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Crystal structures of chiral mesogenic 4-hexylphenyl 4′-[(*S*)-2-methylbutyl]biphenyl-4-carboxylate and 4-[(*S*)-2-methylbutyl]phenyl 4′-hexylbiphenyl-4-carboxylate

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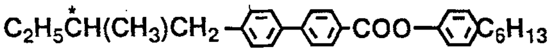
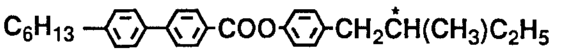
Single crystal X-ray analysis has been carried out for 4-hexylphenyl 4′-[(*S*)-2-methylbutyl]biphenyl-4-carboxylate (**1**), which has a phase sequence of crystal–cholesteric–isotropic, and 4-[(*S*)-2-methylbutyl]phenyl 4′-hexylbiphenyl-4-carboxylate (**2**), which has a phase sequence of crystal–S_A–cholesteric–isotropic. Crystal data:



$C_2H_5\overset{*}{C}H(CH_3)CH_2-C_6H_4-C_6H_4-COO-C_6H_4-C_6H_{13}$ (1)

$M_r = 428{\cdot}61$, $C_{30}H_{36}O_2$, monoclinic, $P2_1$, $T = 298\,K$, $a = 25{\cdot}697(3)$, $b = 5{\cdot}7055(4)$, $c = 18{\cdot}718(1)\,Å$, $\beta = 110{\cdot}124(7)°$, $V = 2576{\cdot}8(4)\,Å^3$, $Z = 4$, $d_x = 1{\cdot}105\,g\,cm^{-3}$, $F(000) = 928{\cdot}00$, $\mu = 4{\cdot}49\,cm^{-1}$;



$C_6H_{13}-C_6H_4-C_6H_4-COO-C_6H_4-CH_2\overset{*}{C}H(CH_3)C_2H_5$ (2)

$M_r = 428{\cdot}61$, $C_{30}H_{36}O_2$, monoclinic, $P2_1$, $T = 239\,K$, $a = 25{\cdot}631(2)$, $b = 10{\cdot}019(1)$, $c = 10{\cdot}081(1)\,Å$, $\beta = 94{\cdot}67(1)°$, $V = 2580{\cdot}1(5)\,Å^3$, $Z = 4$, $d_x = 1{\cdot}103\,g\,cm^{-3}$, $F(000) = 928{\cdot}00$, $\mu = 4{\cdot}48\,cm^{-1}$.

Each crystal has a smectic-like layer structure, in which the molecular tilt angle is 50° in **1**, and 30° in **2**. Chiral groups are disordered in both crystals. Normal alkyl chains are also highly disordered in **2**. The features correspond to the different mesophase sequences. The layer thickness of S_A was measured for **2** by X-ray diffraction.

1. Introduction

In order to elucidate intermolecular interactions controlling various kinds of liquid crystalline phases, we intended to find relations between mesophase characteristics (phase sequences, structures and properties) and molecular interactions revealed in crystal structures by X-ray crystal structure analysis. Some correlations between liquid crystalline behaviour and crystal structures have been found for a series of chiral biphenyl esters having an alkoxy group [1–5], whose crystal structures were interpreted to be controlled by the interaction between an ester group and an ether group [6].

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On the other hand, chiral biphenyl esters having an alkyl group show quite different phase sequences, depending on the position of the chiral chain [7, 8]. This paper describes the crystal structures of the following mesogenic compounds, in which the chiral and the normal chains are exchanged;

4-hexylphenyl 4′-[(*S*)-2-methylbutyl]biphenyl-4-carboxylate (**1**)

$$\mathrm{C} \xrightarrow{60{\cdot}3^{\circ}\mathrm{C}} \mathrm{Ch} \xleftrightarrow{132{\cdot}3^{\circ}\mathrm{C}} \mathrm{I}\ [7]\ \text{and}$$

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

$$\mathrm{C} \xrightarrow{81{\cdot}0^{\circ}\mathrm{C}} \mathrm{S_A} \xleftrightarrow{132{\cdot}6^{\circ}\mathrm{C}} \mathrm{Ch} \xleftrightarrow{146{\cdot}2^{\circ}\mathrm{C}} \mathrm{I}\ [8].$$

2. Experimental

2.1. *Synthesis*

Both compounds were synthesized and purified in a similar manner to those reported previously [1, 2]. Melting points and phase transition temperatures are in good agreements with the reported values [7, 8].

2.2. *Apparatus*

Powder X-ray diffraction patterns were obtained using a Rigaku RAD-RA diffractometer. Melting and the transition points were measured on a Mettler FP 84 differential scanning calorimeter.

2.3. *Crystal structure analysis*

Single crystals appropriate to the structure determination were grown from an ethyl acetate–ethanol solution (**1**) and an ethyl acetate–methanol solution (**2**). Data collection procedures are summarized in table 1. For **2**, the data was collected at room temperature and at 239 K: the data collected at room temperature had insufficient intensity.

Table 1. Experimental conditions.

