  Bull. Chem. Soc. Jpn., 61, 3859—3867 (1988)

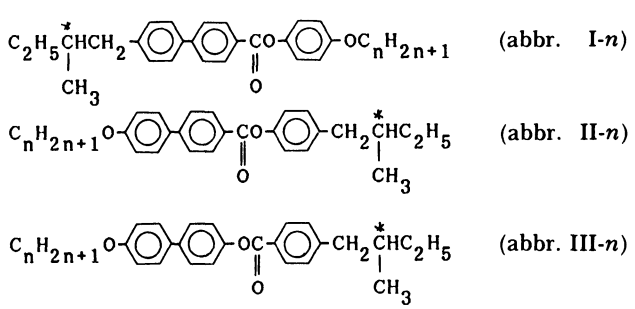
Crystal Structures of Chiral Smectogenic 4-Pentyloxyphenyl and 4-Heptyloxyphenyl 4′-[(*S*)-2-Methylbutyl]biphenyl-4-carboxylates

Kayako HORI* and Yuji OHASHI
Department of Chemistry, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112
(Received June 15, 1988)

Crystal structures of the title compounds, which have a Sm* C phase adjacent to a cholesteric, have been determined by single crystal X-ray analysis. 4-Pentyloxyphenyl 4′-[(*S*)-2-methylbutyl]biphenyl-4-carboxylate: monoclinic, $P2_1$, a=25.085(2), b=5.7522(3), c=18.668(1) Å, β=110.275(9)°, Z=4. 4-Heptyloxyphenyl 4′-[(*S*)-2-methylbutyl]biphenyl-4-carboxylate: triclinic, $P1$, a=14.607(1), b=17.212(2), c=5.7322(8) Å, α=94.84(1), β=84.03(1), γ=108.607(9)°, Z=2. Final R-values were 0.113 and 0.083, respectively. Both crystals have layer structures similar to those of Sm* C phase. Two crystallographically independent molecules in each crystal are related by a pseudo-inversion. Paraffin chains with extended conformations have close contacts between layers.

The Sm* C phase of liquid crystals has become of interest because of its unique ferroelectricity. Precise structures and molecular interaction in the phase, however, are not sufficiently clear, because it is very difficult to obtain microscopic structural information due to rapid molecular motions. So, we intended to find a relationship between the mesophase characteristics (phase sequences, structures and properties) and molecular interaction revealed in the crystal structures, by X-ray crystal structure analysis for a series of compounds with various mesophase characteristics.

For this purpose, three types of compounds containing biphenyl esters were chosen, since their mesophase characteristics have already been examined.[1] The first type, 4-alkoxyphenyl 4′-[(*S*)-2-methylbutyl]biphenyl-4-carboxylates, has a Sm* C phase with iridescent color caused by a short-pitched helical structure, between crystalline and cholesteric phases.[2] Powder X-ray diffraction patterns showed that I-5 and I-7 are isomorphous with I-6 and I-8, respectively.[3] This paper describes the crystal structures of I-5 and I-7 in detail.



Experimental

The compounds were obtained in the same way as described previously.[4] Transparent long parallelepiped crystals were grown from a methanol–chloroform solution. Crystals of dimensions, 0.4×0.3×0.1 mm (I-5) and 0.5×0.4×0.1 mm (I-7) were used. The unit cell dimensions and space groups were determined from oscillation and Weissenberg photographs. Accurate cell parameters were determined by a least-squares fit for 16 reflections within the range $39°<2\theta<52°$ (I-5) and 20 reflections within the range $33°<2\theta<52°$ (I-7), measured on a Rigaku AFC-4 diffractometer with Cu $K\alpha$ radiation (λ=1.54184 Å) monochromatised by graphite. Crystal data. I-5, M_r=430.56, $C_{29}H_{34}O_3$, monoclinic, $P2_1$, T=298 K, a=25.085(2), b=5.7522(3), c=18.668(1) Å, β=110.275(9)°, V=2526.8(4) Å^3, Z=4, d_x=1.131 g cm^{-3}, μ=4.90 cm^{-1}, $F(000)$=928; I-7, M_r=458.61, $C_{31}H_{38}O_3$, triclinic, $P1$, T=298 K, a=14.607(1), b=17.212(2), c=5.7322(8) Å, α=94.84(1), β=84.03(1), γ=108.607(9)°, V=1356.4(3) Å^3, Z=2, d_x=1.123 g cm^{-3}, μ=4.79 cm^{-1}, $F(000)$=496. Intensity data were collected by 2θ–ω scan mode, up to 2θ=125°. Scan width was $\Delta\omega=(1.0+0.15\tan\theta)°$. 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. For I-5, a total of 4497 reflections were collected at a rate of $4°(2\theta)$ min^{-1}, of which 3345 were treated as significant ($|F_o|>3\sigma(|F_o|)$). For I-7, 4345 reflections were collected at a rate of $8°(2\theta)$ min^{-1}, of which 3692 were used in the calculation. The data were corrected for Lorentz and polarization factors but not for absorption.

The structures were determined by applying the program MULTAN78[5] and refined by constrained block-matrix least-squares using SHELX76.[6] The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w=(\sigma(F_o)^2+0.004|F_o|)^{-1}$. In the course of the refinement of both structures, additional peaks of 0.5—1.0 e Å^{-3} were found around the chiral groups, whose atoms revealed considerably large temperature factors. These peaks were included as disordered atoms in further refinement. For I-5, C(22) to C(25) of the molecule A and C(23) to C(25) of B were disordered, whereas only the terminal C(24) atoms of A and B were disordered for I-7. All the non-hydrogen atoms except for the disordered ones of I-7 were refined anisotropically with loosely constrained condition to have normal geometries. Some hydrogen atoms were found in the difference Fourier maps and others were derived geometrically except for the chiral parts and the terminal atoms of the alkyl chains of I-5. Final refinement including the hydrogen atoms were performed with the program HBLS,[7] since the numbers of the parameters became too large for SHELX76. Max. Δ/σ and max. $\Delta\rho$ in the final difference map were 0.52 and 0.25 e Å^{-3} for I-5, and 0.54 and 0.30 e Å^{-3} for I-7. Final R (and R_w) were 0.113 (0.139) and 0.083 (0.098) for I-5 and I-7, respectively. Rather large R-value of I-5 is due to the disordered structures of the chiral parts. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[8] The final

