between layers, as shown in Fig. 5. How-

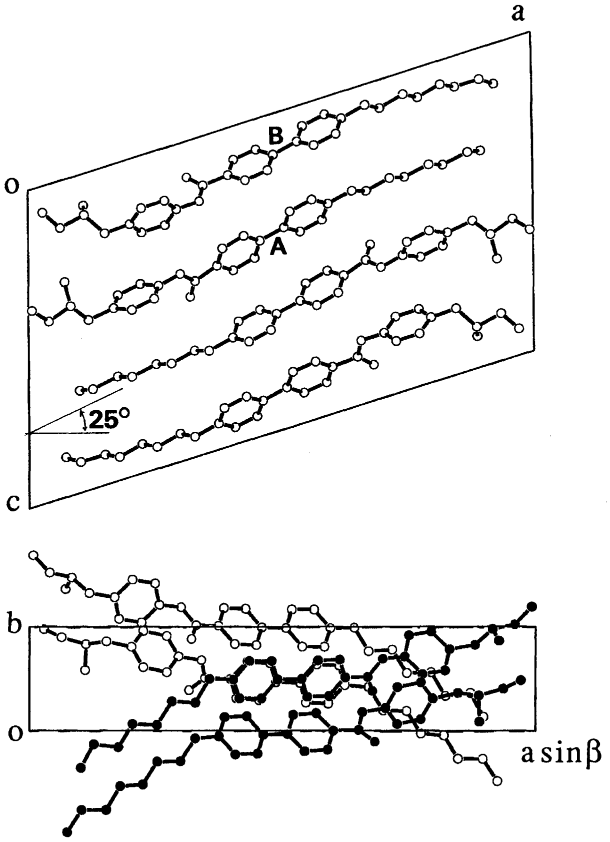


Fig. 2. The crystal structure of **1** viewed along the *b* (upper) and *c* (lower) axes. Atoms of front molecules are denoted by closed circles in the lower figure.

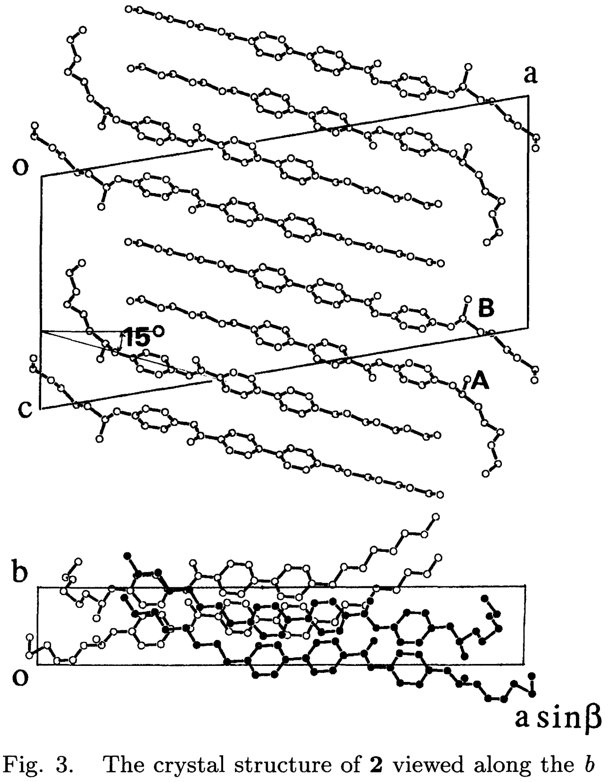


Fig. 3. The crystal structure of **2** viewed along the *b* (upper) and *c* (lower) axes. Atoms of front molecules are denoted by closed circles in the lower figure.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **2**