	1	**2**
X-ray source	Cu K_α mochromated by graphite ($\lambda = 1{\cdot}54184$ Å)	
Diffractometer	Rigaku AFC-4	Rigaku AFC-5
Measuring temperature	298 K	239 K
L.s. for cell const.	20 refl. ($39^\circ < 2\theta < 61^\circ$)	24 refl. ($35^\circ < 2\theta < 51^\circ$)
Scan mode	$2\theta - \omega$	
2θ range	$3^\circ < 2\theta < 125^\circ$	$3^\circ < 2\theta < 110^\circ$
Scan width	$\omega = (1{\cdot}0 + 0{\cdot}15 \tan\theta)^\circ$	$\omega = (1{\cdot}73 + 0{\cdot}15 \tan\theta)^\circ$
Scan rate/°(2θ) min^{-1}	8	16
Backgrounds	5 s at both ends of a scan	
Standard reflections	3 after every 50 reflections	3 after every 100 reflections
Intensity variation	Not significant	
Crystal size/mm	$0{\cdot}4 \times 0{\cdot}3 \times 0{\cdot}02$	$0{\cdot}5 \times 0{\cdot}6 \times 0{\cdot}02$
Total number of reflections	4644	3245
Number of reflections	2085 ($> 4\sigma(\lvert F_o \rvert)$)	1477($> 3\sigma(\lvert F_o \rvert)$)
Correction	Lp but not for absorption	

The structures were solved by applying the programs MULTAN78 [9] for **1** and SHELX86 [10] for **2**, and refined by loosely constrained full-matrix least-squares (in two blocks) using SHELX76 [11]. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w=[\sigma(|F_o|)^2+0{\cdot}004\ |F_o|^2]^{-1}$ for **1** and $w=[\sigma(|F_o|)^2+0{\cdot}016481\ |F_o|^2]^{-1}$ for **2**. Atomic scattering factors were taken from International Tables for X-ray Crystallography [12].

In the course of refinement of **1**, additional peaks were found around the chiral groups, whose temperature factors were remarkably large. These peaks were included as disordered atoms in further refinements. All other non-hydrogen atoms were refined anisotropically. Only 22 hydrogen atoms found in the difference Fourier maps were included in the refinement. Final $R(R_w)$ values were 0·096 (0·107). $(\Delta/\sigma)_{max}$ and $\Delta\rho_{max}$ in the final refinement were 0·36 and 0·38 e Å^{-3}, respectively. The final atomic coordinates of non-hydrogen atoms are given in table 2 [13]. Computations were carried out on an IBM 4381-R24 computer at the Information Processing Center of Ochanomizu University.

For **2**, both of the paraffin chains and the chiral groups were refined by assuming disordering. Some of the atoms in the chains, however, still have large temperature factors, in spite of no significant peaks around them. Besides, it was very difficult to obtain appropriate geometries for these disordered atoms, especially for those with minor occupancies. These facts are considered to be due to the highly disordered structures. Two conformers for each molecule were taken into account in order to restrict the number of the parameters. Thus, the occupation factors were adjusted to have approximately the same temperature factors for the two conformers and were fixed in further refinements. The benzene rings were also fixed to have an ideal shape, because of the small number of reflections. Most of the non-hydrogen atoms without disorder were refined anisotropically, while some of them and disordered atoms were refined isotropically. Hydrogen atoms were not included in the refinement, because of the limited number of reflections. $(\Delta/\sigma)_{max}$ and $\Delta\rho_{max}$ in the final refinement were 0·39 and 0·37 e Å^{-3}, respectively. Final $R(R_w)$ values were 0·132 (0·137). The large R value is due to the highly disordered structure and the limited conditions of the refinements mentioned above. The final atomic coordinates of non-hydrogen atoms are given in table 3 [13]. Computations were carried out on an SPARC Station 2 computer at Tokyo Institute of Technology.

3. Results and discussion

3.1. *Molecular conformations*

All the bond lengths and angles are compatible with those reported earlier [1–5]. There are two crystallographically independent molecules, *A* and *B*, in both crystals. Molecular structures with numbering schemes are shown in figure 1. The molecules have nearly planar biphenyl moieties, whose dihedral angles are 5·1° (*A*) and 4·8° (*B*) in crystal **1**, while in crystal **2** biphenyl moieties are twisted with dihedral angles of 37° (*A*) and 29° (*B*). The chains of the chiral groups are highly disordered around the C_{22} (*A*) and C_{22}(*B*) atoms in crystal **1**, whereas not only the chains of the chiral groups but also the normal alkyl chains have highly disordered conformations in crystal **2**. Table 4 shows torsion angles of the normal chains. The chains in crystal **1** have all-*trans* conformations. On the other hand, the molecule *A* has two nearly all-*trans* conformers, while the molecule *B* has twisted conformers in crystal **2**.

Table 2. Atomic coordinates with their estimated standard deviations for 4-hexylphenyl 4′-[(*S*)-2-methylbutyl]biphenyl-4-carbonylate (**1**).