Table 1. Final Atomic Coordinates with Their Estimated Standard Deviations of 4-Pentyloxyphenyl 4′-[(S)-2-Methylbutyl]biphenyl-4-carboxylate (I-5)

Atom	x	y	z	B_{eq}/Å^{2}[a]
O(1A)	0.1630(2)	1.1093(15)	0.8335(3)	10.7
O(2A)	0.2156(2)	0.8131(11)	0.8180(3)	7.0
O(3A)	0.3178(2)	0.6911(14)	1.1284(3)	8.8
C(1A)	0.0019(4)	0.9993(17)	0.3075(4)	8.1
C(2A)	0.0400(4)	0.8260(19)	0.3413(5)	9.7
C(3A)	0.0702(4)	0.8224(17)	0.4176(5)	8.4
C(4A)	0.0654(3)	1.0052(16)	0.4644(4)	6.9
C(5A)	0.0270(3)	1.1835(17)	0.4305(4)	7.6
C(6A)	−0.0050(4)	1.174(2)	0.3547(5)	8.7
C(7A)	0.0950(3)	0.9984(13)	0.5489(4)	5.8
C(8A)	0.1316(3)	0.818(2)	0.5824(4)	7.8
C(9A)	0.1593(3)	0.8067(15)	0.6603(4)	6.4
C(10A)	0.1507(3)	0.9816(19)	0.7072(5)	8.0
C(11A)	0.1151(4)	1.1695(16)	0.6743(5)	8.0
C(12A)	0.0893(4)	1.1783(18)	0.5943(4)	8.3
C(13A)	0.1759(3)	0.9872(18)	0.7909(4)	7.3
C(14A)	0.2396(3)	0.7904(19)	0.8956(5)	7.5
C(15A)	0.2260(4)	0.5884(19)	0.9269(4)	8.3
C(16A)	0.2527(3)	0.5507(17)	1.0045(5)	8.0
C(17A)	0.2920(3)	0.7064(18)	1.0496(4)	7.3
C(18A)	0.3038(3)	0.9022(17)	1.0173(4)	7.4
C(19A)	0.2790(3)	0.9481(18)	0.9405(4)	7.2
C(21A)	−0.0369(4)	1.001(3)	0.2225(5)	10.5
C(22A)[b]	−0.0059(11)	1.068(4)	0.1677(12)	14.0
C(23A)[b]	−0.0003(8)	1.323(4)	0.1687(9)	11.3
C(24A)[b]	0.0261(11)	1.380(6)	0.1124(14)	17.0
C(25A)[b]	−0.0409(13)	1.005(6)	0.0851(14)	20.6
C(22A′)[b]	−0.0162(11)	1.175(10)	0.1767(11)	23.7
C(23A′)[b]	−0.0581(12)	1.213(7)	0.0960(14)	16.0
C(24A′)[b]	−0.0570(10)	0.989(7)	0.0681(10)	15.6
C(25A′)[b]	0.0454(9)	1.271(7)	0.1978(14)	13.8
C(31A)	0.3075(3)	0.492(2)	1.1657(4)	8.9
C(32A)	0.3334(3)	0.531(2)	1.2536(5)	9.2
C(33A)	0.3248(4)	0.328(3)	1.2994(5)	11.4
C(34A)	0.3494(4)	0.3777(19)	1.3845(5)	10.6
C(35A)	0.3342(4)	0.187(2)	1.4334(6)	10.4
O(1B)	0.3353(2)	0.1458(12)	0.6592(3)	8.5
O(2B)	0.2846(2)	0.4424(10)	0.6757(3)	6.8
O(3B)	0.1813(2)	0.5549(11)	0.3638(3)	7.6
C(1B)	0.4969(3)	0.2217(18)	1.1872(4)	7.3
C(2B)	0.4588(3)	0.401(2)	1.1561(4)	7.8
C(3B)	0.4283(3)	0.4047(18)	1.0785(4)	7.1
C(4B)	0.4358(3)	0.2350(14)	1.0298(4)	5.5
C(5B)	0.4730(4)	0.060(2)	1.0615(5)	8.5
C(6B)	0.5020(4)	0.0443(19)	1.1398(4)	8.2
C(7B)	0.4032(3)	0.2471(16)	0.9455(4)	6.2
C(8B)	0.3675(3)	0.4299(14)	0.9110(4)	5.8
C(9B)	0.3388(3)	0.4366(16)	0.8318(4)	7.0
C(10B)	0.3472(2)	0.2618(12)	0.7872(3)	4.6
C(11B)	0.3820(3)	0.0752(16)	0.8203(4)	6.7
C(12B)	0.4100(3)	0.0686(16)	0.8979(4)	6.4
C(13B)	0.3225(3)	0.2741(14)	0.7016(4)	6.8
C(14B)	0.2602(3)	0.4676(12)	0.5955(4)	5.1
C(15B)	0.2721(3)	0.6659(14)	0.5625(4)	6.0
C(16B)	0.2473(3)	0.6988(16)	0.4842(4)	6.4
C(17B)	0.2096(3)	0.5341(15)	0.4404(4)	5.9
C(18B)	0.1953(3)	0.3408(16)	0.4741(4)	7.2
C(19B)	0.2202(3)	0.3107(16)	0.5528(4)	6.4
C(21B)	0.5329(4)	0.229(3)	1.2725(4)	9.4
C(22B)	0.5002(4)	0.164(3)	1.3246(4)	12.2
C(23B)[b]	0.5383(7)	0.127(4)	1.4079(7)	13.0
C(24B)[b]	0.5650(8)	0.345(7)	1.4361(8)	17.7
C(25B)[b]	0.4627(6)	−0.040(4)	1.3023(7)	9.9
C(23B′)[b]	0.5443(17)	0.230(11)	1.401(3)	26.3
C(24B′)[b]	0.5286(13)	0.222(10)	1.4653(14)	13.6

Table 1. (Continued)

Atom	x	y	z	B_{eq}/Å$^{2a)}$
C(25B')[b]	0.4831(16)	−0.075(10)	1.2994(18)	15.4
C(31B)	0.1963(4)	0.7440(16)	0.3259(4)	7.7
C(32B)	0.1632(4)	0.709(2)	0.2400(4)	9.2
C(33B)	0.1810(3)	0.9026(19)	0.1964(4)	7.5
C(34B)	0.1510(3)	0.873(3)	0.1095(4)	10.3
C(35B)	0.1682(5)	1.066(3)	0.0662(6)	13.0

a) $B_{eq}=(4/3)\sum_{ij}\beta_{ij}(a_i\cdot a_j)$. b) Occupation factors are fixed as 0.55, 0.45, 0.66, and 0.34 for C(22A)–C(25A), C(22A')–C(25A'), C(23B)–C(25B), and C(23B')–C(25B'), respectively.