Atom	x	y	z	$U_{\mathrm{eq}}{}^{\mathrm{a)}}/\text{Å}^2$ or $U_{\mathrm{iso}}{}^{\mathrm{b)}}/\text{Å}^2$
O(1A)	0.6826(2)	1.295(2)	1.1017(5)	0.107(3)
O(2A)	0.6958(2)	0.9539(19)	1.0391(5)	0.087(3)
O(3A)	0.8485(2)	0.973(2)	1.1925(6)	0.111(3)
C(1A)	0.4368(2)	1.0302(15)	0.8089(4)	0.070(3)
C(2A)	0.4633(2)	0.8555(14)	0.7938(4)	0.082(3)
C(3A)	0.5015(2)	0.8695(14)	0.8328(4)	0.077(3)
C(4A)	0.5133(2)	1.0583(16)	0.8870(4)	0.059(3)
C(5A)	0.4868(2)	1.2330(14)	0.9021(4)	0.079(3)
C(6A)	0.4486(2)	1.2190(14)	0.8630(5)	0.086(4)
C(7A)	0.5561(2)	1.0727(16)	0.9275(5)	0.070(3)
C(8A)	0.5830(2)	0.8973(15)	0.9152(5)	0.093(4)
C(9A)	0.6210(2)	0.9157(16)	0.9551(5)	0.097(4)
C(10A)	0.6322(2)	1.1095(18)	1.0075(5)	0.074(3)
C(11A)	0.6053(2)	1.2849(15)	1.0199(5)	0.090(4)
C(12A)	0.5673(2)	1.2665(15)	0.9799(5)	0.091(4)
C(13A)	0.6714(4)	1.133(3)	1.0538(7)	0.079(3)
C(14A)	0.7332(2)	0.9601(17)	1.0786(5)	0.073(3)
C(15A)	0.7583(2)	1.1441(15)	1.0645(4)	0.090(4)
C(16A)	0.7968(2)	1.1371(17)	1.1023(5)	0.097(4)
C(17A)	0.8102(2)	0.9461(19)	1.1542(5)	0.087(4)
C(18A)	0.7850(2)	0.7621(16)	1.1683(4)	0.092(4)
C(19A)	0.7465(2)	0.7691(15)	1.1306(5)	0.077(3)
C(21A)	0.8682(5)	0.780(3)	1.2393(10)	0.154(7)
C(22A)	0.9002(5)	0.903(5)	1.3026(13)	0.239(17)
C(23A)	0.9146(11)	0.760(8)	1.3815(18)	0.330
C(24A)	0.9456(10)	0.926(9)	1.430(2)	0.330
C(25A)	0.9268(10)	1.110(9)	1.481(2)	0.330
C(26A)	0.9437(10)	1.125(9)	1.573(2)	0.330
C(27A)	0.9146(10)	1.310(9)	1.598(2)	0.330
C(28A)	0.8777(5)	0.593(5)	1.1756(17)	0.246(14)
C(31A)	0.3942(3)	1.014(3)	0.7658(7)	0.085(4)
C(32A)	0.3703(3)	1.236(3)	0.7614(7)	0.076(3)
C(33A)	0.3312(3)	1.220(3)	0.7103(8)	0.088(4)
C(34A)	0.3092(3)	1.453(3)	0.7027(7)	0.090(4)
C(35A)	0.2684(3)	1.434(3)	0.6512(7)	0.088(4)
C(36A)	0.2449(4)	1.660(3)	0.6505(8)	0.103(4)
C(37A)	0.2053(4)	1.645(4)	0.5991(10)	0.119(5)
C(38A)	0.1824(5)	1.873(5)	0.5989(13)	0.172(8)
O(1B)	0.6921(3)	0.793(3)	0.7515(6)	0.121(4)
O(2B)	0.6863(2)	0.460(2)	0.8245(5)	0.106(3)
O(3B)	0.8444(2)	0.416(3)	0.9372(6)	0.129(4)
C(1B)	0.4312(2)	0.5462(16)	0.5647(5)	0.073(3)
C(2B)	0.4544(2)	0.7342(14)	0.5447(4)	0.084(4)
C(3B)	0.4934(2)	0.7408(14)	0.5782(5)	0.090(4)
C(4B)	0.5094(2)	0.5594(17)	0.6317(5)	0.064(3)
C(5B)	0.4863(2)	0.3713(14)	0.6517(4)	0.077(3)
C(6B)	0.4472(2)	0.3647(13)	0.6182(5)	0.076(3)
C(7B)	0.5516(2)	0.5769(18)	0.6719(5)	0.072(3)
C(8B)	0.5737(2)	0.7699(16)	0.6516(5)	0.108(5)
C(9B)	0.6126(2)	0.7863(17)	0.6857(5)	0.112(5)
C(10B)	0.6295(2)	0.6097(19)	0.7402(5)	0.080(3)
C(11B)	0.6074(3)	0.4167(16)	0.7605(5)	0.095(4)
C(12B)	0.5685(2)	0.4003(15)	0.7264(5)	0.095(4)
C(13B)	0.6720(4)	0.633(4)	0.7712(9)	0.094(4)
C(14B)	0.7262(2)	0.4551(19)	0.8495(5)	0.086(4)
C(15B)	0.7468(3)	0.2584(17)	0.8267(5)	0.097(4)
C(16B)	0.7863(3)	0.2411(19)	0.8541(5)	0.102(4)
C(17B)	0.8054(2)	0.421(2)	0.9044(6)	0.096(4)
C(18B)	0.7848(3)	0.6174(19)	0.9272(5)	0.102(5)