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$†
O_1A	0·8356(4)	0·592(2)	0·1666(5)	11·6
O_2A	0·7870(3)	0·3096	0·1857(4)	7·2
C_1A	1·0032(4)	0·516(2)	0·6957(5)	4·7
C_2A	0·9676(5)	0·333(2)	0·6647(5)	8·3
C_3A	0·9397(6)	0·319(2)	0·5879(6)	9·9
C_4A	0·9377(4)	0·509(2)	0·5397(5)	5·2
C_5A	0·9759(5)	0·688(2)	0·5709(5)	8·3
C_6A	1·0064(4)	0·696(2)	0·6469(6)	8·1
C_7A	0·9069(3)	0·500(2)	0·4516(4)	3·9
C_8A	0·8713(4)	0·317(2)	0·4233(5)	5·4
C_9A	0·8399(4)	0·305(2)	0·3440(5)	6·0
$C_{10}A$	0·8506(4)	0·467(2)	0·2956(4)	5·7
$C_{11}A$	0·8835(4)	0·663(2)	0·3262(5)	6·9
$C_{12}A$	0·9130(4)	0·676(2)	0·4029(6)	6·6
$C_{13}A$	0·8237(4)	0·478(2)	0·2112(6)	4·7
$C_{14}A$	0·7599(4)	0·275(2)	0·1059(5)	5·0
$C_{15}A$	0·7721(4)	0·089(2)	0·0677(5)	6·5
$C_{16}A$	0·7427(5)	0·067(2)	−0·0091(6)	6·7
$C_{17}A$	0·7059(4)	0·236(2)	−0·0505(5)	6·4
$C_{18}A$	0·6959(4)	0·429(2)	−0·0104(7)	8·0
$C_{19}A$	0·7222(4)	0·445(2)	0·0681(5)	6·5
$C_{21}A$	1·0405(8)	0·507(4)	0·7743(9)	12·9
$C_{22}A$	1·021(1)	0·620(7)	0·850(2)	22·1
$C_{23}A$	1·059(2)	0·477(8)	0·926(2)	5·9(8)‡
$C_{23}A'$	0·995(2)	0·418(10)	0·837(3)	12·6(17)‡
$C_{23}A''$	0·959(2)	0·705(9)	0·810(2)	7·1(10)‡
$C_{24}A$	1·032(2)	0·540(9)	0·958(2)	9·0(11)‡
$C_{24}A'$	1·022(3)	0·550(12)	0·795(4)	10·3(17)‡
$C_{24}A''$	0·976(3)	0·861(14)	0·879(4)	20·6(25)‡
$C_{25}A$	0·976(2)	0·828(8)	0·808(2)	7·3(10)‡
$C_{25}A'$	1·020(3)	0·869(11)	0·819(3)	13·5(20)‡
$C_{25}A''$	1·072(2)	0·620(9)	0·927(2)	7·7(11)‡
$C_{31}A$	0·6795(4)	0·246(3)	−0·1329(6)	5·9
$C_{32}A$	0·6898(5)	0·051(4)	−0·1725(7)	10·4
$C_{33}A$	0·6669(5)	0·055(2)	−0·2587(6)	6·5
$C_{34}A$	0·6722(5)	−0·201(4)	−0·3007(8)	10·7
$C_{35}A$	0·6544(5)	−0·145(3)	−0·3873(6)	7·2
$C_{36}A$	0·6640(6)	−0·323(3)	−0·4342(7)	9·9
O_1B	0·3377(3)	0·124(2)	0·6666(4)	7·7
O_2B	0·2861(3)	0·441(2)	0·6812(4)	5·8
C_1B	0·4974(5)	0·240(3)	1·1886(6)	8·7
C_2B	0·4571(7)	0·409(3)	1·1545(8)	11·6
C_3B	0·4284(4)	0·409(2)	1·0767(7)	7·2
C_4B	0·4367(5)	0·239(2)	1·0292(6)	6·4
C_5B	0·4736(5)	0·064(2)	1·0634(7)	7·3
C_6B	0·5033(5)	0·063(2)	1·1403(7)	8·4
C_7B	0·4029(5)	0·258(2)	0·9486(5)	7·2
C_8B	0·3692(4)	0·444(2)	0·9143(5)	6·0
C_9B	0·3418(4)	0·448(2)	0·8356(5)	5·5
$C_{10}B$	0·3484(4)	0·264(2)	0·7923(6)	6·0
$C_{11}B$	0·3842(4)	0·079(2)	0·8257(6)	6·8
$C_{12}B$	0·4118(5)	0·077(2)	0·9048(6)	7·7
$C_{13}B$	0·3260(5)	0·260(3)	0·7070(7)	7·3
$C_{14}B$	0·2612(4)	0·451(2)	0·6019(6)	6·6