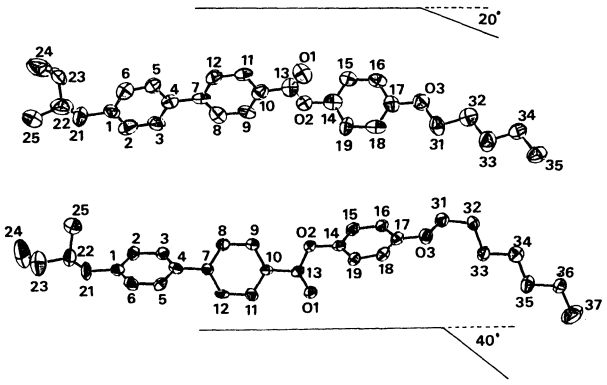


Fig. 1. ORTEP views of the molecules A of 4-pentyloxyphenyl 4'-[(*S*)-2-methylbutyl]biphenyl-4-carboxylate (I-5, upper) and 4-heptyloxyphenyl 4'-[(*S*)-2-methylbutyl]biphenyl-4-carboxylate (I-7, lower) with 50% probability thermal ellipsoids. Only one of the two conformers of the disordered part is shown for simplicity.

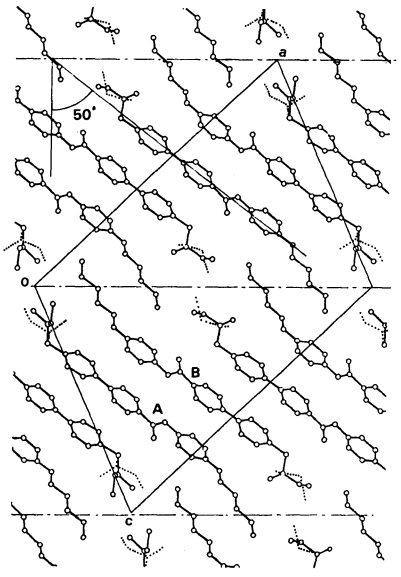


Fig. 2. Crystal structure of I-5 viewed along the b axis. The dot-and-dash lines denote interfaces of the layer. The dotted lines denote disordered conformers.

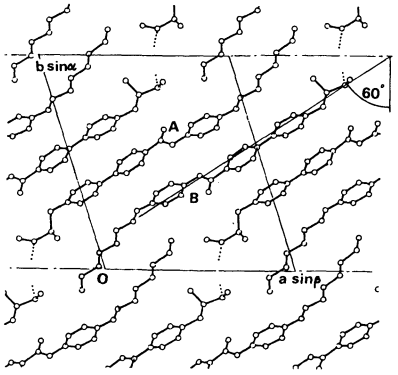


Fig. 3. Crystal structure of I-7 viewed along the c axis. The dot-and-dash lines denote interfaces of the layer. The dotted lines denote disordered conformers.

coordinates of non-hydrogen atoms are given in Tables 1 (I-5) and 2 (I-7).[9] Computations were done on a HITAC M-280H at the Computer Center of the University of Tokyo.

Results and Discussion

Molecular Conformations. There are two crystallographically independent molecules with approximately the same conformation in an asymmetric unit for both crystals. The ORTEP drawings of the molecular structures with numbering schemes are shown in Fig. 1.[10] Chiral parts are highly disordered even in the crystalline state for I-5, while they are only slightly disordered for I-7. All the bond lengths and bond angles, as given in Tables 3 and 4, are compatible with those found in other mesogens.[11] All the phenyl rings are planar within the experimental error.

Table 5 shows torsion angles characteristic to the molecular conformations. Each molecule in the I-5 crystal has an approximately coplanar biphenyl moiety and an all-trans zigzag paraffin chain, while a largely twisted biphenyl moiety and an extended paraffin chain with a twisted O–C–C–C part are found in the I-7 crystal. In each crystal, an extended alkyl chain results in a bent shape of a molecule as a whole, as shown in Fig. 1. The angles between the chains and the other part of the molecules are approximately 20° (I-5) and 40° (I-7).

Crystal Packing. Figures 2 and 3 show the crystal

Table 2. Final Atomic Coordinates with Their Estimated Standard Deviations of 4-Heptyloxyphenyl 4′-[(*S*)-2-Methylbutyl]biphenyl-4-carboxylate (I-7)