Table 3. (Continued)

Atom	x	y	z	$U_{eq}{}^{a)}/Å^2$ or $U_{iso}{}^{b)}/Å^2$
C(19B)	0.7452(3)	0.6346(17)	0.8997(5)	0.097(4)
C(21B)	0.8683(4)	0.236(4)	0.9106(11)	0.173(9)
C(22B)	0.9030(6)	0.244(6)	0.9826(14)	0.233(14)
C(23B)	0.9292(8)	0.025(6)	0.9930(15)	0.35(2)
C(24B)	0.9554(7)	0.004(6)	1.0774(18)	0.38(3)
C(25B)	0.9781(11)	0.228(6)	1.110(2)	0.330
C(26B)	1.0112(9)	0.137(8)	1.177(2)	0.330
C(27B)	1.0173(10)	0.365(8)	1.232(2)	0.330
C(28B)	0.8787(6)	0.327(7)	0.8290(11)	0.229(17)
C(31B)	0.3884(3)	0.530(3)	0.5289(8)	0.089(4)
C(32B)	0.3681(3)	0.757(3)	0.5021(8)	0.099(4)
C(33B)	0.3261(4)	0.745(3)	0.4688(8)	0.094(4)
C(34B)	0.3039(4)	0.963(4)	0.4474(9)	0.115(5)
C(35B)	0.2623(3)	0.941(3)	0.4120(8)	0.103(5)
C(36B)	0.2390(4)	1.166(4)	0.3923(10)	0.138(7)
C(37B)	0.1996(5)	1.138(5)	0.3533(15)	0.175(10)
C(38B)	0.1771(6)	1.345(8)	0.3393(19)	0.247(17)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. b) For C(23A)–C27(A) and C(25B)–C(27B), isotropic temperature factors are fixed to be 0.33.

ever, small inter-layer interaction is suggested by the twisted conformation with large temperature factors.

