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Packing modes in crystals of mesogenic biphenyl esters with normal alkyl and/or alkoxy chains

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Packing modes in crystals of mesogenic biphenyl esters with normal alkyl and/or alkoxy chains

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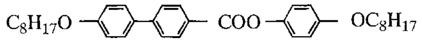
Crystal structures determined for eight compounds R–C_6H_4–C_6H_4–COO–C_6H_4–R', where R and R' are achiral, four with octyloxy and/or octyl chains and four with a methyl or methoxy group at one end, are classified into three modes. First is a smectic-like layer composed of parallel molecules with closely arranged ester linkages; second is a layer comprising two crystallographically independent molecules, among which the ester linkages are close. Compounds with an octyloxy chain take these modes. Thirdly, for molecules with alkyl chains, the ester linkages are far apart among the parallel molecules. Melting and clearing points suggest stronger intermolecular interactions in the former two modes than in the last mode.

1. Introduction

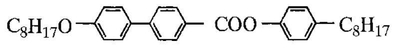
Biphenyl esters are typical mesogens with various mesophases having different degrees of order according to substituents [1]. Relationships between molecular structures and packing modes of molecules are essential for an understanding of the intermolecular interaction controlling the mesophases. It is, however, very difficult to obtain precise structural information on mesophases directly, due to the vigorous thermal motions. Good correlations between the crystal structures and mesophase sequences have been found through systematic crystal structure analysis for chiral biphenyl esters with the general formula, R–C_6H_4–C_6H_4–COO–C_6H_4–R', where R and R' are alkyl and/or alkoxy groups [2]. Two types of local arrangements of ester linkages were found for compounds with R or R' being chiral [3]. For compounds with chiral R (methylbutyl group), ester linkages are arranged in an antiparallel way between neighbouring molecules (mode I), leading to largely tilted smectic-like layer structures, which are related to the nematic (N) or largely tilted smectic C (SmC) phases. For those where R is a normal alkoxy chain on the other hand, ester linkages and alkoxy O atoms of neighbouring molecules are close together (mode II), resulting in largely overlapped smectic-like layer structures, which are related to the smectic A (SmA) phase. The latter mode has been found in many mesogens including antiferroelectric ones [4, 5].

However, an achiral mesogen, 4-methoxyphenyl 4′-octyloxybiphenyl-4-carboxylate (8O-O1), crystallizes in a different way [6]. Therefore, crystal structure analysis has been extended to biphenyl esters with achiral alkyl and/or alkoxy chains for both R and R'. First, crystal structures were determined for the following four compounds with octyloxy and/or octyl chains:

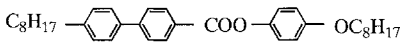
4-Octyloxyphenyl 4′-octyloxybiphenyl-4-carboxylate (8O-O8)



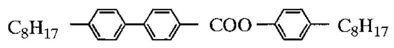
4-Octylphenyl 4′-octyloxybiphenyl-4-carboxylate (8O-8)



4-Octyloxyphenyl 4′-octylbiphenyl-4-carboxylate (8-O8)

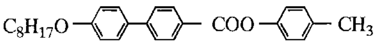


4-Octylphenyl 4′-octylbiphenyl-4-carboxylate (8-8).

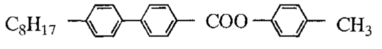


Furthermore, to make clear the influence of chain length in addition to that of alkoxy O atoms, crystal structures were determined for the following four compounds, in which one of chains is replaced by a methoxy or a methyl group:

4-Methylphenyl 4′-octyloxybiphenyl-4-carboxylate (8O-1)



4-Methylphenyl 4′-octylbiphenyl-4-carboxylate (8-1)



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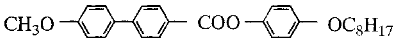
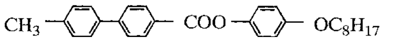
4-Octyloxyphenyl 4′-methoxybiphenyl-4-carboxylate (1O-O8)



4-Octyloxyphenyl 4′-methylbiphenyl-4-carboxylate (1-O8).



Incomplete results were obtained for 4-methoxyphenyl 4′-octylbiphenyl-4-carboxylate (8-O1), 4-octylphenyl 4′-methoxybiphenyl-4-carboxylate (1O-8), and 4-octylphenyl 4′-methylbiphenyl-4-carboxylate (1-8).

This paper describes the crystal structures of 8O-O8, 8O-8, 8-O8, 8-8, 8O-1, 8-1, 1O-O8, and 1-O8, which are classified into three groups, and discusses relationships between the packing modes, molecular configurations, and mesophase behaviour.

2. Experimental

2.1. *Compounds*

All the compounds were synthesized by conventional methods [7]. Single crystals were obtained by slow evaporation from the solutions described in table 1. Transition temperatures and entropies were measured on a Seiko DSC-22C calorimeter. Mesophases of 8-O1, 8-1, 1O-O8, 1O-8, 1-O8, and 1-8 were identified from textures observed on an Olympus POM microscope with a Mettler FP-82 hot stage, and X-ray diffraction patterns obtained on a Rigaku RAD-2A diffractometer with a temperature controller (Rigaku), in addition to the DSC results.

2.2. *X-ray analysis*

Cell parameters and reflection intensities (2θ up to 120° for 8O-O8, 8O-8, and 8-O8, and 135° for others) were measured on a Rigaku AFC-7R diffractometer with CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å). The ω scan mode was applied. Three standard reflections were measured after every 150 reflections. No significant change was observed. The intensity data were corrected for Lorentz and polarization factors. Absorption correction based on the Ψ scan was applied for 8O-O8, 8-8, 8O-1, 1O-O8, and 1-O8. For 8O-8, appropriate Ψ scan curves could not be obtained because of the highly asymmetric profiles of the peaks. Extinction correction was applied for 8O-O8, 8O-1, 1O-O8, and 1-O8. Structures were solved by direct methods [8–11] and refined by full-matrix least squares on F^2 using SHELXL93 [12]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms calculated geometrically were included in the calculation but not refined. Detailed experimental conditions, crystal data, and the results of final refinements are summarized in tables 1 and 2. Final atomic coordinates are shown in tables 3–10.

Table 1. Crystal data.

	Compound							
Parameter	8O-O8	8O-8	8-O8	8-8	8O-1	8-1	1O-O8	1-O8
Formula	$C_{35}H_{46}O_4$	$C_{35}H_{46}O_3$	$C_{35}H_{46}O_3$	$C_{35}H_{46}O_2$	$C_{28}H_{32}O_3$	$C_{28}H_{32}O_2$	$C_{28}H_{32}O_4$	$C_{28}H_{32}O_3$
F.W.	530.72	514.72	514.72	498.72	416.54	400.54	432.54	416.54
Crystal shape	plate	plate	plate	plate	plate	plate	plate	plate
Solvent	$CHCl_3$	$CHCl_3$	ethyl acetate	toluene	diethyl ether	toluene /EtOH	ethyl acetate	ethyl acetate
Crystal size/mm^3	0.3 × 0.3 × 0.05	0.4 × 0.4 × 0.05	0.3 × 0.4 × 0.05	0.4 × 0.2 × 0.03	0.4 × 0.4 × 0.05	0.35 × 0.22 × 0.01	0.4 × 0.4 × 0.03	0.3 × 0.3 × 0.03
1.s. for cell const[a]	21 (40–45)	20 (50–57)	25 (40–45)	22 (45–57)	25 (40–45)	21 (45–57)	24 (40–50)	23 (40–50)
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic
Space group	Ia	Pc	$P\bar{1}$	$Pca2_1$	$P\bar{1}$	Cc	$Pca2_1$	$P2_1/c$
a/Å	69.618(16)	34.774(16)	10.9808(17)	68.784(5)	7.785(18)	5.583(10)	7.46(2)	52.97(2)
b/Å	7.452(18)	7.615(5)	35.606(5)	5.497(6)	50.63(9)	53.563(7)	53.300(15)	7.500(15)
c/Å	5.998(15)	5.731(2)	7.9590(17)	15.838(6)	6.038(5)	15.540(5)	6.044(15)	5.98(2)
α/°	90	90	95.072(14)	90	92.80(14)	90	90	90
β/°	90.38(15)	90.94(4)	90.191(16)	90	95.40(12)	90.32(7)	90	93.7(2)
γ/°	90	90	88.268(11)	90	92.55(18)	90	90	90
V/Å	3112(11)	1517.4(14)	3098.2(9)	5988(7)	2364(7)	4647(9)	2404(9)	2371(9)
Z	4	2	4	8	4	8	4	4
d_x/g cm^{-3}	1.13	1.13	1.10	1.11	1.17	1.15	1.20	1.17
μ/mm	0.565	0.539	0.528	0.506	0.584	0.542	0.625	0.582

[a] The number of reflections with 2θ range in the parenthesis.

Table 2. Data collection, structure solution, and refinement.