Atom	*x*	*y*	*z*	B_{eq}/Å^2[a]
O(1A)	0.5409(3)	0.6614(3)	0.4871(10)	8.1
O(2A)	0.5624(3)	0.5910(2)	0.7792(7)	5.4
O(3A)	0.9550(3)	0.7584(3)	0.7960(8)	6.5
C(1A)	−0.0876(5)	0.3158(4)	0.6937(12)	5.8
C(2A)	−0.0458(4)	0.3625(4)	0.8884(11)	5.3
C(3A)	0.0513(4)	0.4097(4)	0.8781(11)	5.5
C(4A)	0.1104(5)	0.4036(3)	0.6759(10)	5.0
C(5A)	0.0717(5)	0.3561(4)	0.4795(11)	5.8
C(6A)	−0.0261(6)	0.3098(4)	0.4955(13)	6.7
C(7A)	0.2150(4)	0.4544(3)	0.6554(9)	4.5
C(8A)	0.2724(4)	0.4566(4)	0.8358(10)	4.9
C(9A)	0.3702(4)	0.5029(3)	0.8238(9)	4.5
C(10A)	0.4071(4)	0.5554(3)	0.6412(9)	4.4
C(11A)	0.3492(4)	0.5584(4)	0.4661(10)	5.2
C(12A)	0.2536(4)	0.5072(4)	0.4747(8)	4.2
C(13A)	0.5090(4)	0.6095(3)	0.6267(9)	4.6
C(14A)	0.6606(4)	0.6377(4)	0.7734(10)	5.2
C(15A)	0.6923(5)	0.6835(4)	0.9767(11)	5.8
C(16A)	0.7902(5)	0.7255(4)	0.9897(11)	5.6
C(17A)	0.8560(4)	0.7205(3)	0.8013(11)	5.2
C(18A)	0.8243(4)	0.6707(3)	0.6024(11)	5.3
C(19A)	0.7258(4)	0.6333(4)	0.5830(10)	5.1
C(21A)	−0.1963(5)	0.2705(6)	0.705(2)	9.4
C(22A)	−0.2246(6)	0.1784(6)	0.702(2)	10.6
C(23A)	−0.3300(8)	0.1327(9)	0.665(3)	14.2
C(24A)[c]	−0.4035(14)	0.1466(19)	0.848(6)	24.0
C(24A′)[c]	−0.377(5)	0.045(4)	0.624(13)	13.6[b]
C(25A)	−0.2021(10)	0.1475(12)	0.918(3)	18.2
C(31A)	0.9944(5)	0.8083(4)	0.9954(12)	6.6
C(32A)	1.1016(5)	0.8473(4)	0.9336(12)	6.1
C(33A)	1.1223(5)	0.9038(4)	0.7312(14)	6.7
C(34A)	1.2282(6)	0.9579(5)	0.7175(15)	7.3
C(35A)	1.2522(5)	1.0167(5)	0.5165(18)	8.3
C(36A)	1.3572(5)	1.0740(5)	0.5039(14)	7.3
C(37A)	1.3874(11)	1.1303(8)	0.298(3)	14.2
O(1B)	0.6751(3)	0.3699(3)	1.3815(8)	6.6
O(2B)	0.6558(3)	0.4456(3)	1.1017(7)	6.0
O(3B)	0.2640(3)	0.2769(2)	1.0858(7)	4.8
C(1B)	1.3041(4)	0.7262(4)	1.1888(14)	6.6
C(2B)	1.2670(5)	0.6770(5)	0.9950(14)	6.7
C(3B)	1.1681(4)	0.6356(3)	0.9974(10)	4.8
C(4B)	1.1073(4)	0.6345(4)	1.2028(9)	4.5
C(5B)	1.1447(5)	0.6859(4)	1.3936(11)	6.4
C(6B)	1.2432(5)	0.7298(5)	1.3905(12)	7.0
C(7B)	1.0029(4)	0.5811(3)	1.2090(8)	4.4
C(8B)	0.9425(4)	0.5841(3)	1.0401(9)	4.4
C(9B)	0.8464(4)	0.5337(4)	1.0465(10)	4.9
C(10B)	0.8099(4)	0.4817(3)	1.2312(9)	4.5
C(11B)	0.8690(4)	0.4799(3)	1.4052(9)	4.9
C(12B)	0.9648(4)	0.5296(4)	1.3919(12)	5.6
C(13B)	0.7087(4)	0.4264(4)	1.2565(11)	5.4
C(14B)	0.5561(4)	0.4003(4)	1.0975(10)	4.8
C(15B)	0.5245(4)	0.3529(4)	0.8954(10)	5.4
C(16B)	0.4265(5)	0.3107(4)	0.8871(10)	5.4
C(17B)	0.3611(4)	0.3148(3)	1.0777(9)	4.4
C(18B)	0.3952(4)	0.3605(3)	1.2803(9)	4.5
C(19B)	0.4919(4)	0.4071(4)	1.2869(10)	4.9
C(21B)	1.4135(6)	0.7675(5)	1.1815(16)	8.2
C(22B)	1.4536(7)	0.8318(8)	1.006(3)	15.9
C(23B)	1.5638(9)	0.8652(9)	0.971(4)	18.2
C(24B)[c]	1.5997(16)	0.8910(16)	1.209(8)	27.2
C(24B′)[c]	1.576(5)	0.931(4)	1.153(12)	18.1[b]
C(25B)	1.4050(9)	0.8958(6)	1.037(3)	15.2
C(31B)	0.2278(5)	0.2276(4)	0.8827(12)	6.3
C(32B)	0.1202(6)	0.1843(5)	0.9355(15)	7.7

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å[2a)]
C(33B)	0.0991(5)	0.1236(4)	1.1306(14)	7.0
C(34B)	−0.0091(5)	0.0788(4)	1.1801(14)	7.1
C(35B)	−0.0324(6)	0.0154(4)	1.3635(12)	7.0
C(36B)	−0.1397(7)	−0.0322(5)	1.387(2)	9.8
C(37B)	−0.1582(7)	−0.0970(6)	1.5671(17)	9.5

a) $B_{eq}=(4/3)\sum_{ij}\beta_{ij}(a_i \cdot a_j)$. b) Isotropic temperature factors. c) Occupation factors are fixed as 0.8, 0.2, 0.7, and 0.3 for C(24A), C(24A′),C(24B), and C(24B′), respectively.

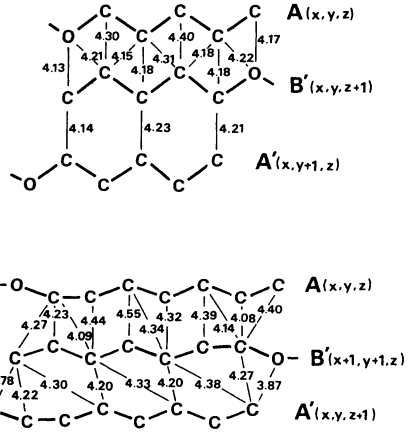


Fig. 4. Inter-chain distances (Å) of I-5 (upper) and I-7 (lower). Symmetry codes are shown in parentheses.

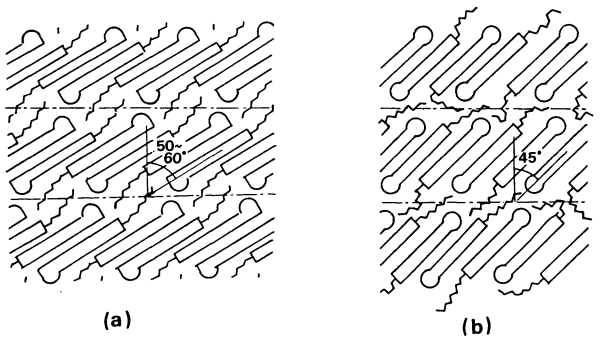


Fig. 5. Schematic diagrams of the structures of the crystal (a) and Sm* C (b). In the latter, the tilt direction forms a slightly helical distribution on moving from layer to layer. A half-rounded head in (a) denotes a static bulky 2-methylbutyl group, while a round head in (b) denotes a rotating one.

structures of I-5 and I-7, respectively. They have a similar packing mode. Layer structures similar to those of smectics are composed of two crystallographically independent molecules A and B, which are related by a pseudo-inversion except for the chiral parts. In a crystal of an achiral compound, 4,4′-bis(pentyloxy)azoxybenzene had a layer structure composed of equivalent molecules, in which a layer plane was very clear, corresponding to the existence of an "intermediately highly ordered smectics".[12] In the present case, layer planes, although less clear, are parallel to the (10$\bar{1}$) plane (I-5) and the (010) plane (I-7). The molecular long axis is largely tilted in the layer. The tilt angles are estimated to be 50° (I-5) and 60° (I-7).