Thus, we conclude that both crystals have very similar packing modes except for the different chiral groups. In other words, the different phase sequences between the two compounds may be ascribable to the different circumstances of the chiral groups. Powder X-ray diffraction showed that the layer thickness of **2** increases only very slightly (about 0.6 Å) at the cryst.-S_B transition point, although this does not necessarily mean that

Table 4. Torsion Angles ($\tau/°$) of Chiral Chains in **2**

	A	B
O(3)–C(21)–C(22)–C(23)	156(3)	161(4)
C(28)–C(21)–C(22)–C(23)	−84(4)	−87(4)
C(21)–C(22)–C(23)–C(24)	180(3)	−163(3)
C(22)–C(23)–C(24)–C(25)	85(5)	−49(6)
C(23)–C(24)–C(25)–C(26)	128(5)	−161(3)
C(24)–C(25)–C(26)–C(27)	−176(4)	−152(4)

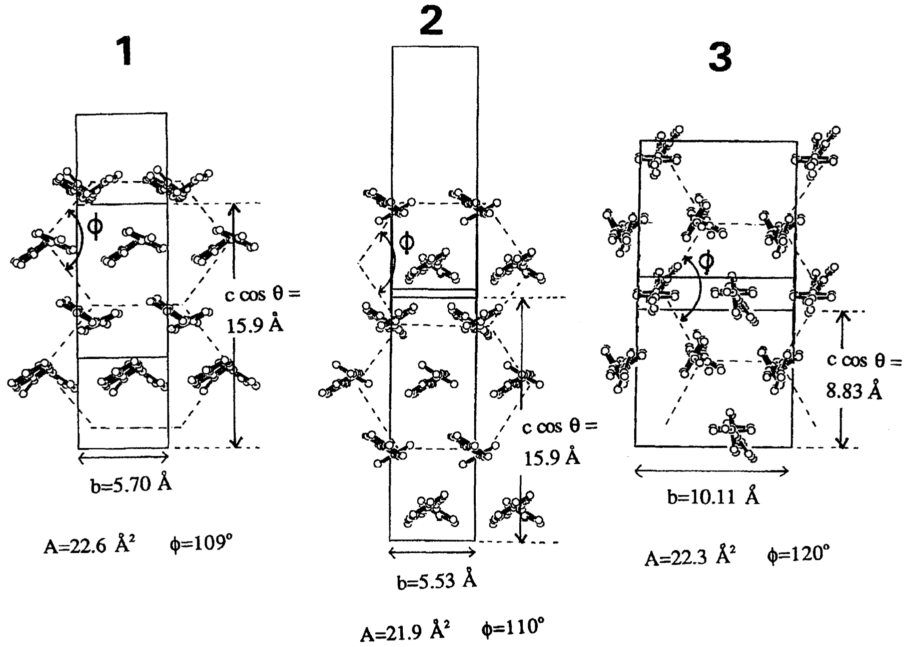


Fig. 4. Schematic diagrams of in-plane packing modes of the core moieties along the molecular long axis for crystals, **1**, **2**, and **3**. For **3**, crystal data at room temperature, a=25.65(1), b=10.109(6), c=10.199(6) Å, β=94.55(6)°, are used. Dashed lines denote pseudo-hexagonal array for the core moieties. θ is a tilt angle of molecular long axis. ϕ is an apex angle of a hexagon denoted in each figure. A is a cross-section area per molecule.

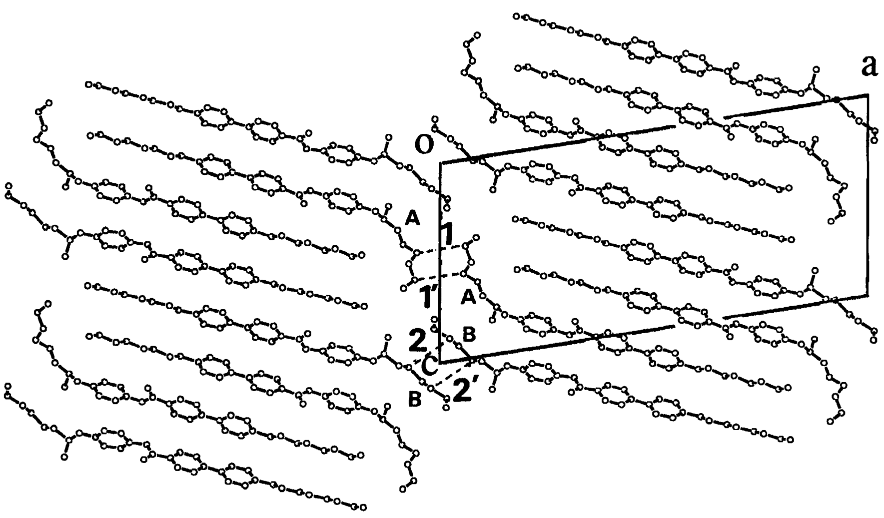
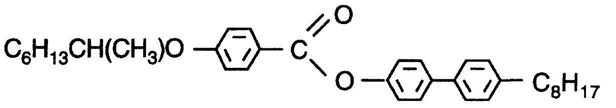