Parameter	Compound 8O-O8	 8O-8	 8-O8	 8-8	 8O-1	 8-1	 1O-O8	 1-O8
No. of refl. measd.	2996	2751	9738	6984	9108	5078	3107	4221
No. of indep. refl.	2037	2545	9180	5511	8296	4563	2277	4199
$R(\mathrm{int})$	0.0262	0.1346	0.0243	0.1070	0.0737	0.0572	0.0506	—
No. of obs. refl., $I > 2\sigma(I)$	1095	1581	4674	2177	3957	1350	1633	2015
$T_{\mathrm{min}}/T_{\mathrm{max}}$	0.708	—	0.949	0.825	0.891	0.904	0.864	0.864
Program for str. soln.	SAPI91 [8]	SAPI90	SIR88 [9]	SHELXS-86 [10]	MULTAN-88 [11]	SAPI90	SHELXS-86	SAPI90
R_1[a]	0.0686	0.1091	0.1014	0.0691	0.0892	0.0817	0.0719	0.0808
R_{w2}[b]	0.1806	0.2945	0.2078	0.1731	0.2707	0.1626	0.1900	0.2269
S	1.030	1.048	1.123	1.029	1.023	0.974	1.007	1.028
No. of refl. used for refinement	2034	2529	9067	5458	8097	4555	2249	4141
No. of parameters	317	343	685	655	560	469	290	281
Extinction coef.	0.0003(2)	none	none	none	0.0006(3)	none	0.0014(5)	0.0010(4)
$(\Delta/\sigma)_{\mathrm{max}}$	− 0.363	0.204	0.205	− 0.362	0.075	− 0.474	− 0.273	0.132
$\Delta\rho_{\mathrm{max}}$	0.192	0.452	0.378	0.209	0.288	0.159	0.280	0.290
$\Delta\rho_{\mathrm{min}}$	− 0.202	− 0.341	− 0.245	− 0.276	− 0.270	− 0.187	− 0.225	− 0.246

[a] $R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$ for observed reflections, $I > 2\sigma(I)$.
[b] $R_{w2} = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{0.5}$ for observed reflections, $I > 2\sigma(I)$.
[c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

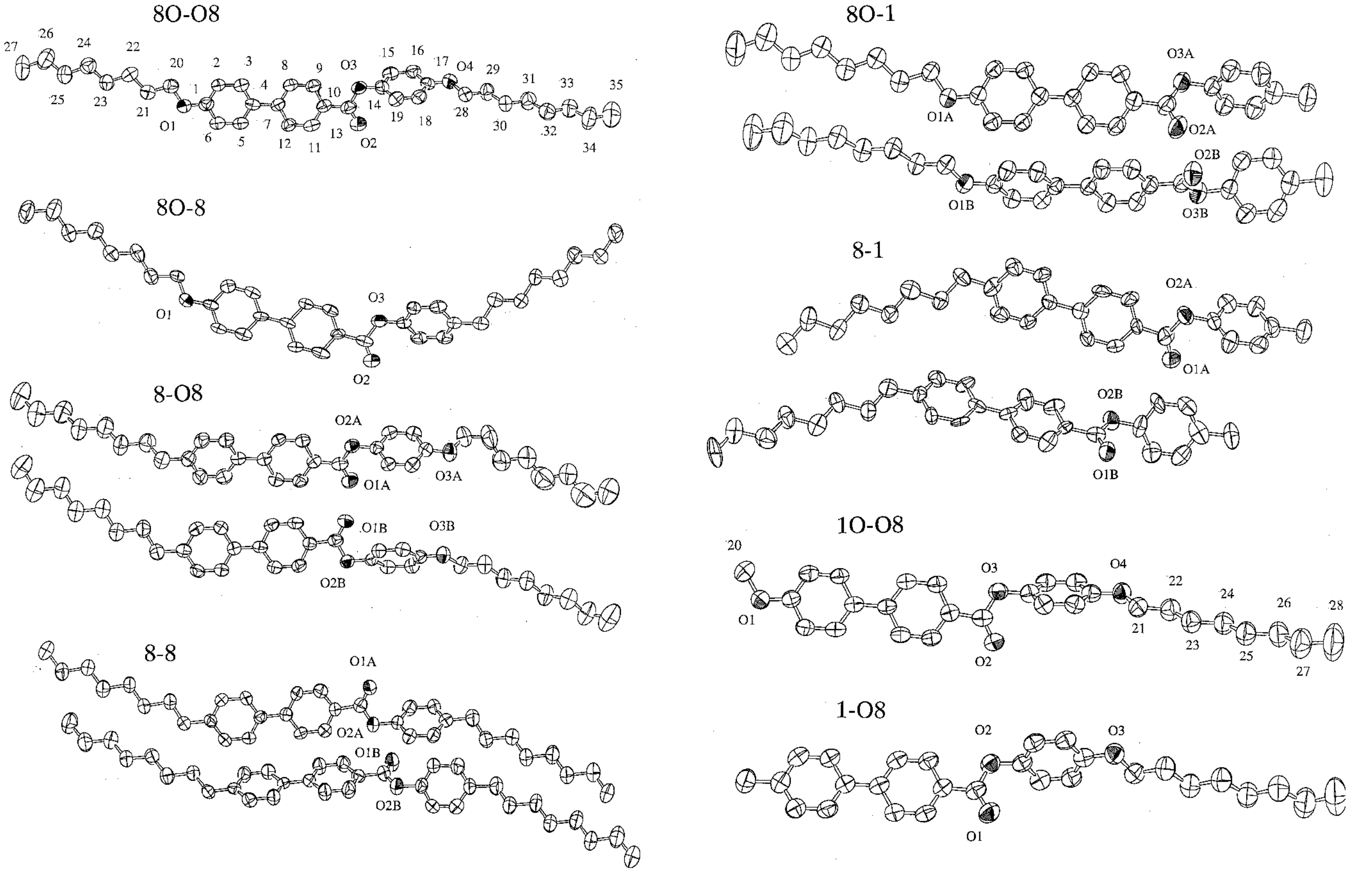


Figure 1. Molecular structures with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for simplicity. Atoms in all the molecules are numbered similarly.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters for 8O-O8. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}/Å^2
O(1)	0.0843(1)	0.5203(12)	0.3537(13)	0.083(3)
O(2)	−0.0521(1)	0.6183(13)	1.1140(16)	0.110(3)
O(3)	−0.0626(1)	0.4753(11)	0.8120(13)	0.080(2)
O(4)	−0.1389(1)	0.5300(13)	1.0518(13)	0.093(3)
C(1)	0.0658(1)	0.5019(11)	0.4205(11)	0.078(4)
C(2)	0.0514(1)	0.4076(10)	0.3097(10)	0.069(3)
C(3)	0.0329(1)	0.4060(9)	0.3937(12)	0.075(3)
C(4)	0.0287(1)	0.4988(10)	0.5886(12)	0.064(3)
C(5)	0.0431(1)	0.5931(9)	0.6994(10)	0.079(4)
C(6)	0.0617(1)	0.5947(10)	0.6154(11)	0.074(3)
C(7)	0.0082(1)	0.4955(10)	0.6848(12)	0.072(3)
C(8)	−0.0072(1)	0.4343(10)	0.5578(10)	0.073(3)
C(9)	−0.0258(1)	0.4482(11)	0.6394(12)	0.082(4)
C(10)	−0.0290(1)	0.5233(11)	0.8481(13)	0.074(3)
C(11)	−0.0135(1)	0.5846(10)	0.9751(11)	0.086(4)
C(12)	0.0051(1)	0.5707(10)	0.8935(11)	0.075(3)
C(13)	−0.0485(2)	0.5384(18)	0.945(2)	0.088(4)
C(14)	−0.0813(1)	0.4893(11)	0.8847(12)	0.080(4)
C(15)	−0.0942(1)	0.5831(10)	0.7501(10)	0.078(3)
C(16)	−0.1135(1)	0.5925(10)	0.8076(12)	0.079(3)
C(17)	−0.1199(1)	0.5079(11)	0.9997(13)	0.069(4)
C(18)	−0.1071(1)	0.4141(11)	1.1344(11)	0.089(4)
C(19)	−0.0878(1)	0.4048(11)	1.0769(12)	0.082(4)
C(20)	0.0894(2)	0.451(2)	0.1360(19)	0.083(4)
C(21)	0.1089(2)	0.530(2)	0.087(2)	0.091(4)
C(22)	0.1186(2)	0.4563(19)	−0.1234(19)	0.090(4)
C(23)	0.1384(2)	0.538(2)	−0.154(2)	0.090(4)
C(24)	0.1491(2)	0.456(2)	−0.353(2)	0.101(4)
C(25)	0.1694(2)	0.531(3)	−0.376(3)	0.122(5)
C(26)	0.1805(3)	0.450(3)	−0.567(3)	0.155(7)
C(27)	0.2008(3)	0.516(4)	−0.584(4)	0.202(12)
C(28)	−0.1459(2)	0.460(2)	1.257(2)	0.085(4)
C(29)	−0.1655(2)	0.535(2)	1.284(2)	0.094(4)
C(30)	−0.1753(2)	0.464(2)	1.489(2)	0.092(4)
C(31)	−0.1957(2)	0.540(2)	1.518(3)	0.110(5)
C(32)	−0.2062(2)	0.461(2)	1.717(3)	0.111(5)
C(33)	−0.2265(2)	0.536(3)	1.739(3)	0.124(5)
C(34)	−0.2376(2)	0.452(3)	1.932(3)	0.162(8)
C(35)	−0.2578(3)	0.524(4)	1.951(4)	0.227(13)

For 8O-8, the first data set converged to the final R-value of 13.5%. The second run for another crystal showed the length of the a axis to be twice (69.5 Å) that obtained in the first run. However, the data set could not be solved. Data was collected for the third crystal assuming the longer a axis (69.5 Å), which gave very weak intensities for $h = 2n + 1$ of $h\ k\ l$. Therefore, we considered that the crystal suffered from pseudo-symmetry and solved for the third data set after transformation to the shorter unit cell given in table 1. The resultant R-value was still large, which was considered to be due to the pseudo-symmetry in addition to the poor crystallinity mentioned above.