Atom	x	y	z	$B_{eq}/Å^2$†
$C_{15}B$	0·2691(4)	0·653(2)	0·5670(7)	6·7
$C_{16}B$	0·2477(5)	0·670(2)	0·4877(6)	8·1
$C_{17}B$	0·2087(4)	0·503(2)	0·4471(5)	6·2
$C_{18}B$	0·1962(5)	0·314(2)	0·4851(5)	6·9
$C_{19}B$	0·2226(5)	0·283(2)	0·5623(7)	7·3
$C_{21}B$	0·5365(5)	0·235(3)	1·2751(6)	9·0
$C_{22}B$	0·5046(7)	0·190(3)	1·3272(6)	8·7
$C_{23}B$	0·505(1)	−0·745(6)	0·1333(2)	8·6(8)‡
$C_{23}B'$	0·467(1)	−0·033(6)	0·1318(2)	9·3(8)‡
$C_{24}B$	0·551(2)	0·071(10)	0·1409(2)	6·0(9)‡
$C_{24}B''$	0·547(5)	−0·095(24)	0·1414(5)	13·8(35)‡
$C_{24}B'$	0·437(2)	−0·065(14)	0·1372(3)	10·6(17)‡
$C_{24}B'''$	0·491(3)	−0·165(14)	0·1399(3)	11·3(20)‡
$C_{25}B$	0·572(1)	0·246(7)	0·1413(2)	9·2(8)‡
$C_{25}B'$	0·540(2)	0·260(10)	0·1424(2)	14·6(14)‡
$C_{31}B$	0·1769(8)	0·501(3)	0·3590(7)	12·0
$C_{32}B$	0·1905(5)	0·731(2)	0·3168(6)	7·0
$C_{33}B$	0·1623(5)	0·731(4)	0·2281(7)	10·1
$C_{34}B$	0·1828(6)	0·919(2)	0·1929(6)	7·3
$C_{35}B$	0·1469(8)	0·892(4)	0·1027(9)	14·4
$C_{36}B$	0·1696(8)	1·111(3)	0·0721(9)	14·2

†$B_{eq}=(8\pi^2/3)\Sigma_i\Sigma_j U_{ij}\mathbf{a}_i\mathbf{a}_j$.

‡Occupancies were fixed as follows. $C_{23}A$–$C_{25}A''$, 0·33333; $C_{23}B$, $C_{23}B'$, $C_{25}B$ and $C_{25}B'$, 0·5; $C_{24}B$, 0·3; $C_{24}B''$, 0·2; $C_{24}B'$ and $C_{24}B'''$, 0·25. Isotropic temperature factors are applied to these atoms.

Table 3. Atomic coordinates with their estimated standard deviations for 4-[(*S*)-2-methylbutyl]phenyl 4′-hexylbiphenyl-4-carboxylate (**2**).

Atom	x	y	z	$B_{eq}/Å^2$†
O_1A	0·3248(5)	1·03750	1·278(1)	9·3(4)‡
O_2A	0·3005(5)	0·846(2)	1·189(1)	8·3(3)‡
C_1A	0·6113(4)	0·919(1)	0·780(1)	6·2
C_2A	0·5637(4)	0·880(1)	0·715(1)	7·5
C_3A	0·5182(4)	0·882(1)	0·782(1)	8·3
C_4A	0·5203(4)	0·922(1)	0·915(1)	7·6
C_5A	0·5680(4)	0·961(1)	0·980(1)	8·0
C_6A	0·6134(4)	0·959(1)	0·913(1)	7·1
C_7A	0·4701(4)	0·931(1)	0·9955(9)	5·2
C_8A	0·4320(4)	0·832(1)	0·9764(9)	5·4
C_9A	0·3880(4)	0·835(1)	1·0491(9)	7·9
$C_{10}A$	0·3821(4)	0·937(1)	1·1410(9)	6·6
$C_{11}A$	0·4203(4)	1·036(1)	1·1601(9)	7·5
$C_{12}A$	0·4643(4)	1·033(1)	1·0874(9)	6·6
$C_{13}A$	0·3331(7)	0·949(2)	1·203(2)	7·3(5)‡
$C_{14}A$	0·2552(6)	0·855(2)	1·251(2)	9·9
$C_{15}A$	0·2550(6)	0·797(2)	1·377(2)	8·4
$C_{16}A$	0·2102(6)	0·804(2)	1·447(2)	9·6
$C_{17}A$	0·1654(6)	0·868(2)	1·390(2)	15(1)‡
$C_{18}A$	0·1656(6)	0·925(2)	1·264(2)	19(1)‡
$C_{19}A$	0·2104(6)	0·918(2)	1·194(2)	20
$C_{21}A$	0·1202(7)	0·899(3)	1·476(2)	17(1)‡
$C_{22}A$	0·0698(7)	0·855(3)	1·396(3)	23(2)‡
$C_{23}A$	0·0231(9)	0·876(4)	1·477(4)	28(3)‡
$C_{24}A$	−0·005(4)	1·00(1)	1·43(1)	26(5)§