Fig. 5. Interlayer arrangement of long chains in chiral groups for **2**. The shortest inter-chain distances shown by broken lines are 4.23(6) Å for C24A ($x-1$, y, $z-1$)···C26A ($-x+1$, $y-0.5$, $-z+2$) (**1**) and C26A ($x-1$, y, $z-1$)···C24A ($-x+1$, $y+0.5$, $-z+2$) (**1′**) and 4.22(6) Å for C23B ($x-1$, y, z)···C25B ($-x+1$, $y-0.5$, $-z+2$) (**2**) and C25B ($x-1$, y, z)···C23B ($-x+1$, $y+0.5$, $-x+2$) (**2′**). The next shortest distances are 4.32(6) Å for C23B ($x-1$, y, z)···C26B ($-x+1$, $y-0.5$, $-z+2$) and C26B ($x-1$, y, z)···C23B ($-x+1$, $y+0.5$, $-z+2$) and 4.41 Å for C24B ($x-1$, y, z)···C25B ($-x+1$, $y-0.5$, $-z+2$) and C25B ($x-1$, y, z)···C24B ($-x+1$, $y+0.5$, $-z+2$).

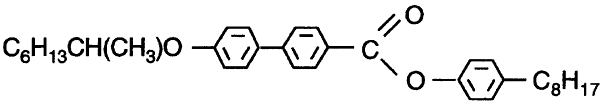
the structural change at the transition is small.

Comparison of the Crystal Structures with Those of Related Compounds. It was reported⁷⁾ that the crystal structure of the 4′-hexyl homologue (**3**) of **1** has a similar packing mode of core moieties to those of **1** and **2**. Two crystallographically independent molecules form a parallel pair, and the pairs are arranged in an antiparallel manner by the 2-fold screw axis, within a smectic-like layer, in which both the core moiety and normal paraffin chain contribute to the lateral overlapping of molecules, leading to the small tilt angle of molecular long axes, 30°. However, molecular conformations are significantly different; twisted biphenyl moieties and highly disordered paraffin chains even at −30 °C, which were interpreted to be responsible to that the crystal transforms directly to $\mathrm{S_A}$. Figure 4(c) shows a lateral packing of crystal **3** viewed along the molecular long axis. Compared to **1** and **2**, **3** has a more regular hexagonal packing, showing more isotropic arrangement within a layer. It is also pointed out that disordered chains result in more straight shape of molecules in **3** than in **1** and **2**. This favors molecular rotation around the molecular long axes and/or mutual shift of molecules along their long axes. Thus, the behavior of **3**, direct transformation from crystal to $\mathrm{S_A}$, is well understood.