Table 4. Atomic coordinates and equivalent isotropic displacement parameters for 8O-8. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}/Å^2
O(1)	0.1488(2)	0.7690(11)	0.3794(14)	0.065(2)
O(2)	−0.1394(3)	0.8515(14)	−0.2708(17)	0.090(3)
O(3)	−0.1518(2)	0.7132(11)	0.0585(14)	0.068(2)
C(1)	0.1104(4)	0.7598(14)	0.3184(18)	0.052(3)
C(2)	0.0984(3)	0.8414(14)	0.1167(19)	0.059(3)
C(3)	0.0598(4)	0.8416(11)	0.046(2)	0.056(3)
C(4)	0.0329(3)	0.7436(14)	0.1732(17)	0.051(3)
C(5)	0.0457(4)	0.6584(15)	0.371(2)	0.065(3)
C(6)	0.0838(3)	0.6593(14)	0.447(2)	0.060(3)
C(7)	−0.0087(3)	0.7524(11)	0.0962(18)	0.047(3)
C(8)	−0.0205(4)	0.8189(15)	−0.1131(18)	0.055(3)
C(9)	−0.0597(4)	0.8293(11)	−0.180(2)	0.062(4)
C(10)	−0.0871(3)	0.7595(16)	−0.0305(18)	0.055(3)
C(11)	−0.0758(4)	0.6911(16)	0.176(2)	0.062(3)
C(12)	−0.0375(3)	0.6766(15)	0.2446(19)	0.057(3)
C(13)	−0.1285(4)	0.7891(15)	−0.100(2)	0.061(3)
C(14)	−0.1907(3)	0.7297(13)	0.0362(19)	0.051(3)
C(15)	−0.2121(4)	0.6693(17)	−0.146(2)	0.070(3)
C(16)	−0.2526(4)	0.6842(16)	−0.144(2)	0.070(3)
C(17)	−0.2706(3)	0.7717(18)	0.035(2)	0.069(3)
C(18)	−0.2479(4)	0.8235(17)	0.226(2)	0.071(4)
C(19)	−0.2090(3)	0.8169(15)	0.222(2)	0.061(3)
C(20)	0.1615(4)	0.7125(19)	0.597(2)	0.068(3)
C(21)	0.2017(4)	0.7736(18)	0.637(3)	0.077(4)
C(22)	0.2222(4)	0.715(2)	0.847(3)	0.089(5)
C(23)	0.2621(4)	0.780(2)	0.883(3)	0.084(4)
C(24)	0.2857(4)	0.715(2)	1.086(3)	0.095(5)
C(25)	0.3254(4)	0.778(2)	1.106(3)	0.094(5)
C(26)	0.3486(5)	0.711(3)	1.307(4)	0.129(8)
C(27)	0.3891(5)	0.764(3)	1.329(4)	0.175(13)
C(28)	−0.3128(4)	0.795(2)	0.028(3)	0.084(4)
C(29)	−0.3359(4)	0.7249(19)	0.225(3)	0.077(4)
C(30)	−0.3773(4)	0.7774(19)	0.228(3)	0.076(4)
C(31)	−0.4007(4)	0.712(2)	0.427(3)	0.087(4)
C(32)	−0.4407(4)	0.780(2)	0.436(3)	0.101(5)
C(33)	−0.4642(4)	0.710(2)	0.627(3)	0.099(5)
C(34)	−0.5056(4)	0.782(3)	0.639(3)	0.114(7)
C(35)	−0.5295(4)	0.718(3)	0.833(4)	0.141(9)

3. Results and discussion

3.1. *Molecular conformations*

All the bond lengths and angles are normal within experimental errors. Molecular structures with numbering schemes are shown in figure 1. While 8O-O8, 8-O8, and 8-8 have zig-zag structures, 8O-8 has a bow-shaped structure. Octyloxy and octyl chains have the all-*trans*-conformation except for the octyloxy chain in molecule A of 8-O8, where the torsion angle O(3)–C(28)–C(29)–C(30) is 64.2(11)°. Dihedral angles between planar moieties, i.e. the C–C–C backbones of the chains, benzene rings, and ester linkages, are summarized in table 11. It is noteworthy that the angle

Table 5. Atomic coordinates and equivalent isotropic displacement parameters for 8-O8. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}/Å^2
O(1A)	0.7470(4)	0.0253(1)	0.4329(6)	0.093(2)
O(2A)	0.9078(4)	0.0390(1)	0.2785(5)	0.067(1)
O(3A)	0.8312(5)	0.1907(1)	0.4722(6)	0.086(1)
C(1A)	0.9153(7)	−0.2179(2)	−0.0460(9)	0.075(2)
C(2A)	0.9962(7)	−0.1920(2)	−0.0909(9)	0.083(2)
C(3A)	0.9873(6)	−0.1546(2)	−0.0266(8)	0.076(2)
C(4A)	0.8973(5)	−0.1415(2)	0.0860(7)	0.058(2)
C(5A)	0.8191(7)	−0.1687(2)	0.1350(9)	0.084(2)
C(6A)	0.8281(7)	−0.2055(2)	0.0698(10)	0.089(2)
C(7A)	0.8835(5)	−0.1014(2)	0.1513(7)	0.056(2)
C(8A)	0.9706(5)	−0.0749(2)	0.1246(7)	0.062(2)
C(9A)	0.9561(5)	−0.0375(2)	0.1817(7)	0.064(2)
C(10A)	0.8510(6)	−0.0249(2)	0.2707(7)	0.058(2)
C(11A)	0.7643(6)	−0.0505(2)	0.2999(8)	0.068(2)
C(12A)	0.7792(6)	−0.0877(2)	0.2404(7)	0.066(2)
C(13A)	0.8284(6)	0.0147(2)	0.3374(8)	0.065(2)
C(14A)	0.8867(6)	0.0771(2)	0.3301(7)	0.059(2)
C(15A)	0.9672(6)	0.0948(2)	0.4425(8)	0.066(2)
C(16A)	0.9523(6)	0.1324(2)	0.4917(7)	0.068(2)
C(17A)	0.8555(6)	0.1531(2)	0.4310(7)	0.063(2)
C(18A)	0.7753(6)	0.1347(2)	0.3188(7)	0.067(2)
C(19A)	0.7903(5)	0.0972(2)	0.2685(7)	0.063(2)
C(20A)	0.9188(7)	−0.2585(2)	−0.1242(10)	0.094(2)
C(21A)	1.0210(8)	−0.2830(2)	−0.0738(10)	0.104(3)
C(22A)	1.0179(8)	−0.3229(2)	−0.1616(11)	0.110(3)
C(23A)	1.1199(9)	−0.3485(2)	−0.1220(13)	0.130(3)
C(24A)	1.1192(9)	−0.3874(2)	−0.2125(13)	0.134(4)
C(25A)	1.2214(10)	−0.4138(3)	−0.1756(16)	0.167(5)
C(26A)	1.2208(12)	−0.4523(3)	−0.2684(18)	0.198(6)
C(27A)	1.3253(13)	−0.4780(4)	−0.227(2)	0.284(10)
C(28A)	0.9122(8)	0.2109(2)	0.5773(11)	0.107(3)
C(29A)	0.8916(10)	0.2529(3)	0.5629(14)	0.156(4)
C(30A)	0.7688(9)	0.2679(3)	0.6232(14)	0.150(4)
C(31A)	0.7659(11)	0.3111(3)	0.6067(17)	0.177(5)
C(32A)	0.6537(11)	0.3325(3)	0.6699(17)	0.192(5)
C(33A)	0.6583(11)	0.3747(3)	0.6605(18)	0.169(5)
C(34A)	0.5478(13)	0.3947(4)	0.732(2)	0.237(7)
C(35A)	0.5495(13)	0.4363(4)	0.725(2)	0.234(8)
O(1B)	0.7484(4)	1.0263(1)	0.9335(6)	0.093(2)
O(2B)	0.5845(4)	1.0399(1)	0.7794(5)	0.064(1)
O(3B)	0.6357(4)	1.1913(1)	0.9775(6)	0.078(1)
C(1B)	0.6269(6)	0.7828(2)	0.4530(8)	0.066(2)
C(2B)	0.7112(7)	0.7956(2)	0.5729(9)	0.086(2)
C(3B)	0.7127(6)	0.8329(2)	0.6384(9)	0.080(2)
C(4B)	0.6298(5)	0.8595(2)	0.5869(7)	0.055(2)
C(5B)	0.5437(6)	0.8463(2)	0.4701(8)	0.073(2)
C(6B)	0.5420(6)	0.8094(2)	0.4074(8)	0.071(2)
C(7B)	0.6364(5)	0.8996(2)	0.6511(7)	0.055(2)
C(8B)	0.7374(6)	0.9133(2)	0.7416(7)	0.064(2)
C(9B)	0.7460(6)	0.9503(2)	0.7999(8)	0.069(2)
C(10B)	0.6537(5)	0.9761(2)	0.7724(7)	0.056(2)
C(11B)	0.5514(6)	0.9637(2)	0.6840(7)	0.064(2)
C(12B)	0.5427(5)	0.9260(2)	0.6262(7)	0.064(2)
C(13B)	0.6691(6)	1.0159(2)	0.8376(8)	0.064(2)
C(14B)	0.5983(5)	1.0783(2)	0.8310(7)	0.056(2)
C(15B)	0.6907(6)	1.0980(2)	0.7699(7)	0.064(2)
C(16B)	0.7008(5)	1.1353(2)	0.8213(7)	0.064(2)
C(17B)	0.6179(6)	1.1539(2)	0.9347(7)	0.061(2)
C(18B)	0.5245(6)	1.1337(2)	0.9944(7)	0.065(2)
C(19B)	0.5153(5)	1.0957(2)	0.9432(7)	0.061(2)
C(20B)	0.6252(7)	0.7423(2)	0.3768(9)	0.084(2)
C(21B)	0.7413(7)	0.7192(2)	0.3931(10)	0.090(2)
C(22B)	0.7385(8)	0.6805(2)	0.2980(10)	0.101(3)
C(23B)	0.8493(8)	0.6558(2)	0.3260(11)	0.110(3)
C(24B)	0.8481(9)	0.6171(2)	0.2368(12)	0.127(3)
C(25B)	0.9549(10)	0.5912(3)	0.2767(14)	0.143(4)
C(26B)	0.9533(12)	0.5526(3)	0.1928(18)	0.191(6)
C(27B)	1.0580(12)	0.5275(3)	0.2366(18)	0.220(7)
C(28B)	0.5449(7)	1.2124(2)	1.0763(9)	0.084(2)
C(29B)	0.5727(7)	1.2536(2)	1.0817(10)	0.093(2)
C(30B)	0.4726(8)	1.2788(2)	1.1580(10)	0.099(2)
C(31B)	0.4862(8)	1.3199(2)	1.1529(11)	0.105(3)
C(32B)	0.3837(8)	1.3444(2)	1.2239(12)	0.117(3)
C(33B)	0.3918(9)	1.3859(3)	1.2139(14)	0.138(4)
C(34B)	0.2884(11)	1.4095(3)	1.2856(16)	0.169(5)
C(35B)	0.2957(13)	1.4506(4)	1.272(2)	0.252(8)

between the octyl chain and the benzene ring of molecule A is quite different from that of molecule B in 8-O8. Thus, two crystallographically independent molecules of 8-O8 have largely different conformations. It is also pointed out that the angle between the ring and the octyl chain in 8O-8 (63°) is considerably larger than in other molecules.