Atom	x	y	z	B_{eq}/Å^2†
$C_{24}A'$	−0·027(1)	0·85(2)	1·392(8)	26(6)§
$C_{24}A''$	0·018(5)	0·76(1)	1·57(1)	21(7)§
$C_{25}A$	0·076(1)	0·707(3)	1·367(4)	23(2)‡
$C_{31}A$	0·6570(7)	0·921(3)	0·696(2)	11·7(8)‡
$C_{32}A$	0·7066(9)	0·867(4)	0·765(3)	7·(1)§
$C_{32}A'$	0·710(1)	0·937(6)	0·770(4)	7·(1)§
$C_{33}A$	0·750(1)	0·852(8)	0·675(5)	15(3)§
$C_{33}A'$	0·752(1)	0·894(8)	0·679(5)	8(2)§
$C_{34}A$	0·802(1)	0·817(5)	0·752(4)	9(1)§
$C_{34}A'$	0·807(1)	0·905(7)	0·750(5)	9(2)§
$C_{35}A$	0·843(2)	0·790(9)	0·650(5)	18(2)§
$C_{35}A'$	0·848(2)	0·89(1)	0·654(6)	15(3)§
$C_{36}A$	0·896(1)	0·786(7)	0·728(6)	16(2)§
$C_{36}A'$	0·902(2)	0·91(1)	0·728(8)	16(3)§
O_1B	0·3918(5)	0·751(1)	0·431(1)	8·1(3)‡
O_2B	0·4188(5)	0·620(2)	0·598(1)	8·2(3)‡
C_1B	0·7329(5)	0·606(2)	0·220(2)	10·2(6)‡
C_2B	0·7251(5)	0·597(2)	0·355(2)	12
C_3B	0·6747(5)	0·607(2)	0·397(2)	6·5
C_4B	0·6321(5)	0·627(2)	0·304(2)	7·0
C_5B	0·6399(5)	0·637(2)	0·169(2)	8·1
C_6B	0·6903(5)	0·626(2)	0·127(2)	9·0
C_7B	0·5779(4)	0·643(1)	0·355(1)	7·5
C_8B	0·5653(4)	0·580(1)	0·471(1)	5·1
C_9B	0·5154(4)	0·595(1)	0·515(1)	7·8
$C_{10}B$	0·4781(4)	0·673(1)	0·442(1)	5·5
$C_{11}B$	0·4908(4)	0·736(1)	0·326(1)	7·6
$C_{12}B$	0·5407(4)	0·721(1)	0·282(1)	7·5
$C_{13}B$	0·4259(6)	0·685(2)	0·487(1)	6·0(4)‡
$C_{14}B$	0·3713(4)	0·617(1)	0·6512(9)	5·7
$C_{15}B$	0·3496(4)	0·495(1)	0·6847(9)	8·5
$C_{16}B$	0·3059(4)	0·492(1)	0·7585(9)	11
$C_{17}B$	0·2839(4)	0·611(1)	0·7988(9)	8·7
$C_{18}B$	0·3056(4)	0·733(1)	0·7653(9)	8·8
$C_{19}B$	0·3493(4)	0·736(1)	0·6914(9)	7·8(5)‡
$C_{21}B$	0·2379(7)	0·592(3)	0·882(2)	11·2(7)‡
$C_{22}B$	0·1871(9)	0·616(3)	0·809(3)	12·8(8)‡
$C_{23}B$	0·142(1)	0·592(4)	0·901(3)	17(1)‡
$C_{24}B$	0·095(2)	0·67(1)	0·837(9)	23(4)§
$C_{24}B'$	0·130(2)	0·718(6)	0·971(7)	18(3)§
$C_{25}B$	0·176(1)	0·522(4)	0·688(2)	16(1)‡
$C_{31}B$	0·782(1)	0·566(4)	0·164(3)	14·3(9)‡
$C_{32}B$	0·823(1)	0·662(4)	0·160(5)	25(2)‡
$C_{33}B$	0·875(1)	0·579(7)	0·156(9)	26(4)§
$C_{33}B'$	0·866(2)	0·638(6)	0·071(6)	14(2)§
$C_{34}B$	0·920(2)	0·675(9)	0·176(9)	30·0
$C_{34}B'$	0·894(3)	0·508(7)	0·092(9)	18(3)§
$C_{35}B$	0·955(2)	0·653(8)	0·058(7)	20(3)§
$C_{35}B'$	0·950(2)	0·527(9)	0·04(1)	20(4)§
$C_{36}B$	0·986(4)	0·52(1)	0·094(9)	29(5)§
$C_{36}B'$	0·971(4)	0·39(1)	0·01(2)	30·0

† $B_{eq}=(8\pi^2/3)\Sigma_i\Sigma_j U_{ij}\mathbf{a}_i\mathbf{a}_j$.

‡Isotropic temperature factors.

§Occupancies were fixed as follows. $C_{24}A$, 0·4; $C_{24}A'$, 0·35; $C_{24}A''$, 0·25; $C_{24}B$, 0·52; $C_{24}B'$, 0·48; $C_{32}A$–$C_{36}A$, 0·591; $C_{32}A'$–$C_{36}A'$, 0·409; $C_{33}B$–$C_{36}B$, 0·6; $C_{33}B'$–$C_{36}B'$, 0·4. Isotropic temperature factors are applied to these atoms. Temperature factors of $C_{34}B$ and $C_{36}B'$ were fixed.