The structural isomers of **2**, 4’-octylbiphenyl-4-yl 4-[(*S*)-1-methylheptyloxy]benzoate (**4**),

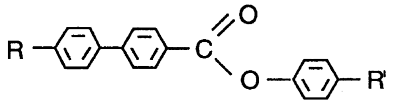


and 4-octylphenyl 4’-[(*S*)-1-methylheptyloxy]biphenyl-4-carboxylate (**5**),



have phase sequences of cryst.-$\mathrm{S_C^*}$-chol.-iso. and cryst.-$\mathrm{S_C^*}$-$\mathrm{S_A}$-chol.-iso., respectively.³⁾ Both crystals have smectic-like layer structures with large (65°) (**4**) and small (10°) (**5**) tilt angles, corresponding to those in $\mathrm{S_C^*}$; 42° for **4** and 29—0° (temperature dependent) for **5**.⁸⁾ In both crystals, two polar groups, O (in an alkoxyl chain) and COO, come close to each other at two points between neighboring molecules, forming antiparallel arrangements of the molecules. The lengths of sandwiched moieties between the two groups, which are short (1 benzene ring) in **4** and long (2 benzene rings) in **5**, determine overlapping of molecules (small (**4**) and large (**5**)) and hence the tilt angles (large (**4**) and small (**5**)). Thus, it was interpreted that the molecular geometry is closely related to the crystal structures and furthermore to the mesophase behavior. The crystal of **2**, discussed in the previous section, shows no such association of the two groups. The difference is assumed to be due to the different direction of COO with respect to O. Goodby pointed out that when C=O in a carbonyloxy group and O in an ether linkage are conjugated within a molecule, the resonance structure favors the association of the two groups.¹⁸⁾ This is the case of **4** and **5**. In the case of **2**, where C=O and O are not conjugated, the O atom seems to behave as only a part of a chain, because the crystal packings of **1**, **2**, and **3** have a common feature, irrespective of whether a terminal chiral group has an O atom or not.

Table 5. Tilt Angles in the Crystal Structures and Phase Sequences for



R	R′	Tilt angle/°	Phase sequence	Ref.
$C_6H_{13}CH(CH_3)O$–	–C_8H_{17}	10	cryst.-S_C^*-S_A-chol.	8)
$C_7H_{15}O$–	–$CH_2CH(CH_3)C_2H_5$	30	cryst.-S_C^*-S_A-chol.	17)
$C_8H_{17}O$–	–$CH_2CH(CH_3)C_2H_5$	30	cryst.-S_C^*-S_A-chol.	17)
C_6H_{13}–	–$CH_2CH(CH_3)C_2H_5$	30	cryst.-S_A-chol.	7)
C_8H_{17}–	–$CH_2CH(CH_3)C_2H_5$	25	cryst.-S_G-S_J^*-S_F^*-S_I^*-S_C^*-S_A-chol.	This work
C_8H_{17}–	–$OCH(CH_3)C_6H_{13}$	15	cryst.-S_B-S_A	This work
$C_2H_5CH(CH_3)CH_2$–	–C_6H_{13}	50	cryst.-chol.	7)
$C_2H_5CH(CH_3)CH_2$–	–OC_5H_{11}	50	cryst.-(S_C^*)-chol.[a)]	14)
$C_2H_5CH(CH_3)CH_2$–	–OC_7H_{15}	60	cryst.-S_C^*-chol.	14)

a) (): monotropic phase.

To make the situation clearer, the tilt angles in crystal structures and phase sequences are summarized in Table 5. There are three groups. In the compounds of the first group, in which C=O and O are conjugated and the sandwiched moiety is long, tilt angles are small (degrees of overlapping within a layer are large). In the second group, molecules with no conjugation between C=O and O still have small tilt angles. In the third group, molecules with no conjugation between C=O and O have large tilt angles. Here, two compounds with hexyl and pentyloxy chains have isomorphous crystals, irrespective of the presence of an O atom in the chain. The difference of the latter two groups is attributed to the different molecular shapes, as follows. The compounds in the second group have biphenyl moieties attached by normal paraffin chains. Thus, it is easy for the biphenyl moieties to overlap largely between neighboring molecules, leading to the small tilt angles. On the other hand, the compounds in the third group have biphenyl moieties attached by bulky chiral groups. Thus, it is difficult for the biphenyl moieties to overlap largely, leading to the small tilt angles. The tilt angle values (degrees of overlapping within a layer) are closely related to the phase sequences; i.e., the smaller one to smectics represented by S_A and the larger one to largely tilted S_C^* and/or chol.