3.2. *Packing modes*

Figure 2 shows the crystal structures of 8O-O8, 8O-8, 1O-O8, and 1-O8. They have very similar packing modes with large overlappings of parallel molecules, resulting in distinct smectic-like layer structures with separate aggregation of cores and chains. The crystal of 8O-O1 [6] also belongs to this mode. Figure 3 shows that ester linkages in all the crystals are closely arranged in one-dimensional chains. The distances are 3.16–3.40 Å for C … O (in the double bond) and 3.34–3.51 Å for O (in the double bond) … O (in the single bond). The former values are close to van der Waals contact C .. O (3.2 Å), while the latter are a little further from van der Waals contact of O .. O (3.0 Å).

Figure 4 shows the crystal structures of 8-O8 and 8O-1; they have very similar packing modes. Ester linkages come close between the crystallographically independent molecules A and B, which are parallel to each other. Figure 5 shows that the ester linkages in these crystals again form one-dimensional chains. The distances are, however, 3.39–3.47 Å for C … O (in the double bond) and 3.26–3.37 Å for O (in the double bond) … O (in the single bond), the former being longer

Table 6. Atomic coordinates and equivalent isotropic displacement parameters for 8-8. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U_{eq}/\text{Å}^2$
O(1A)	0.16963(8)	− 0.0418(12)	0.6685(4)	0.090(2)
O(2A)	0.16831(7)	0.2846(11)	0.5829(4)	0.081(2)
C(1A)	0.3029(1)	0.1576(16)	0.6029(5)	0.062(2)
C(2A)	0.2921(1)	0.3419(17)	0.5692(5)	0.074(3)
C(3A)	0.2719(1)	0.3394(15)	0.5703(5)	0.066(2)
C(4A)	0.2616(1)	0.1567(15)	0.6101(5)	0.057(2)
C(5A)	0.2725(1)	− 0.0225(16)	0.6481(6)	0.074(3)
C(6A)	0.2931(1)	− 0.0229(16)	0.6449(6)	0.077(3)
C(7A)	0.2400(1)	0.1453(15)	0.6115(5)	0.057(2)
C(8A)	0.2287(1)	0.3204(16)	0.5715(5)	0.074(3)
C(9A)	0.2085(1)	0.3090(17)	0.5729(5)	0.073(3)
C(10A)	0.1992(1)	0.1273(16)	0.6159(5)	0.060(2)
C(11A)	0.2105(1)	− 0.0453(17)	0.6566(6)	0.082(3)
C(12A)	0.2304(1)	− 0.0349(17)	0.6550(6)	0.085(3)
C(13A)	0.1779(1)	0.1074(18)	0.6253(5)	0.067(2)
C(14A)	0.14802(5)	0.2860(11)	0.5896(4)	0.068(2)
C(15A)	0.13911(7)	0.4792(9)	0.6309(4)	0.083(3)
C(16A)	0.11896(7)	0.4887(9)	0.6368(3)	0.075(2)
C(17A)	0.10772(5)	0.3050(11)	0.6014(4)	0.068(2)
C(18A)	0.11663(7)	0.1118(9)	0.5601(3)	0.077(3)
C(19A)	0.13677(7)	0.1023(9)	0.5542(3)	0.081(3)
C(20A)	0.3250(1)	0.1631(15)	0.5986(6)	0.078(3)
C(21A)	0.33551(9)	− 0.0718(16)	0.6096(6)	0.080(3)
C(22A)	0.35714(9)	− 0.0528(16)	0.5951(6)	0.072(2)
C(23A)	0.36810(9)	− 0.2859(16)	0.6066(6)	0.079(3)
C(24A)	0.3899(1)	− 0.2708(17)	0.5932(6)	0.090(3)
C(25A)	0.4012(1)	− 0.4971(16)	0.6096(7)	0.090(3)
C(26A)	0.4226(1)	− 0.4820(18)	0.5959(8)	0.114(4)
C(27A)	0.4342(1)	− 0.7085(18)	0.6131(8)	0.135(5)
C(28A)	0.0857(1)	0.3027(16)	0.6100(6)	0.088(3)
C(29A)	0.0757(1)	0.5453(16)	0.6109(7)	0.084(3)
C(30A)	0.0538(1)	0.5355(18)	0.6111(7)	0.091(3)
C(31A)	0.0435(1)	0.7726(19)	0.6168(7)	0.096(3)
C(32A)	0.0216(1)	0.757(2)	0.6107(7)	0.103(3)
C(33A)	0.0108(1)	0.9945(19)	0.6174(7)	0.097(3)
C(34A)	− 0.0111(1)	0.976(2)	0.6106(8)	0.109(4)
C(35A)	− 0.0213(1)	1.218(2)	0.6210(8)	0.126(4)
O(1B)	0.15266(8)	0.4379(13)	0.2967(4)	0.093(2)
O(2B)	0.15059(7)	0.7769(11)	0.3743(4)	0.078(2)
C(1B)	0.2855(1)	0.6871(14)	0.3660(5)	0.059(2)
C(2B)	0.2738(1)	0.8554(16)	0.4050(5)	0.071(2)
C(3B)	0.2538(1)	0.8406(16)	0.4039(5)	0.076(3)
C(4B)	0.24431(9)	0.6572(14)	0.3617(5)	0.055(2)
C(5B)	0.2560(1)	0.4855(16)	0.3214(6)	0.076(3)
C(6B)	0.2760(1)	0.5022(17)	0.3246(6)	0.078(3)
C(7B)	0.2228(1)	0.6423(15)	0.3575(5)	0.059(2)
C(8B)	0.2108(1)	0.8102(18)	0.3970(6)	0.085(3)
C(9B)	0.1906(1)	0.7960(19)	0.3913(6)	0.089(3)
C(10B)	0.1817(1)	0.6161(17)	0.3480(5)	0.061(2)
C(11B)	0.1932(1)	0.4419(17)	0.3117(6)	0.082(3)
C(12B)	0.2133(1)	0.4546(17)	0.3160(6)	0.078(3)
C(13B)	0.1603(1)	0.594(2)	0.3362(6)	0.077(3)
C(14B)	0.1299(1)	0.7759(17)	0.3645(6)	0.074(2)
C(15B)	0.1219(1)	0.9702(17)	0.3269(6)	0.079(3)
C(16B)	0.1019(1)	0.9819(19)	0.3191(6)	0.090(3)
C(17B)	0.0900(1)	0.805(2)	0.3521(6)	0.082(3)
C(18B)	0.0990(1)	0.6164(18)	0.3924(6)	0.084(3)
C(19B)	0.1191(1)	0.5973(17)	0.3994(6)	0.078(3)
C(20B)	0.3073(1)	0.7069(16)	0.3699(6)	0.070(2)
C(21B)	0.3187(1)	0.4767(16)	0.3488(6)	0.074(3)
C(22B)	0.3404(1)	0.5041(17)	0.3638(6)	0.076(3)
C(23B)	0.35166(9)	0.2731(17)	0.3519(6)	0.083(3)
C(24B)	0.37327(9)	0.2923(17)	0.3660(6)	0.084(3)
C(25B)	0.3846(1)	0.0637(18)	0.3484(6)	0.087(3)
C(26B)	0.4060(1)	0.0839(19)	0.3633(7)	0.109(4)
C(27B)	0.4173(1)	− 0.147(2)	0.3486(8)	0.124(4)
C(28B)	0.0681(1)	0.8120(18)	0.3456(8)	0.115(4)
C(29B)	0.0582(1)	1.0482(17)	0.3654(6)	0.087(3)
C(30B)	0.0364(1)	1.0374(17)	0.3583(7)	0.100(3)
C(31B)	0.0258(1)	1.2756(17)	0.3699(7)	0.093(3)
C(32B)	0.0040(1)	1.2537(16)	0.3643(8)	0.112(4)
C(33B)	− 0.0068(1)	1.4919(18)	0.3701(7)	0.108(4)
C(34B)	− 0.0286(1)	1.464(2)	0.3657(9)	0.141(5)
C(35B)	− 0.0398(1)	1.694(2)	0.3698(9)	0.156(5)