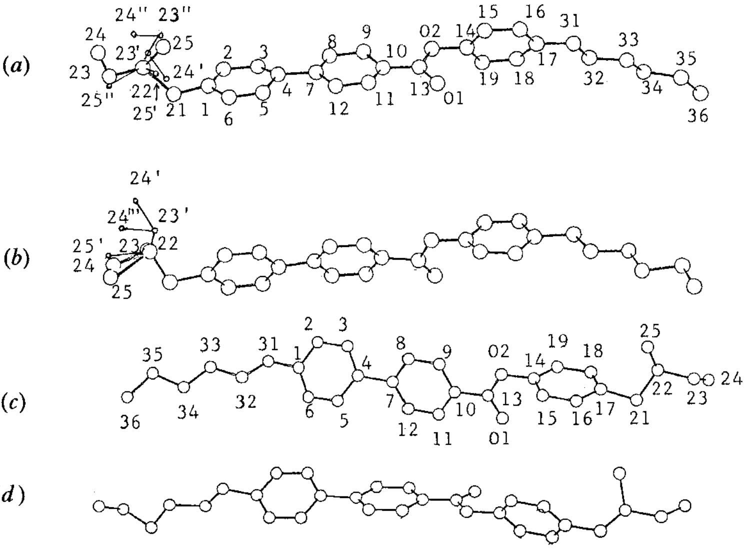


Figure 1. Molecular structures with numbering schemes. (*a*) The molecule *A* of **1**, (*b*) the molecule of *B* of **1**, (*c*) the molecule *A* of **2** and (*d*) the molecule *B* of **2**. The molecules *B* are numbered in the same way as the corresponding molecules *A*. For (*a*) and (*b*), disordered atoms with minor occupancies are denoted by small circles. $C_{23}B$ is almost hidden by $C_{22}B$ and $C_{24}B'$ is also hidden by $C_{24}B$. Disordered structures of **2** are shown in figure 4.

Table 4. Torsion angles (τ/°).

	1		**2**			
Alkyl chains	*A*	*B*	*A*		*B*	
C^*–C_{31}–C_{32}–C_{33}	176	−176	163	172	156	−163
C_{31}–C_{32}–C_{33}–C_{34}	170	170	−179	172	−170	−163
C_{32}–C_{33}–C_{34}–C_{35}	172	178	−168	174	−127	−155
C_{33}–C_{34}–C_{35}–C_{36}	−169	−176	177	168	−77	−156

C^* means C_{17} for **1** and C_1 for **2**. For **2**, torsion angles of two conformers are shown for two molecules, *A* and *B*; C_{31}–C_{36} (left) and C'_{31}–C'_{36} (right).

3.2. *Crystal packing*

Figure 2 shows the crystal structure of **1** viewed along the *b* axis. The crystal has a smectic-like layer structure. The layer plane is parallel to the (10$\bar{1}$) plane, which is denoted by dot-and-dash lines. Molecular long axes are largely tilted (50°) in the smectic-like layer. Paraffin chains are in close contact with each other between layers. Nearest neighbour phenyl rings in adjacent molecules make an angle of 60°, on average.

Figure 3 shows the crystal structure of **2** viewed along the *b* and *c* axes. The disordered atoms are denoted by shadowed circles. This crystal also has a smectic-like layer structure, whose layer plane is parallel to the *bc* plane. Here, the whole molecule including a normal chain contributes to the lateral packing within a layer, resulting in a more distinct layer structure than that in crystal **1**. A tilt angle of the molecular long axis is 30°, which is smaller than that of **1**. The phenyl rings between adjacent molecules in

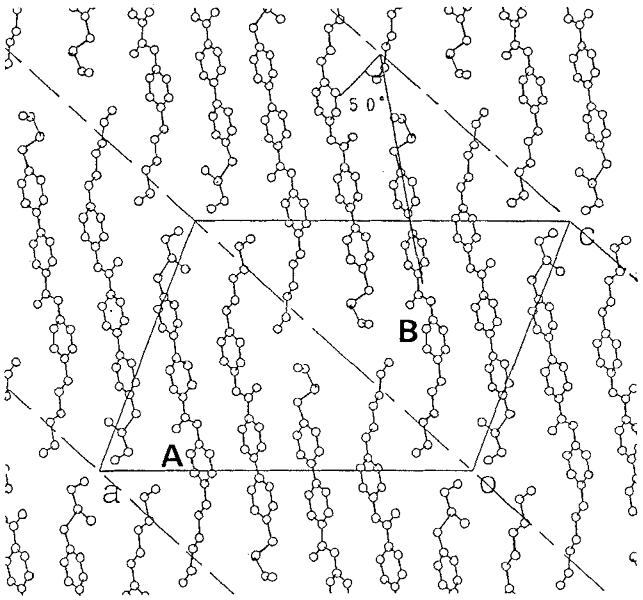


Figure 2. The crystal structure of **1** viewed along the *b* axis. Layer planes are denoted by dashed lines. Disordered atoms with minor occupancies are omitted for clarity.