It was found that three compounds with C_nH_{2n+1}-$C_6H_4C_6H_4COOC_6H_4$– (n=6 or 8) crystallize in a similar manner. Among these, only **1** has a very complicated phase sequence beginning from highly ordered S_G, while the other two have only orthogonal smectics (S_B and S_A). The reason for this is not clear, but it should be pointed out that the crystal of **1** has a well-ordered structure with ideally strainless molecular conformation. On the other hand, for **2**, the chains of the chiral groups between layers may be interpreted to work as "lubricant", because they have twisted conformations with large temperature factors. For **3** with a shorter chain, which is highly disordered, less intermolecular interaction than for **1** and **2** within a layer is assumed, in accordance with its direct transformation to S_A from the crystal.

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References

1) J. W. Goodby, R. Blinc, N. A. Clark, S. T. Lagerwall, M. A. Osipov, S. A. Pikin, T. Sakurai, K. Yoshino, and B. Zeks, "Ferroelectric Liquid Crystals," Gordon and Breach, Philadelphia (1991).

2) W. Kuczynski and H. Stegemyer, *Liq. Cryst.*, **5**, 553 (1989). Helical structures were confirmed for S_J, S_F, S_I, and S_C, but not for S_G.

3) T. Inukai, S. Saitoh, H. Inoue, K. Miyazawa, K. Terashima, and K. Furukawa, *Mol. Cryst. Liq. Cryst.*, **141**, 251 (1986).

4) J. Budai, R. Pindak, S. C. Davey, and J. W. Goodby, *J. Phys. Lett.*, (*Orsay, Fr.*), **45**, L1053 (1984).

5) S. Gierlotka, J. Przedmojski, and B. Pura, *Liq. Cryst.*, **11**, 1535 (1988).

6) Z. Paszeuski, J. Rutkowska, J. Kedzierski, P. Perkouski, W. Piecek, J. Zielinski, J. Zmija, and R. Dabrowski, *Ferroelectrics*, **147**, 281 (1993).

7) K. Ito, K. Endo, K. Hori, T. Nemoto, H. Uekusa, and Y. Ohashi, *Liq. Cryst.*, **17**, 747 (1994).

8) K. Hori and Y. Ohashi, *J. Mater. Chem.*, **1**, 667 (1991).

9) M. C. Burla, M. Camall, C. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, and D. Viterbo, "SIR88, structure analysis programs," (1988).

10) G. J. Gilmore, "MITHRIL90, structure analysis programs," (1990).

11) G. M. Sheldrick, "SHELXL93. A program for the refinement of the crystal structure," University of Göttingen

(1993).

12) A. J. C. Wilson, "International Tables for Crystallography," Kluwer Academic Publishers, Dordrecht (1993), Vol. C.

13) The tables of the bond lengths and angles, anisotropic temperature factors of the non-hydrogen atoms, the atomic parameters for hydrogen atoms and the F_o–F_c list have been deposited as Document No. 68064 at the Office of the Editor of Bull. Chem. Soc. Jpn.

14) K. Hori and Y. Ohashi, *Bull. Chem. Soc. Jpn.*, **61**, 3859 (1988).

15) K. Hori and Y. Ohashi, *Bull. Chem. Soc. Jpn.*, **62**, 3216 (1989).

16) K. Hori and Y. Ohashi, *Liq. Cryst.*, **9**, 383 (1991).

17) K. Hori, M. Takamatsu, and Y. Ohashi, *Bull. Chem. Soc. Jpn.*, **62**, 1751 (1989).

18) J. W. Goodby, in Ref. 1, pp. 147 and 174.