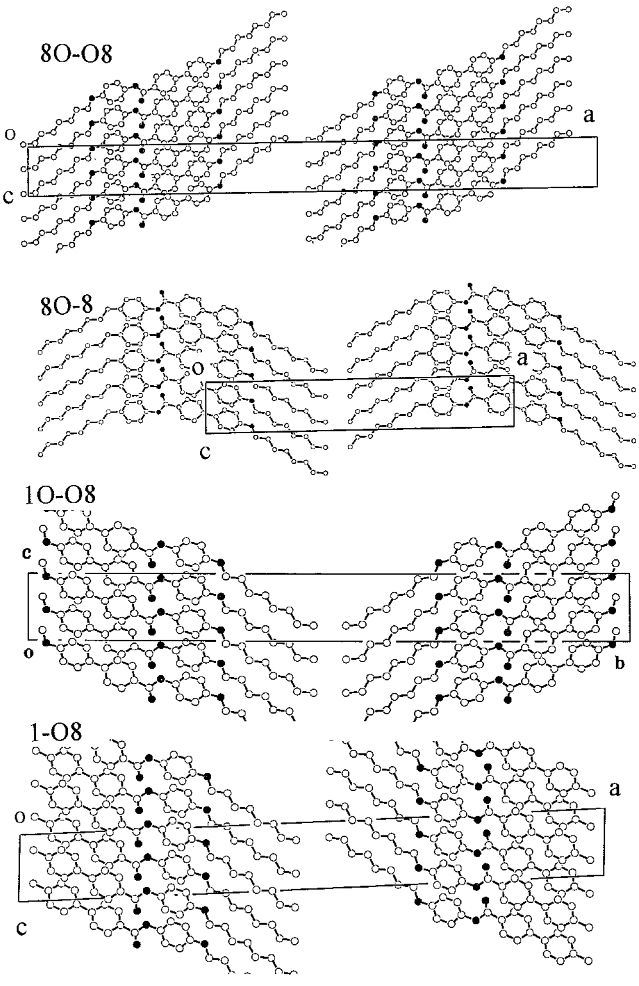


Figure 2. Crystal structures of 8O-O8, 8O-8, 1O-O8, and 1-O8. Closed circles denote O atoms.

Table 7. Atomic coordinates and equivalent isotropic displacement parameters for 8O-1. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U_{eq}/\text{Å}^2$
O(1A)	1.5086(5)	0.19165(7)	−0.0011(6)	0.082(1)
O(2A)	1.1602(7)	0.36813(9)	0.8049(8)	0.118(2)
O(3A)	1.3484(5)	0.38820(7)	0.6016(6)	0.083(1)
C(1A)	1.4805(7)	0.2169(1)	0.0695(8)	0.067(1)
C(2A)	1.3932(7)	0.2192(1)	0.2570(9)	0.075(1)
C(3A)	1.3567(7)	0.2436(1)	0.3444(9)	0.073(1)
C(4A)	1.4101(6)	0.2670(1)	0.2485(8)	0.064(1)
C(5A)	1.4978(7)	0.2641(1)	0.0607(8)	0.070(1)
C(6A)	1.5364(7)	0.2395(1)	−0.0284(9)	0.074(2)
C(7A)	1.3683(6)	0.2931(1)	0.3479(8)	0.064(1)
C(8A)	1.2855(8)	0.2949(1)	0.5407(9)	0.080(2)
C(9A)	1.2472(7)	0.3189(1)	0.6348(9)	0.080(2)
C(10A)	1.2964(7)	0.3421(1)	0.5423(9)	0.073(1)
C(11A)	1.3793(7)	0.3410(1)	0.3512(9)	0.076(2)
C(12A)	1.4139(7)	0.3167(1)	0.2529(9)	0.073(1)
C(13A)	1.2554(8)	0.3672(1)	0.6625(10)	0.081(2)
C(14A)	1.3332(8)	0.4119(1)	0.7266(10)	0.078(2)
C(15A)	1.4117(9)	0.4153(1)	0.9396(10)	0.090(2)
C(16A)	1.3983(9)	0.4390(1)	1.0545(11)	0.096(2)
C(17A)	1.3057(9)	0.4591(1)	0.9632(12)	0.092(2)
C(18A)	1.2273(10)	0.4550(1)	0.7493(13)	0.109(2)
C(19A)	1.2410(9)	0.4313(1)	0.6301(11)	0.095(2)
C(20A)	1.5858(8)	0.1868(1)	−0.2043(9)	0.082(2)
C(21A)	1.5546(11)	0.1578(1)	−0.2587(11)	0.106(2)
C(22A)	1.6251(10)	0.1475(1)	−0.4633(11)	0.097(2)
C(23A)	1.5890(10)	0.1181(1)	−0.5082(12)	0.105(2)
C(24A)	1.6598(11)	0.1065(1)	−0.7109(12)	0.109(2)
C(25A)	1.6271(12)	0.0773(1)	−0.7494(13)	0.121(3)
C(26A)	1.6936(15)	0.0652(2)	−0.9525(16)	0.167(4)
C(27A)	1.6641(17)	0.0364(2)	−0.989(2)	0.215(6)
C(28A)	1.2863(11)	0.4846(1)	1.1002(14)	0.133(3)
O(1B)	1.0787(5)	0.17350(7)	0.4299(6)	0.079(1)
O(2B)	0.6677(6)	0.36220(8)	0.9260(7)	0.094(1)
O(3B)	0.8861(5)	0.36053(7)	1.1899(6)	0.081(1)
C(1B)	1.0225(7)	0.1971(1)	0.5053(9)	0.067(1)
C(2B)	1.1001(7)	0.2068(1)	0.7104(9)	0.070(1)
C(3B)	1.0561(7)	0.2308(1)	0.7995(8)	0.068(1)
C(4B)	0.9379(6)	0.24627(9)	0.6856(8)	0.063(1)
C(5B)	0.8606(7)	0.2359(1)	0.4828(9)	0.077(2)
C(6B)	0.9016(7)	0.2117(1)	0.3924(9)	0.077(2)
C(7B)	0.8965(7)	0.2729(1)	0.7776(8)	0.064(1)
C(8B)	0.9621(7)	0.2825(1)	0.9897(9)	0.072(1)
C(9B)	0.9276(7)	0.3076(1)	1.0675(9)	0.073(1)
C(10B)	0.8256(7)	0.3237(1)	0.9396(9)	0.068(1)
C(11B)	0.7574(7)	0.3140(1)	0.7319(9)	0.074(1)
C(12B)	0.7956(7)	0.2892(1)	0.6498(9)	0.073(1)
C(13B)	0.7818(8)	0.3504(1)	1.0137(10)	0.074(1)
C(14B)	0.8577(7)	0.3870(1)	1.2571(9)	0.073(1)
C(15B)	0.7854(9)	0.3917(1)	1.4488(10)	0.093(2)
C(16B)	0.7601(9)	0.4178(1)	1.5172(11)	0.101(2)
C(17B)	0.8114(9)	0.4384(1)	1.3932(12)	0.095(2)
C(18B)	0.8879(9)	0.4327(1)	1.1999(11)	0.099(2)
C(19B)	0.9151(8)	0.4070(1)	1.1326(10)	0.083(2)
C(20B)	1.0246(8)	0.1644(1)	0.2050(9)	0.077(2)
C(21B)	1.1284(9)	0.1410(1)	0.1554(10)	0.092(2)
C(22B)	1.0691(9)	0.1268(1)	−0.0669(10)	0.093(2)
C(23B)	1.1650(10)	0.1019(1)	−0.1058(12)	0.106(2)
C(24B)	1.1031(11)	0.0858(1)	−0.3150(12)	0.117(2)
C(25B)	1.1954(13)	0.0601(2)	−0.3387(15)	0.148(3)
C(26B)	1.1380(16)	0.0441(2)	−0.5441(19)	0.190(5)
C(27B)	1.2336(19)	0.0192(2)	−0.569(2)	0.266(9)
C(28B)	0.7795(11)	0.4667(1)	1.4692(15)	0.148(4)

than the latter in contrast to the cases of the previous group of 8O-O8, 8O-8, 1O-O8, 1-O8, and 8O-O1. The crystal of 4-octyloxyphenyl 4′-(1-methylheptyloxy)-biphenyl-4-carboxylate (8*O-O8) [2] belongs to this mode with corresponding distances of 3.39–3.58 Å for C … O and 3.33–3.39 Å for O … O.

Figure 6 shows the crystal structures of 8-8 and 8-1; they have very similar packing modes. The crystallographically independent molecules A and B have large overlappings of the octyl chains and the biphenyl moieties, which are further arranged in an antiparallel way. Ester linkages form one-dimensional chains, as shown in figure 7. The distances between ester linkages are, however, longer than 3.8 Å, between O (in the double bond) … O (in the single bond), suggesting that intermolecular interactions between ester linkages are not very significant. Similar packing modes were found in the crystals of 4-[(*S*)-2-methylbutyl]phenyl and 4-[(*S*)-1-methylheptyloxy]phenyl 4′-octylbiphenyl-4-carboxylates (8-5* and 8-O8*, respectively) [13], and also in that of 4-[(*S*)-1-methylheptylcarbonyloxy]phenyl 4′-dodecylbiphenyl-4-carboxylate (10-COO8*) [14].

3.3. *Relationships between molecular structures, packing modes, and mesophase behaviour*

In the previous section the crystal packings are classified into three groups, which are different from the previously notified two modes, I and II; we designate them as modes III, IV, and V.