Paraffin chains of adjacent molecules are in contact with each other between layers. The inter-chain distances are shown in Fig. 4. The molecules A and B′ are contact in the range of 4.13—4.40 Å for I-5 and 4.08—4.55 Å for I-7. The wider range of I-7 is caused by the twisted O–C–C–C parts. Neverthless, the inter-chain distances in the two crystals are very close to the values found in the crystalline long-chain compounds; 4.14 and 4.20 Å for hexatriacontane[13] or 4.13 and 4.20 Å for normal-chain fatty acids.[14] Furthermore, the chains of the molecules B′ and A′ are also relatively close, though the zigzag chains are out of phase each other. Therefore, the inter-chain association between layers plays an important role in molecular aggregation in these crystals. The bent shape of each molecule mentioned above is resulted from this inter-chain contact. This bending also favors the packing of bulky 2-methylbutyl groups.

Concerning a packing mode within a layer, there are two kinds of intermolecular overlapping. Each molecule overlaps largely, i.e., from head to tail, with one of the nearest neighbor molecules. On the contrary, the overlaps with the other molecule is small and alkyl chains are related to the interlayer aggregation. So, the two molecules displace largely each other along their long axes, and the large displacement leads to a large tilt angle of the molecule in a layer. Nearest phenyl rings between adjacent molecules make angles of 60° (I-5) and 54° (I-7) in average. This fact also suggests that lateral intermolecular forces are not so strong as in the case of 4,4′-bis(pentyloxy)azoxybenzene with a more ordered smectic than Sm* C, since nearest phenyl rings of the latter crystal are parallel between adjacent molecules.

Relationship between the Crystal and Sm* C Structures. Characteristic features of the two crystal structures are summarized schematically in Fig. 5(a). This is compared with a Sm* C structure shown in Fig. 5(b), which was estimated in the previous study[4] by measuring temperature dependence of the interlayer distances in the Sm* C phase in the series I (n=6, 7, 8, 9, 10, 12, 14, and 16) by X-ray diffraction. Linear

Table 3. Bond Lengths (l/Å) and Bond Angles (ϕ/°) of I-5

Bond	l/Å or ϕ/°	Bond	l/Å or ϕ/°
O(1A)-C(13A)	1.187(14)	O(1B)-C(13B)	1.205(11)
O(2A)-C(13A)	1.379(13)	O(2B)-C(13B)	1.326(10)
O(2A)-C(14A)	1.369(13)	O(2B)-C(14B)	1.415(9)
O(3A)-C(17A)	1.389(13)	O(3B)-C(17B)	1.364(11)
O(3A)-C(31A)	1.412(16)	O(3B)-C(31B)	1.417(12)
C(1A)-C(2A)	1.374(16)	C(1B)-C(2B)	1.391(16)
C(1A)-C(6A)	1.387(16)	C(1B)-C(6B)	1.386(16)
C(2A)-C(3A)	1.362(15)	C(2B)-C(3B)	1.385(16)
C(3A)-C(4A)	1.398(14)	C(3B)-C(4B)	1.391(13)
C(4A)-C(5A)	1.399(14)	C(4B)-C(5B)	1.362(14)
C(5A)-C(6A)	1.364(16)	C(5B)-C(6B)	1.392(17)
C(7A)-C(8A)	1.382(15)	C(7B)-C(8B)	1.387(13)
C(7A)-C(12A)	1.376(13)	C(7B)-C(12B)	1.407(13)
C(8A)-C(9A)	1.378(15)	C(8B)-C(9B)	1.403(12)
C(9A)-C(10A)	1.400(14)	C(9B)-C(10B)	1.367(12)
C(10A)-C(11A)	1.401(15)	C(10B)-C(11B)	1.386(12)
C(11A)-C(12A)	1.408(14)	C(11B)-C(12B)	1.373(13)
C(14A)-C(15A)	1.396(16)	C(14B)-C(15B)	1.377(11)
C(14A)-C(19A)	1.389(15)	C(14B)-C(19B)	1.379(12)
C(15A)-C(16A)	1.386(15)	C(15B)-C(16B)	1.390(13)
C(16A)-C(17A)	1.381(15)	C(16B)-C(17B)	1.387(13)
C(17A)-C(18A)	1.358(15)	C(17B)-C(18B)	1.385(13)
C(18A)-C(19A)	1.376(15)	C(18B)-C(19B)	1.393(13)
C(1A)-C(21A)	1.547(18)	C(1B)-C(21B)	1.535(18)
C(4A)-C(7A)	1.492(13)	C(4B)-C(7B)	1.503(13)
C(10A)-C(13A)	1.468(16)	C(10B)-C(13B)	1.503(11)
C(21A)-C(22A)	1.53(3)	C(21B)-C(22B)	1.52(2)
C(21A)-C(22A′)	1.52(6)	C(22B)-C(23B)	1.53(3)
C(22A)-C(23A)	1.48(4)	C(22B)-C(25B)	1.47(3)
C(22A)-C(25A)	1.53(4)	C(22B)-C(23B′)	1.51(7)
C(23A)-C(24A)	1.46(4)	C(22B)-C(25B′)	1.47(6)
C(22A′)-C(23A′)	1.52(7)	C(23B)-C(24B)	1.44(5)
C(22A′)-C(25A′)	1.56(7)	C(23B′)-C(24B′)	1.40(9)
C(23A′)-C(24A′)	1.39(6)	C(31B)-C(32B)	1.543(16)
C(31A)-C(32A)	1.558(19)	C(32B)-C(33B)	1.534(17)
C(32A)-C(33A)	1.51(2)	C(33B)-C(34B)	1.544(19)
C(33A)-C(34A)	1.52(2)	C(34B)-C(35B)	1.52(2)
C(34A)-C(35A)	1.555(18)		
C(13A)-O(2A)-C(14A)	117.0(8)	C(13B)-O(2B)-C(14B)	117.0(6)
C(17A)-O(3A)-C(31A)	118.4(9)	O(1B)-C(13B)-O(2B)	121.9(8)
O(1A)-C(13A)-O(2A)	120.9(10)	O(1B)-C(13B)-C(10B)	124.4(8)
O(1A)-C(13A)-C(10A)	127.5(11)	O(2B)-C(13B)-C(10B)	113.7(7)
O(2A)-C(13A)-C(10A)	111.3(9)	O(2B)-C(14B)-C(15B)	118.4(7)
O(2A)-C(14A)-C(15A)	116.2(10)	O(2B)-C(14B)-C(19B)	120.4(7)
O(2A)-C(14A)-C(19A)	122.5(10)	O(3B)-C(17B)-C(16B)	124.0(8)
O(3A)-C(17A)-C(16A)	125.2(9)	O(3B)-C(17B)-C(18B)	115.1(8)
O(3A)-C(17A)-C(18A)	115.4(9)	C(17B)-O(3B)-C(31B)	117.3(7)
C(2A)-C(1A)-C(6A)	117.0(10)	C(2B)-C(1B)-C(6B)	118.8(10)
C(1A)-C(2A)-C(3A)	122.5(10)	C(1B)-C(2B)-C(3B)	119.9(10)
C(2A)-C(3A)-C(4A)	120.4(10)	C(2B)-C(3B)-C(4B)	121.5(9)
C(3A)-C(4A)-C(5A)	117.5(9)	C(3B)-C(4B)-C(5B)	117.7(9)
C(4A)-C(5A)-C(6A)	120.4(10)	C(4B)-C(5B)-C(6B)	122.2(11)
C(1A)-C(6A)-C(5A)	122.0(11)	C(1B)-C(6B)-C(5B)	119.6(11)
C(8A)-C(7A)-C(12A)	118.6(9)	C(8B)-C(7B)-C(12B)	117.4(8)
C(7A)-C(8A)-C(9A)	121.8(10)	C(7B)-C(8B)-C(9B)	121.6(8)
C(8A)-C(9A)-C(10A)	119.7(9)	C(8B)-C(9B)-C(10B)	119.3(8)
C(9A)-C(10A)-C(11A)	119.5(10)	C(9B)-C(10B)-C(11B)	120.3(8)
C(10A)-C(11A)-C(12A)	118.8(9)	C(10B)-C(11B)-C(12B)	120.3(8)
C(7A)-C(12A)-C(11A)	121.2(9)	C(7B)-C(12B)-C(11B)	121.1(9)
C(15A)-C(14A)-C(19A)	121.1(10)	C(15B)-C(14B)-C(19B)	120.7(7)
C(14A)-C(15A)-C(16A)	118.0(10)	C(14B)-C(15B)-C(16B)	119.7(8)
C(15A)-C(16A)-C(17A)	121.3(10)	C(15B)-C(16B)-C(17B)	119.5(9)
C(16A)-C(17A)-C(18A)	119.1(10)	C(16B)-C(17B)-C(18B)	120.7(9)
C(17A)-C(18A)-C(19A)	122.1(10)	C(17B)-C(18B)-C(19B)	119.2(9)
C(14A)-C(19A)-C(18A)	118.4(10)	C(14B)-C(19B)-C(18B)	119.9(8)
C(2A)-C(1A)-C(21A)	124.4(10)	C(2B)-C(1B)-C(21B)	119.0(10)
C(6A)-C(1A)-C(21A)	118.4(10)	C(6B)-C(1B)-C(21B)	122.2(10)