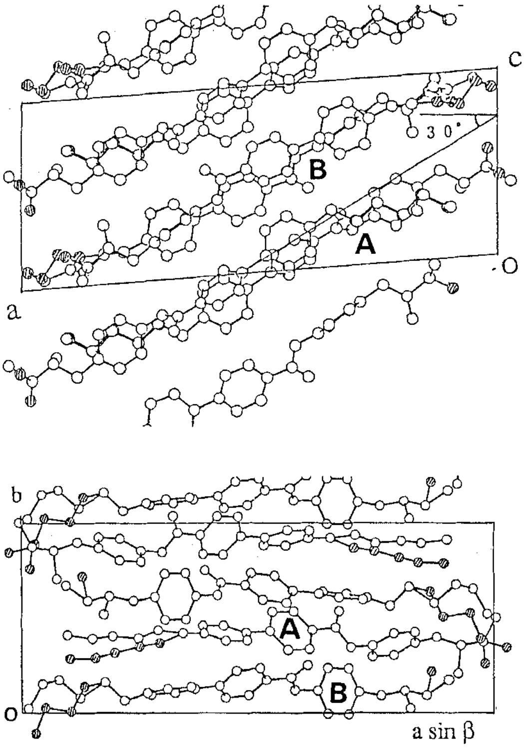


Figure 3. The crystal structure of **2** viewed along the *b* axis (upper) and along the *c* axis (lower). Disordered atoms are shown with shadowed circles.

crystal **2** are arranged more irregularly, i.e. with a wider range of contact angles (18–86°), than in crystal **1**.

The crystal data of **2** at room temperature are $P2_1$, $a = 25{\cdot}65(1)$, $b = 10{\cdot}109(6)$, $c = 10{\cdot}199(6)$ Å, $\beta = 94{\cdot}55(6)°$, $V = 2636(2)$ Å^3. Comparing these data with those at 239 K, coefficients of thermal expansion along the a, b and c axes are calculated to be 8×10^{-4}, 9×10^{-3} and 1×10^{-2} K^{-1}, respectively. This means that the expansion parallel to the layer plane is ten times larger than that along the direction of the layer stacking.

3.3. *S_A layer thickness of 2*

In order to elucidate a structural change at the melting point (C–S_A) of **2**, the thickness of the layer was measured by X-ray diffraction, as shown in figure 4. The layer thickness in the crystal is 24·5 Å. The thickness in the S_A phase at the melting point is 27·5 Å. The molecules tilt to the layer by 30° in the crystal, giving the molecular length to be 28·3 Å, which is comparable to the layer thickness in S_A. This indicates that the molecules change their tilt angle from 30 to 0° at the C–S_A transition. In the S_A phase, layer thickness slightly decreases as the temperature increases. This temperature dependence, which was also observed in the S_A of 4-[(*S*)-2-methylbutyl]phenyl 4′-alkoxybiphenyl-4-carboxylate series [2] and *p*-octylphenyl 4′-[(*S*)-1-methylheptyloxy]biphenyl-4-carboxylate [5], is attributable to the melting of paraffin chains and/or the increasing of the precession amplitudes of the molecules. For the present compound, the paraffin chains are found to have highly disordered conformations even in the crystal. Thus, it is suggested that the latter effect is dominant.

On cooling, the S_A phase supercooled to 59°C: subsequently, diffraction peaks corresponding to $d = 24{\cdot}5$ and 19 Å appeared. The former had a greater intensity than the latter and became higher as the temperature decreased, while the latter vanished at room temperature. Therefore, the former corresponds to the crystalline state and the latter to a metastable phase. The thickness of 19 Å corresponds to the tilt angle of 45°, which is contradictory to the statement that the compound has a S_B phase as a supercooled phase [8]. However, the fact that it always appeared as a minor portion with the crystalline phase prevented us from analysing the phase in detail.

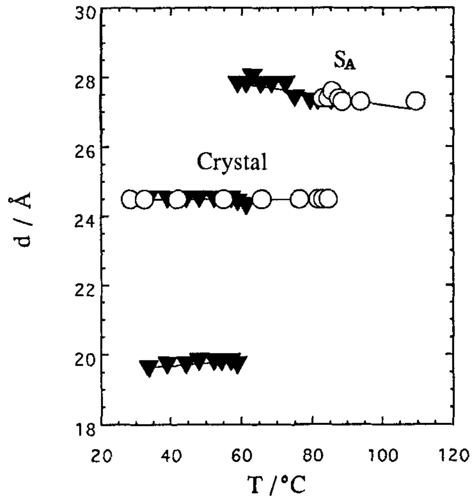
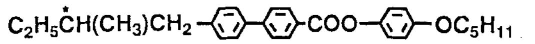


Figure 4. Temperature dependence of the layer thickness. Open circles and closed triangles give the values on heating and cooling, respectively.

3.4. *Comparison with the alkoxy compounds*

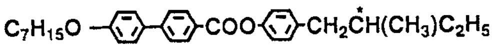
Figure 5 shows a comparison of the crystal structures of **1** and 4-pentyloxyphenyl 4′-[(*S*)-2-methylbutyl]biphenyl-4-carbonylate (**3**):



(**3**)