In order to correlate the packing modes and mesophase behaviour, mesophase sequencies were studied. The reported behaviour [1, 7] was confirmed for 8O-O8, 8-O8, 8O-O1, and 8O-1. For 8O-8, a phase transition at 99.5°C with a large entropy change (42 J K^{-1} mol^{-1}) was found between the melting point (73.4°C, with $\Delta S = 88$ J K^{-1} mol^{-1}) and SmB–SmC transition point (110.5°C), showing an additional smectic phase (SmX) below the SmB. For 1O-O8, 1O-8, 1-O8, and 1-8, the textures and low transition entropies at the clearing

Table 8. Atomic coordinates and equivalent isotropic displacement parameters for 8-1. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U_{eq}/\text{Å}^2$
O(1A)	0.6332(18)	0.3748(2)	0.1123(6)	0.090(3)
O(2A)	0.2982(19)	0.3722(2)	0.0302(5)	0.081(3)
C(1A)	0.385(2)	0.5444(1)	0.0433(6)	0.069(4)
C(2A)	0.2098(15)	0.5302(2)	0.0026(5)	0.071(4)
C(3A)	0.2251(15)	0.5043(2)	0.0034(5)	0.075(4)
C(4A)	0.4157(18)	0.4926(1)	0.0448(6)	0.053(3)
C(5A)	0.5910(14)	0.5069(2)	0.0856(5)	0.069(4)
C(6A)	0.5757(16)	0.5328(2)	0.0848(5)	0.075(4)
C(7A)	0.4311(18)	0.4639(1)	0.0503(6)	0.057(3)
C(8A)	0.2534(14)	0.4496(2)	0.0116(5)	0.077(4)
C(9A)	0.2673(14)	0.4237(2)	0.0144(5)	0.076(5)
C(10A)	0.4588(17)	0.4121(1)	0.0559(6)	0.055(3)
C(11A)	0.6365(13)	0.4265(2)	0.0946(5)	0.073(4)
C(12A)	0.6227(15)	0.4524(2)	0.0918(5)	0.068(4)
C(13A)	0.479(3)	0.3847(2)	0.0700(8)	0.070(4)
C(14A)	0.289(2)	0.3460(1)	0.0422(6)	0.064(4)
C(15A)	0.0886(17)	0.3363(2)	0.0832(5)	0.073(4)
C(16A)	0.0592(17)	0.3106(2)	0.0895(5)	0.100(5)
C(17A)	0.230(2)	0.2946(1)	0.0548(6)	0.085(5)
C(18A)	0.4296(18)	0.3044(2)	0.0138(5)	0.089(5)
C(19A)	0.4590(16)	0.3301(2)	0.0075(5)	0.086(5)
C(20A)	0.361(2)	0.5730(2)	0.0385(8)	0.071(4)
C(21A)	0.583(3)	0.5876(2)	0.0589(7)	0.070(4)
C(22A)	0.559(3)	0.6161(2)	0.0427(8)	0.088(5)
C(23A)	0.790(3)	0.6298(2)	0.0573(8)	0.078(4)
C(24A)	0.768(3)	0.6581(2)	0.0434(9)	0.087(5)
C(25A)	1.006(3)	0.6722(2)	0.0655(8)	0.080(5)
C(26A)	0.975(4)	0.7002(2)	0.0504(11)	0.119(6)
C(27A)	1.210(3)	0.7142(3)	0.0727(13)	0.158(8)
C(28A)	0.202(3)	0.2662(2)	0.0633(10)	0.134(7)
O(1B)	1.1089(18)	0.3968(2)	0.7429(6)	0.084(3)
O(2B)	0.7816(17)	0.3953(2)	0.8262(5)	0.070(3)
C(1B)	0.9079(19)	0.5675(1)	0.8044(5)	0.058(4)
C(2B)	0.7209(15)	0.5539(2)	0.8402(4)	0.070(4)
C(3B)	0.7219(14)	0.5280(2)	0.8360(5)	0.065(4)
C(4B)	0.9098(17)	0.5156(1)	0.7961(6)	0.061(4)
C(5B)	1.0967(13)	0.5292(2)	0.7603(5)	0.071(4)
C(6B)	1.0958(15)	0.5551(2)	0.7645(5)	0.062(4)
C(7B)	0.9215(18)	0.4873(1)	0.7964(5)	0.051(4)
C(8B)	0.7467(15)	0.4731(2)	0.8369(5)	0.083(5)
C(9B)	0.7585(15)	0.4472(2)	0.8347(5)	0.077(4)
C(10B)	0.9452(18)	0.4354(1)	0.7919(6)	0.056(3)
C(11B)	1.1201(14)	0.4496(2)	0.7514(5)	0.080(5)
C(12B)	1.1082(15)	0.4755(2)	0.7536(5)	0.067(4)
C(13B)	0.955(3)	0.4076(2)	0.7853(7)	0.057(4)
C(14B)	0.782(2)	0.3692(1)	0.8197(6)	0.078(5)
C(15B)	0.5816(16)	0.3587(2)	0.7802(5)	0.076(4)
C(16B)	0.5619(17)	0.3329(2)	0.7728(5)	0.080(5)
C(17B)	0.743(2)	0.3176(1)	0.8049(6)	0.098(5)
C(18B)	0.9428(18)	0.3281(2)	0.8443(5)	0.086(5)
C(19B)	0.9625(16)	0.3539(2)	0.8517(5)	0.087(5)
C(20B)	0.907(3)	0.5958(2)	0.8104(8)	0.083(5)
C(21B)	1.142(3)	0.6102(2)	0.7956(9)	0.089(5)
C(22B)	1.114(3)	0.6382(2)	0.8150(8)	0.070(4)
C(23B)	1.346(3)	0.6521(2)	0.8023(8)	0.089(5)
C(24B)	1.324(3)	0.6797(2)	0.8180(8)	0.088(5)
C(25B)	1.549(3)	0.6945(2)	0.7979(10)	0.106(5)
C(26B)	1.527(4)	0.7226(3)	0.8183(13)	0.159(9)
C(27B)	1.756(4)	0.7366(2)	0.7965(14)	0.174(9)
C(28B)	0.723(4)	0.2892(2)	0.7968(10)	0.118(6)

Table 9. Atomic coordinates and equivalent isotropic displacement parameters for 1O-O8. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U_{eq}/\text{Å}^2$
O(1)	− 0.0086(6)	0.02989(8)	0.4554(9)	0.078(1)
O(2)	− 0.1193(7)	0.20525(9)	− 0.3681(10)	0.101(2)
O(3)	0.0267(5)	0.22000(8)	− 0.0707(8)	0.072(1)
O(4)	− 0.0294(7)	0.31873(8)	− 0.3357(9)	0.083(1)
C(1)	0.0009(7)	0.0542(1)	0.3812(12)	0.064(2)
C(2)	− 0.0916(8)	0.0588(1)	0.1842(12)	0.069(2)
C(3)	− 0.0925(7)	0.0824(1)	0.0959(11)	0.066(2)
C(4)	− 0.0014(7)	0.1024(1)	0.1886(12)	0.059(1)
C(5)	0.0902(7)	0.0971(1)	0.3868(12)	0.063(2)
C(6)	0.0929(8)	0.0735(1)	0.4777(12)	0.069(2)
C(7)	− 0.0023(7)	0.1279(1)	0.0926(11)	0.060(2)
C(8)	− 0.0739(8)	0.1321(1)	− 0.1182(11)	0.067(2)
C(9)	− 0.0856(7)	0.1559(1)	− 0.2071(11)	0.066(2)
C(10)	− 0.0221(7)	0.1765(1)	− 0.0925(12)	0.062(2)
C(11)	0.0537(8)	0.1727(1)	0.1162(12)	0.070(2)
C(12)	0.0643(8)	0.1490(1)	0.2029(12)	0.067(2)
C(13)	− 0.0462(9)	0.2013(1)	− 0.1941(12)	0.070(2)
C(14)	0.0108(8)	0.2447(1)	− 0.1491(12)	0.068(2)
C(15)	0.0961(8)	0.2519(1)	− 0.3398(13)	0.076(2)
C(16)	0.0878(8)	0.2767(1)	− 0.4058(12)	0.074(2)
C(17)	− 0.0076(8)	0.2940(1)	− 0.2810(12)	0.069(2)
C(18)	− 0.0921(8)	0.2862(1)	− 0.0881(13)	0.073(2)
C(19)	− 0.0833(8)	0.2615(1)	− 0.0224(12)	0.070(2)
C(20)	0.0891(10)	0.0237(1)	0.6524(14)	0.096(2)
C(21)	0.0373(10)	0.3272(1)	− 0.5432(14)	0.081(2)
C(22)	− 0.0365(10)	0.3531(1)	− 0.5820(17)	0.090(2)
C(23)	0.0371(10)	0.3657(1)	− 0.7896(16)	0.089(2)
C(24)	− 0.0361(10)	0.3920(1)	− 0.8224(17)	0.095(2)
C(25)	0.0371(12)	0.4057(1)	− 1.0178(18)	0.103(3)
C(26)	− 0.0343(13)	0.4324(1)	− 1.0451(19)	0.116(3)
C(27)	0.0487(16)	0.4464(2)	− 1.238(2)	0.152(5)
C(28)	− 0.0126(19)	0.4732(2)	− 1.257(4)	0.230(9)

points showed that they have only the N phase. Similarly, the highest phases of 8-O1 and 8-1 were concluded to be N. The lower phases were determined to be SmA for 8-O1 and SmA and SmB for 8-1 from X-ray diffraction patterns. Layer spacings were 28.3 Å for 8-O1 and 27.1 Å (SmB) and 26.4 Å (SmA) for 8-1. Figure 8 shows the mesophase temperature ranges of members belonging to modes III, IV, and V. It is hard to correlate the packing modes directly with the mesophase behaviour. Roughly speaking, however, the average values of melting points, 105 (mode III), 100 (mode IV), and 80°C (mode V) suggest stronger intermolecular interaction for modes III and IV than for mode V in the crystalline states. Similarly, clearing points (203, 185, and 160°C, on average, for modes III, IV, and V, respectively) may be regarded as the measure of intermolecular interaction working in the mesophases (III > IV > V). On the other hand, the fact that 1O-O8 and 1-O8 belonging to mode III have only the N phase suggests a significant role for