Table 3. (Continued)

Bond	ϕ/°	Bond	ϕ/°
C(3A)-C(4A)-C(7A)	121.5(8)	C(3B)-C(4B)-C(7B)	120.2(8)
C(5A)-C(4A)-C(7A)	120.7(8)	C(5B)-C(4B)-C(7B)	122.1(8)
C(4A)-C(7A)-C(8A)	120.5(8)	C(4B)-C(7B)-C(8B)	123.5(8)
C(4A)-C(7A)-C(12A)	120.8(8)	C(4B)-C(7B)-C(12B)	119.1(8)
C(9A)-C(10A)-C(13A)	125.4(10)	C(9B)-C(10B)-C(13B)	121.2(7)
C(11A)-C(10A)-C(13A)	115.1(10)	C(11B)-C(10B)-C(13B)	118.3(7)
C(1A)-C(21A)-C(22A)	113.8(14)	C(1B)-C(21B)-C(22B)	113.7(12)
C(1A)-C(21A)-C(22A')	111(2)	C(21B)-C(22B)-C(23B)	113.5(16)
C(21A)-C(22A)-C(23A)	108(2)	C(21B)-C(22B)-C(25B)	116.7(15)
C(21A)-C(22A)-C(25A)	112(2)	C(21B)-C(22B)-C(23B')	99(3)
C(23A)-C(22A)-C(25A)	106(2)	C(21B)-C(22B)-C(25B')	101(3)
C(22A)-C(23A)-C(24A)	106(2)	C(23B)-C(22B)-C(25B)	107(2)
C(21A)-C(22A')-C(23A')	113(4)	C(23B')-C(22B)-C(25B')	125(4)
C(21A)-C(22A')-C(25A')	126(4)	C(22B)-C(23B)-C(24B)	107(2)
C(23A')-C(22A')-C(25A')	119(4)	C(22B)-C(23B')-C(24B')	118(5)
C(22A')-C(23A')-C(24A')	98(4)	O(3B)-C(31B)-C(32B)	106.2(8)
O(3A)-C(31A)-C(32A)	108.6(10)	C(31B)-C(32B)-C(33B)	107.8(10)
C(31A)-C(32A)-C(33A)	113.2(11)	C(32B)-C(33B)-C(34B)	110.7(10)
C(32A)-C(33A)-C(34A)	111.2(12)	C(33B)-C(34B)-C(35B)	110.9(12)
C(33A)-C(34A)-C(35A)	112.9(11)		