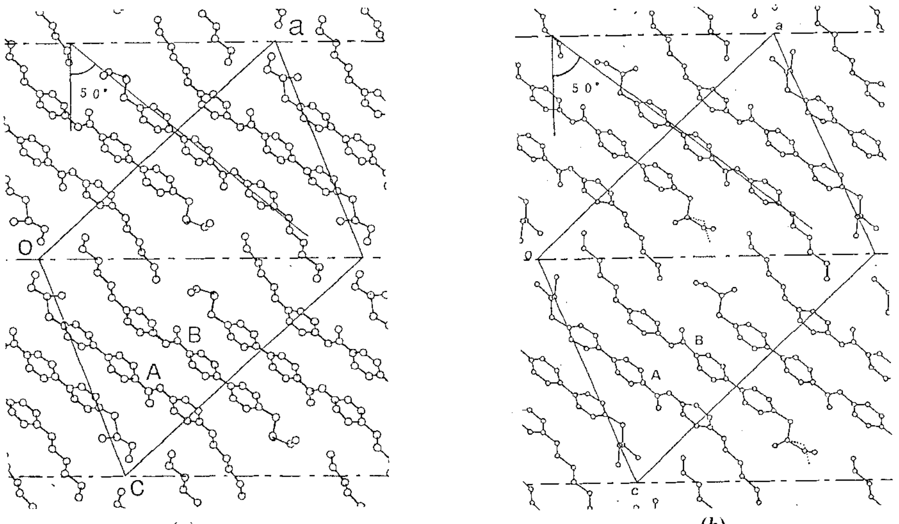
The chain lengths are almost the same between the two compounds, since the hexyl group in **1** is replaced by the pentyloxy group in **3**. These crystal structures are very similar to each other except for the conformations of the chiral groups. In the previous paper, we simply assumed that the chain is so short that the crystal **3** transforms directly to the cholesteric phase, while the longer chain homologues transform to the S_c^* phase [1]. For the hexyl compound also, inter-chain interaction between layers is assumed to be insufficient to have the S_C^* phase. More precisely, however, the pentyloxy compound has a monotropic S_C^* phase [7]. This may indicate that the interaction between the ether group and the phenyl ring in **3** is of significant importance.

In figure 6, the crystal structure of **2** is compared with the heptyloxy homologue (**4**) of the counterpart series, 4-[(*S*)-2-methylbutyl]phenyl 4′-alkoxybiphenyl-4-carboxylates,



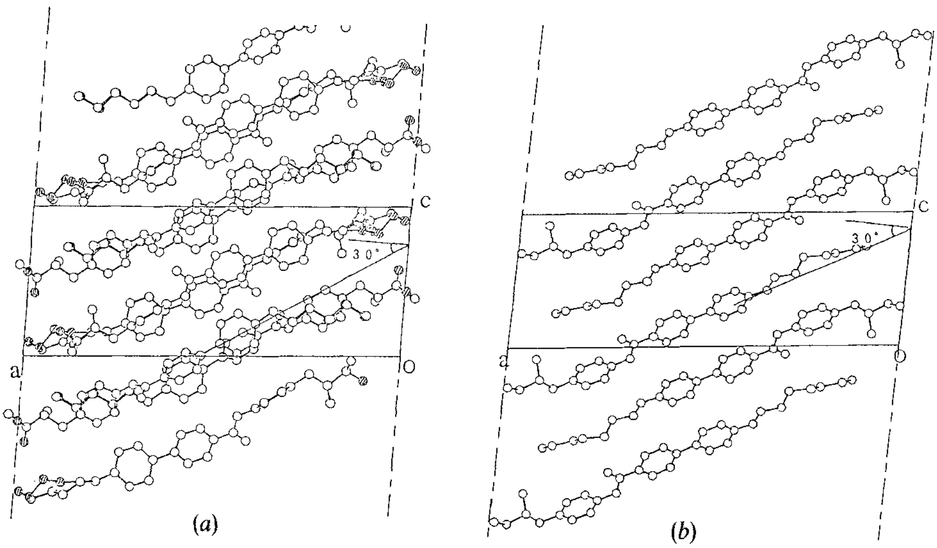
(**4**)

because the crystal structure of the pentyloxy compound has not been determined. The compound **4** has a phase sequence of C–S_C^*–S_A-chol. [14]. In crystal **4** [2], each molecule has a coplanar biphenyl moiety and a twisted paraffinic chain. The twisting in the chain causes a straighter shape of the molecule as a whole than those in crystals **1** and **3**. The whole molecule including the paraffinic chain contributes to the lateral overlapping, which forms a distinct smectic-like layer structure. The tilt angle is estimated to be 30°. Thus, the layer structure of **4** is very similar to that of **2**. It seems reasonable to say that both crystals, with large extent of molecular overlapping within a layer, transform to smectics. A significant difference is, however, found between the two crystals. The paraffinic chain has a well-defined structure, although twisted, in



(*a*) (*b*)

Figure 5. Comparison of the structures of **1** (*a*) and **3** (*b*).



(*a*) (*b*)

Figure 6. Comparison of the structures of **2** (*a*) and **4** (*b*).

crystal **4**, while it is highly disordered in crystal **2** even at low temperature. This fact indicates that the intermolecular interaction within a layer in crystal **2** is weaker than that in crystal **4**. The intra-layer interaction in crystal **4** was also enhanced by the close arrangement of the ester and the ether groups at two points between adjacent molecules [6]. On the other hand, no such interactions between the polar groups are found in crystal **2** because of the lack of the ester group. The above structural differences may be responsible for the fact that crystal **4** transforms to S_C^* and then to S_A, while crystal **2** transforms directly to S_A.

In summary, the exchange of the chiral group and the normal chain brings about the different tilt angles in the smectic-like layer structures and the different organizations of the normal alkyl chains. Such differences appear to explain the different liquid crystalline behaviour of the two compounds.

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