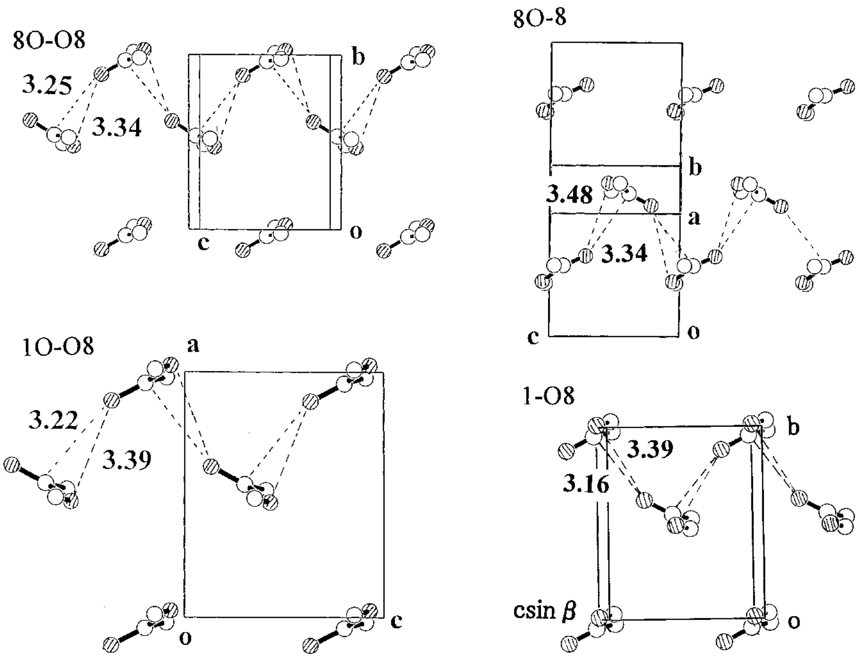


Figure 3. Arrangements of ester linkages of 8O-O8, 8O-8, 1O-O8, and 1-O8. The moiety C–COO–C is shown with hatched and open circles for O and C atoms, respectively. Numerical values are interatomic distances (Å).

Table 10. Atomic coordinates and equivalent isotropic displacement parameters for 1-O8. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U_{eq}/\text{Å}^2$
O(1)	0.20176(7)	0.6208(5)	0.7101(6)	0.102(1)
O(2)	0.21683(6)	0.4733(4)	0.4212(5)	0.077(1)
O(3)	0.31662(6)	0.5297(5)	0.7459(6)	0.087(1)
C(1)	0.0501(1)	0.4842(7)	− 0.1441(8)	0.078(1)
C(2)	0.0709(1)	0.4085(6)	− 0.2387(8)	0.079(1)
C(3)	0.09478(9)	0.4147(6)	− 0.1288(8)	0.074(1)
C(4)	0.09886(9)	0.4971(6)	0.0768(7)	0.065(1)
C(5)	0.0781(1)	0.5742(7)	0.1680(8)	0.080(1)
C(6)	0.0541(1)	0.5670(7)	0.0599(9)	0.085(2)
C(7)	0.12447(9)	0.5020(5)	0.1959(7)	0.063(1)
C(8)	0.14566(9)	0.4336(6)	0.0996(8)	0.075(1)
C(9)	0.16958(9)	0.4436(6)	0.2063(8)	0.074(1)
C(10)	0.17297(8)	0.5240(6)	0.4131(7)	0.066(1)
C(11)	0.15218(9)	0.5911(6)	0.5140(7)	0.070(1)
C(12)	0.12841(9)	0.5800(6)	0.4075(7)	0.070(1)
C(13)	0.19810(9)	0.5466(6)	0.5347(8)	0.072(1)
C(14)	0.24192(9)	0.4904(6)	0.5166(7)	0.068(1)
C(15)	0.2588(1)	0.5828(7)	0.3964(8)	0.078(1)
C(16)	0.2838(1)	0.5926(6)	0.4793(8)	0.077(1)
C(17)	0.2913(1)	0.5077(6)	0.6770(8)	0.073(1)
C(18)	0.2742(1)	0.4131(7)	0.7956(8)	0.079(1)
C(19)	0.2492(1)	0.4044(6)	0.7114(8)	0.077(1)
C(20)	0.0240(1)	0.4722(9)	− 0.2641(10)	0.105(2)
C(21)	0.32503(9)	0.4621(7)	0.9607(9)	0.086(2)
C(22)	0.3514(1)	0.5346(8)	1.0112(10)	0.098(2)
C(23)	0.3640(1)	0.4634(8)	1.2267(10)	0.100(2)
C(24)	0.3907(1)	0.5361(8)	1.2694(10)	0.102(2)
C(25)	0.4047(1)	0.4610(9)	1.4756(11)	0.114(2)
C(26)	0.4314(1)	0.5320(10)	1.5156(12)	0.125(2)
C(27)	0.4458(1)	0.4513(13)	1.7151(14)	0.164(3)
C(28)	0.4724(2)	0.5180(18)	1.756(2)	0.243(6)

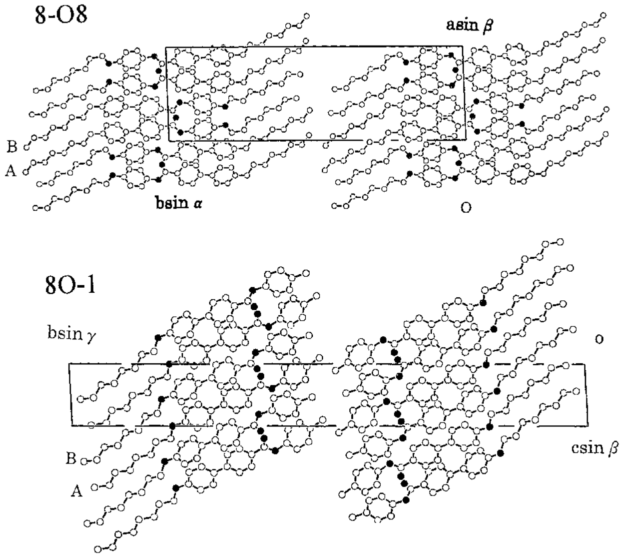


Figure 4. Crystal structures of 8-O8 and 8O-1. Closed circles denote O atoms.

the long chain attaching to the biphenyl moiety in maintaining lateral intermolecular interaction in layer structures.

Finally, the relationship between the packing modes, molecular structures and mesophase sequencies are summarized in table 12. Compounds with the 2-methylbutyl group as *R* crystallize in mode I. Those with an alkoxy group as *R* crystallize in mode II when *R*′ is a chiral group, while they take mode III or IV when *R*′ is a normal chain. Those with an alkyl group as *R* crystallize

Table 11. Dihedral angles (°) between planar moieties in R–C_6H_4–C_6H_4–COO–C_6H_4–R'.

Planar moieties	Compound											
			8-O8		8-8		8O-1		8-1			
	8O-O8	8O-8	A	B	A	B	A	B	A	B	1O-O8	1-O8
R–C_6H_4	6.9(13)	7.9(13)	70.5(5)	11.5(9)	18.2(7)	19.4(7)	10.9(6)	4.9(7)	16.8(10)	14.1(11)	—	—
C_6H_4–C_6H_4	11.2(5)	9.9(5)	11.1(3)	12.4(3)	3.4(5)	1.8(5)	2.2(4)	7.5(4)	1.3(6)	3.9(5)	9.9(3)	3.0(3)
C_6H_4–COO	7.4(10)	1.9(8)	10.0(6)	10.9(6)	5.7(6)	3.8(6)	17.2(6)	16.5(7)	5.8(8)	4.7(7)	3.6(5)	7.8(4)
COO–C_6H_4	63.2(5)	56.4(4)	72.1(3)	71.9(3)	67.7(3)	63.3(3)	74.8(4)	75.0(3)	64.2(4)	36.2(3)	63.4(3)	64.1(3)
C_6H_4–R′	11.4(16)	63.2(7)	twisted chain	17.7(7)	25.8(6)	39.1(5)	—	—	—	—	7.1(8)	7.1(7)

Table 12. Relationships of packing modes, molecular structures, and mesophase sequencies.

Mode	Characteristics	Molecule		Mesophase sequences	Ref. for cryst. structure
		R	R'		
I	1. Antiparallel molecules in a layer.	5*	O5	N	[15]
	2. Antiparallel arrangement of ester linkages.	5*	O7	C^{a}–N	
	3. Large tilt.	5*	6	N	[16]
II	1. Antiparallel molecules in a layer.	7O	5*	C–A–N	[17]
	2. Association of an ester linkage and an alkoxy O atom.	8O	5*	C–A–N	
	3. Small tilt.	8O	COO8*	C_A–C_γ–C–C_α–A	[4]
		8O	COO7*	C–A	[18]
		8O	COO6*	C_A–A	
		8O	O8*	X–C–A	[2]
III	1. Parallel molecules in a layer.	8O	O8	B–C–A	This work.
	2. 1-D chain of closely arranged ester linkages.	8O	8	X–B–C–A	
	3. $d(\mathrm{C..O}) < d(\mathrm{O..O})$	1O	O8	N	
	4. Small tilt.	1	O8	N	
		8O	O1	A–N	[6]
IV	1. 1-D chain of closely arranged ester linkages.	8	O8	B–C–A–N	This work.
	2. $d(\mathrm{C..O}) > d(\mathrm{O..O})$.	8O	1	A–N	
	3. Small tilt.	8*O	O8	C–N	[2]
V	1. Antiparallel arrangement of units composed of parallel molecules.	8	8	G–B–A	This work.
	2. 1-D chain of ester linkages.	8	1	A–N	
	3. $d(\mathrm{O..O}) > 3.8$ Å (long).	8	O8*	B–A–N	[13]
	4. Small tilt.	8	5*	G–J–F–I–C–A–N	
		10	COO8*	C_A–C–A	[14]

[a] C denotes SmC, A denotes SmA, etc; N denotes nematic.

in mode III or IV when R' is a normal alkoxy group, while they take mode V when R' is an alkyl or chiral chain. Therefore, modes III and IV are formed by compounds with normal chains on both sides in which one, at least, is an alkoxy group. The exception is 8*O-O8. On the other hand, mode V is taken by compounds with normal alkyl chains as R and normal alkyl chains or chiral chains as R'. These two facts suggest that the chiral chains play a similar role to that of the normal alkyl chain, probably because intermolecular interaction is reduced by the protrusion of the chiral methyl group.