Table 4. Bond Lengths (l/Å) and Bond Angles (ϕ/°) of I-7

Bond	l/Å	Bond	l/Å
O(1A)-C(13A)	1.197(9)	O(1B)-C(13B)	1.200(9)
O(2A)-C(13A)	1.349(8)	O(2B)-C(13B)	1.361(9)
O(2A)-C(14A)	1.402(8)	O(2B)-C(14B)	1.418(8)
O(3A)-C(17A)	1.382(8)	O(3B)-C(17B)	1.356(7)
O(3A)-C(31A)	1.425(11)	O(3B)-C(31B)	1.425(9)
C(1A)-C(2A)	1.393(10)	C(1B)-C(2B)	1.385(11)
C(1A)-C(6A)	1.391(10)	C(1B)-C(6B)	1.394(11)
C(1A)-C(21A)	1.526(14)	C(1B)-C(21B)	1.525(13)
C(2A)-C(3A)	1.390(10)	C(2B)-C(3B)	1.391(10)
C(3A)-C(4A)	1.389(9)	C(3B)-C(4B)	1.396(9)
C(4A)-C(5A)	1.392(9)	C(4B)-C(5B)	1.390(10)
C(4A)-C(7A)	1.497(8)	C(4B)-C(7B)	1.507(8)
C(5A)-C(6A)	1.393(11)	C(5B)-C(6B)	1.393(11)
C(7A)-C(8A)	1.389(9)	C(7B)-C(8B)	1.390(8)
C(7A)-C(12A)	1.388(8)	C(7B)-C(12B)	1.384(9)
C(8A)-C(9A)	1.394(9)	C(8B)-C(9B)	1.393(8)
C(9A)-C(10A)	1.390(8)	C(9B)-C(10B)	1.394(9)
C(10A)-C(11A)	1.393(9)	C(10B)-C(11B)	1.393(9)
C(10A)-C(13A)	1.480(9)	C(10B)-C(13B)	1.481(9)
C(11A)-C(12A)	1.392(9)	C(11B)-C(12B)	1.386(9)
C(14A)-C(15A)	1.385(9)	C(14B)-C(15B)	1.389(10)
C(14A)-C(19A)	1.386(9)	C(14B)-C(19B)	1.381(9)
C(15A)-C(16A)	1.388(10)	C(15B)-C(16B)	1.388(10)
C(16A)-C(17A)	1.385(9)	C(16B)-C(17B)	1.386(9)
C(17A)-C(18A)	1.393(9)	C(17B)-C(18B)	1.390(8)
C(18A)-C(19A)	1.387(9)	C(18A)-C(19B)	1.387(9)
C(21A)-C(22A)	1.504(18)	C(21B)-C(22B)	1.50(2)
C(22A)-C(23A)	1.52(2)	C(22B)-C(23B)	1.53(3)
C(22A)-C(25A)	1.50(3)	C(22B)-C(25B)	1.48(3)
C(23A)-C(24A)	1.48(4)	C(23B)-C(24B)	1.50(6)
C(23A)-C(24A')	1.45(7)	C(23B)-C(24B')	1.45(6)
C(31A)-C(32A)	1.511(13)	C(31B)-C(32B)	1.519(13)
C(32A)-C(33A)	1.520(13)	C(32B)-C(33B)	1.535(14)
C(33A)-C(34A)	1.528(14)	C(33B)-C(34B)	1.530(13)
C(34A)-C(35A)	1.537(15)	C(34B)-C(35B)	1.515(13)
C(35A)-C(36A)	1.534(14)	C(35B)-C(36B)	1.518(17)
C(36A)-C(37A)	1.53(2)	C(36B)-C(37B)	1.523(19)

Table 4. (Continued)

Bond	ϕ/°	Bond	ϕ/°
C(13A)-O(2A)-C(14A)	116.6(5)	C(13B)-O(2B)-C(14B)	118.8(5)
C(17A)-O(3A)-C(31A)	118.9(6)	C(17B)-O(3B)-C(31B)	116.6(5)
C(2A)-C(1A)-C(6A)	117.5(6)	C(2B)-C(1B)-C(6B)	119.7(7)
C(2A)-C(1A)-C(21A)	120.4(7)	C(2B)-C(1B)-C(21B)	117.8(7)
C(6A)-C(1A)-C(21A)	122.1(7)	C(6B)-C(1B)-C(21B)	122.1(7)
C(1A)-C(2A)-C(3A)	121.8(6)	C(1B)-C(2B)-C(3B)	119.8(7)
C(2A)-C(3A)-C(4A)	118.9(6)	C(2B)-C(3B)-C(4B)	120.8(6)
C(3A)-C(4A)-C(5A)	120.7(6)	C(3B)-C(4B)-C(5B)	118.3(6)
C(3A)-C(4A)-C(7A)	120.7(6)	C(3B)-C(4B)-C(7B)	119.8(5)
C(5A)-C(4A)-C(7A)	118.3(6)	C(5B)-C(4B)-C(7B)	121.9(6)
C(4A)-C(5A)-C(6A)	118.7(6)	C(4B)-C(5B)-C(6B)	120.8(7)
C(1A)-C(6A)-C(5A)	121.8(7)	C(1B)-C(6B)-C(5B)	119.9(8)
C(4A)-C(7A)-C(8A)	119.3(5)	C(4B)-C(7B)-C(8B)	121.8(5)
C(4A)-C(7A)-C(12A)	121.8(5)	C(4B)-C(7B)-C(12B)	119.3(5)
C(8A)-C(7A)-C(12A)	118.5(6)	C(8B)-C(7B)-C(12B)	118.8(5)
C(7A)-C(8A)-C(9A)	121.2(6)	C(7B)-C(8B)-C(9B)	121.2(5)
C(8A)-C(9A)-C(10A)	118.7(6)	C(8B)-C(9B)-C(10B)	118.8(5)
C(9A)-C(10A)-C(11A)	120.9(5)	C(9B)-C(10B)-C(11B)	120.4(6)
C(9A)-C(10A)-C(13A)	121.1(5)	C(9B)-C(10B)-C(13B)	123.3(6)
C(11A)-C(10A)-C(13A)	118.0(5)	C(11B)-C(10B)-C(13B)	116.3(6)
C(10A)-C(11A)-C(12A)	118.9(6)	C(10B)-C(11B)-C(12B)	119.4(6)
C(7A)-C(12A)-C(11A)	121.4(6)	C(7B)-C(12B)-C(11B)	121.2(6)
O(1A)-C(13A)-O(2A)	124.0(6)	O(1B)-C(13B)-O(2B)	122.2(7)
O(1A)-C(13A)-C(10A)	123.2(6)	O(1B)-C(13B)-C(10B)	128.2(7)
O(2A)-C(13A)-C(10A)	112.7(5)	O(2B)-C(13B)-C(10B)	109.4(6)
O(2A)-C(14A)-C(15A)	116.8(6)	O(2B)-C(14B)-C(15B)	118.5(6)
O(2A)-C(14A)-C(19A)	122.4(6)	O(2B)-C(14B)-C(19B)	119.9(6)
C(15A)-C(14A)-C(19A)	120.6(6)	C(15B)-C(14B)-C(19B)	121.5(6)
C(14A)-C(15A)-C(16A)	119.7(6)	C(14B)-C(15B)-C(16B)	118.8(7)
C(15A)-C(16A)-C(17A)	120.1(6)	C(15B)-C(16B)-C(17B)	120.8(7)
O(3A)-C(17A)-C(16A)	125.1(6)	O(3B)-C(17B)-C(16B)	125.3(6)
O(3A)-C(17A)-C(18A)	115.0(6)	O(3B)-C(17B)-C(18B)	115.5(5)
C(16A)-C(17A)-C(18A)	119.9(6)	C(16B)-C(17B)-C(18B)	119.2(6)
C(17A)-C(18A)-C(19A)	119.8(6)	C(17B)-C(18B)-C(19B)	120.8(5)
C(14A)-C(19A)-C(18A)	119.5(6)	C(14B)-C(19B)-C(18B)	118.7(6)
C(1A)-C(21A)-C(22A)	115.6(10)	C(1B)-C(21B)-C(22B)	114.9(10)
C(21A)-C(22A)-C(23A)	115.7(12)	C(21B)-C(22B)-C(23B)	115.8(15)
C(21A)-C(22A)-C(25A)	113.4(13)	C(21B)-C(22B)-C(25B)	112.1(14)
C(23A)-C(22A)-C(25A)	107.0(14)	C(23B)-C(22B)-C(25B)	114.2(16)
C(22A)-C(23A)-C(24A)	116.9(18)	C(22B)-C(23B)-C(24B)	107(3)
C(22A)-C(23A)-C(24A′)	129(3)	C(22B)-C(23B)-C(24B′)	97(3)
O(3A)-C(31A)-C(32A)	107.5(7)	O(3B)-C(31B)-C(32B)	108.4(7)
C(31A)-C(32A)-C(33A)	112.6(7)	C(31B)-C(32B)-C(33B)	112.9(8)
C(32A)-C(33A)-C(34A)	110.2(8)	C(32B)-C(33B)-C(34B)	112.8(8)
C(33A)-C(34A)-C(35A)	112.0(8)	C(33B)-C(34B)-C(35B)	114.3(8)
C(34A)-C(35A)-C(36A)	113.2(9)	C(34B)-C(35B)-C(36B)	111.5(9)
C(35A)-C(36A)-C(37A)	115.7(11)	C(35B)-C(36B)-C(37B)	109.2(11)