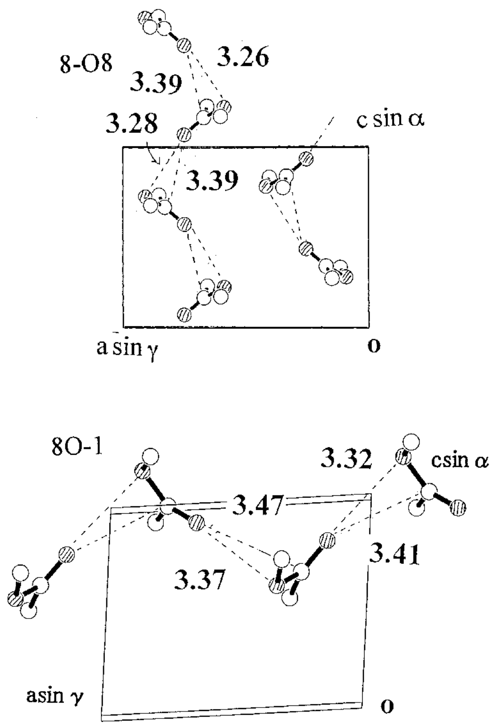


Figure 5. Arrangements of ester linkages of 8-O8 and 8O-1. The moiety C–COO–C is shown with hatched and open circles for O and C atoms, respectively. Numerical values are interatomic distances (Å).

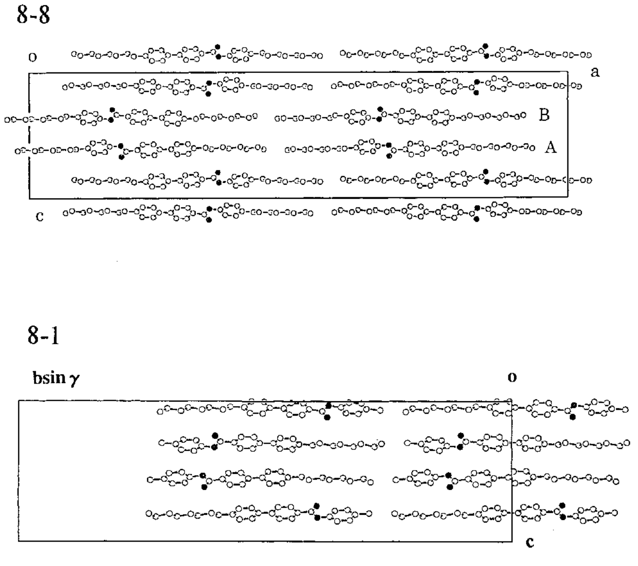


Figure 6. Crystal structures of 8-8 and 8-1. Closed circles denote O atoms.

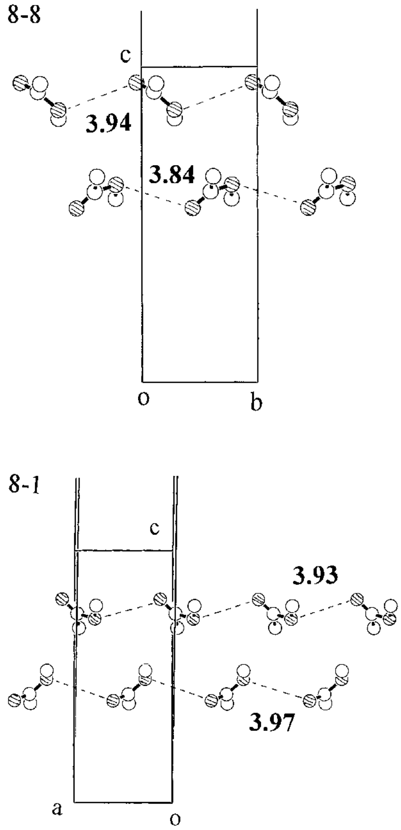


Figure 7. Arrangements of ester linkages of 8-8 and 8-1. The moiety C–COO–C is shown with hatched and open circles for O and C atoms, respectively. Numerical values are interatomic distances (Å).

4. Conclusion

Crystal structures have been determined for eight biphenyl esters with achiral chains, four with octyloxy and/or octyl chains and four with a methyl or methoxy group in one end. All the molecules have smectic-like layer structures, which are classified into three modes. In the first mode, a layer is composed of parallel molecules with one-dimensional chains of close arrangements of ester linkages (3.16–3.40 Å for C…O and 3.34–3.51 Å for O…O). In the second mode, one dimensional chains of closely arranged ester linkages are formed (3.39–3.47 Å for C… O and 3.26–3.37 Å for O…O) between parallel molecules. Compounds with at least one alkoxy chain take these modes. On the other hand, those with alkyl chains take a third arrangement: biphenyl moieties come close among parallel molecules with rather long distances between ester linkages (O…O) > 3.8 Å, which form an antiparallel arrangement in a layer. Melting and clearing points, on average, suggest stronger intermolecular interactions in the former two modes than in the last mode in both crystals and mesophases.

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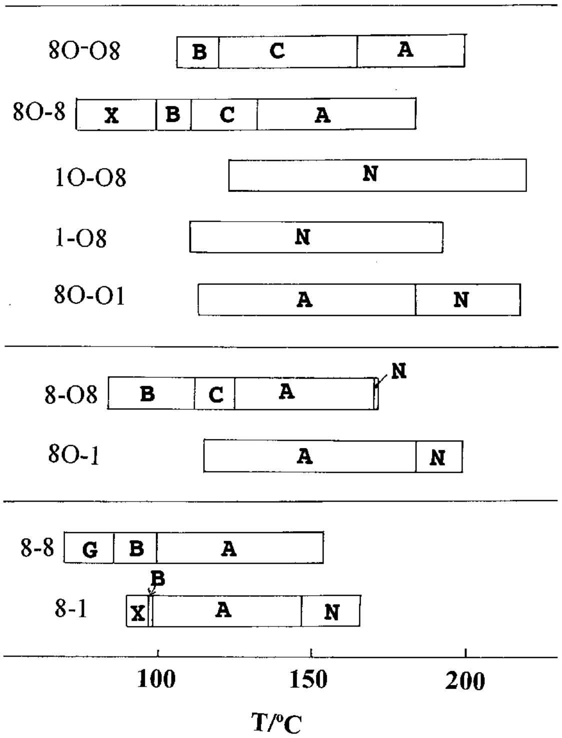

Figure 8. Temperature ranges of mesophases of compounds belonging to modes III (upper), IV (middle), and V (lower). X etc. are used instead of SmX etc. for simplicity. For 8-8, the SmG–SmB transition point was reported to be 67°C [1]. Crystal–crystal transitions were found for 8-O8 (72°C), 8-8 (44°C), 8O-O1 (89°C), and 1-O8 (76°C). Phase sequences for 8-O1, 1O-8, and 1-8 are Cr–100–SmA–143–N–189–I, Cr–107–N–198–I, and Cr–86–Cr–88–N–168–I, respectively.

References

[1] Goodby, J. W., 1991, in *Ferroelectric Liquid Crystals* (Gordon & Breach), p. 131; Goodby, J. W., Gray, G. W., and McDonnel, D. G., 1977, *Mol. Cryst. liq. Cryst.*, **34,** 183.

[2] Kurogoshi, S., and Hori, K., 1997, *Liq. Cryst.*, **23,** 127.

[3] Hori, K., and Ohashi, Y., 1993, *Mol. Cryst. liq. Cryst.*, **203,** 171.

[4] Hori, K., and Endo, K., 1993, *Bull. chem. Soc. Jpn.*, **66,** 46.

[5] Allouchi, H., Cotrait, M., Laguerre, M., Rouillon, J. C., Marcerou, J. P., and Nguyen, H. T., 1998, *Liq. Cryst.*, **25,** 207.

[6] Oki, M., and Hori, K., 1998, *Bull. chem. Soc. Jpn.*, **71,** 543.

[7] Takeda, H., Sakurai, Y., Takenaka, S., Miyake, H., Doi, T., and Kusabayashi, S., 1990, *J. chem. Soc. Faraday Trans.*, **86,** 3429.

[8] Hai-Fu, F., 1988, R-SAPI88: Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan.

[9] Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R., and Viterbo, D., 1989, *J. appl. Cryst.*, **22,** 389.

[10] Sheldrick, G. M., 1986, SHELXS86 Program for the Solution of Crystal Structures, University of Göttingen, Germany.

[11] Debaedemaeker T., Tate, C., and Woolfson, M. M., 1985, *Acta Cryst.*, **A41,** 286.

[12] Sheldrick, G. M., 1993, SHELXL93 Program for the Refinement of Crystal Structures, University of Göttingen, Germany.

[13] Ito, K., and Hori, K., 1995, *Bull. chem. Soc. Jpn.*, **68,** 3347.

[14] Okuyama, K., Kawano, N., Uehori, S., Noguchi, K., Okabe, N., Suzuki, Y., and Kawamura, I., 1996, *Mol. Cryst. liq. Cryst.*, **276,** 193.

[15] Hori, K., and Ohashi, Y., 1988, *Bull. chem. Soc. Jpn.*, **61,** 3859.

[16] Ito, K., Endo, K., Hori, K., Nemoto, T., Uekusa, H., and Ohashi, Y., 1994, *Liq. Cryst.*, **17,** 747.

[17] Hori, K., Takamatsu, M., and Ohashi, Y., 1989, *Bull. chem. Soc. Jpn.*, **62,** 1751.

[18] Hori, K., and Kawahara, S., 1996, *Liq. Cryst.*, **20,** 311.