Table 5. Torsion Angles (ϕ/°)

	I-5		I-7	
	A	B	A	B
Phenyl groups				
ring(C1-C6)-ring(C7-C12)	5.5	2.9	51.5	−52.5
ring(C7-C12)-ring(C14-C19)	59.2	−59.6	54.2	−54.4
Alkyl chains				
O(3)-C(31)-C(32)-C(33)	180.0	183.5	62.7	−64.6
C(31)-C(32)-C(33)-C(34)	181.5	178.0	165.4	181.1
C(32)-C(33)-C(34)-C(35)	172.0	179.5	180.7	177.2
C(33)-C(34)-C(35)-C(36)	—	—	177.9	185.4
C(34)-C(35)-C(36)-C(37)	—	—	176.2	182.0

increase in the interlayer distances with increase in temperature was attributed mainly to the large change of paraffin chain organization. However, the tilt angle of the core part is kept constant (45°), until the transition to a cholesteric phase occurs. This behavior is well interpreted by the crystal structures, as follows. The tilt angles in the crystal structures (50° and 60°) are close to that in the Sm* C phase. This fact suggests that molecular arrangements as a whole do not change largely at the transition, though the transition is of first-order with a large enthalpy change (6—7 kcal mol^{-1}).[2] Transition from crystals to Sm* C is caused by melting of the paraffin chains, which are regularly organized in the crystalline states. Each molecule begins to rotate around its long molecular axis, because the packing between adjacent phenyl rings is not so close, as is suggested by their nonparallel contact. In Sm* C phase, the chains would change their conformations largely, while the inclination angle of molecular axis should be kept relatively constant, owing to the interaction between the alkyl chains. When the chains are sufficiently disordered, molecules no longer have smectic layers because of relatively small molecular interaction of the core part. Then the transition to a cholesteric phase should occur. In the case of I-5, the chains are so short that Sm* C phase appears only monotropically; with increase in temperature the I-5 crystal transforms directly to a cholesteric phase.

It is concluded that the Sm* C phase behavior observed in a series of biphenyl esters is well interpreted by the molecular packing modes in the crystals. This fact suggests that single crystal X-ray analyses give powerful and useful information to elucidate precise mesophase structures.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 60540280 from the Ministry of Education, Science and Culture.

References

1) J. W. Goodby and T. M. Leslie, *Mol. Cryst. Liq. Cryst.*, **110**, 175 (1984).

2) G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **37**, 189 (1976).

3) K. Hori, M. Takamatsu, and Y. Ohashi, *Ferroelectrics*, in press.

4) K. Hori, *Mol. Cryst. Liq. Cryst.*, **123**, 321 (1985).

5) P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson, MULTAN78. A System of Computor Programs for the Automatic Solution of X-ray Diffraction Data. Univs. of York, England and Loivain, Belgium (1978).

6) G. M. Sheldrick, SHELX76. A Program for Crystal Structure Determination. Univ. of Cambridge (1976).

7) Y. Ohashi, Unpublished version of an original program by T. Ashida.

8) "International Tables for X-ray Crystallography," Birmingham, Kynoch Press (1974), Vol. IV.

9) The tables for the anisotropic temperature factors for non-hydrogen atoms, the tables for the atomic parameters for the hydrogen atoms and the F_o—F_c list are deposited as Document No. 8844 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

10) C. Johnson, ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Tennessee (1965).

11) P. Mandal, S. Paul, H. Shenk, and K. Goubitz, *Mol. Cryst. Liq. Cryst.*, **135**, 35 (1986).

12) N. C. Shivaprakash, M. M. M. Abdoh, and J. Shashidhara Prasad, *Z. Kristallogr.*, **172**, 79 (1985).

13) H. M. M. Shearer and V. Vand, *Acta Crystallogr.*, **9**, 379 (1956).

14) E. von Sydow, *Ark. Kemi*, **9**, 231 (1955).