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Diversity in the packing modes of mesogenic diphenylpyrimidines with two chiral centres in their crystal structures: the role of interactions between the pyrimidine rings

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Various different crystal structures were found for four mesogenic diphenylpyrimidines with two chiral centres and these have been compared with the previously determined crystal structure of 2-{4-[(*R*)-2-fluorohexyloxy]phenyl}-5-{4-[(*S*)-2-fluoro-2-methyldecanoyloxy]phenyl}pyrimidine (**1**) which shows an isotropic mesophase. 2-{4-[(*S*)-2-Fluoro-2-methyldecanoyloxy]phenyl}-5-{4-[(*R*)-2-fluorohexyloxy]phenyl}pyrimidine (**2**) and 2-{4-[(*R*)-2-fluorohexyloxy]biphenyl-4′-yl}-5-[(*S*)-2-fluoro-2-methyldecanoyloxy]pyrimidine (**3**), which are isomers of **1** with different N positions, have a structure comprising L-shaped molecules with the chains associated between layers (MHPOBC-type) and a polar structure of stacked monolayers of parallel molecules, respectively. Two diastereomers, 2-{4-[(*R*)-2-fluorohexyloxy]phenyl}-5-{4-[(*R*)-2-butyloxypropanoyloxy]phenyl}pyrimidine (**4**) and 2-{4-[(*S*)-2-fluorohexyloxy]phenyl}-5-{4-[(*R*)-2-butyloxypropanoyloxy]phenyl}pyrimidine (**5**) with the same core as **1** but a different chain, have similar structures with crossed core moieties. It is concluded that electrostatic or dipole–dipole interactions between pyrimidine rings, maximizing the overlap of the core moieties, and the bulkiness of the chains are competing tendencies which produce the diversity of the crystal structures. In striking contrast to **1**, chiral interactions are not dominant in these crystals, confirming the uniqueness of the crystal structure of **1**.

1. Introduction

Chiral interaction plays an important role in the structures and properties of materials. In liquid crystalline phases, helical structures and various properties such as ferro- and antiferro-electricity are induced by the interaction. Of particular interest is an isotropic mesophase (IsoX) induced by chiral interaction and shown by 2-{4-[(*R*)-2-fluorohexyloxy]phenyl}-5-{4-[(*S*)-2-fluoro-2-methyldecanoyloxy]phenyl}pyrimidine (**1**), see table 1 [1]. The crystal structure of **1** revealed a unique feature of molecular packing. There are four crystallographically independent molecules, A, B, C, and D. One-dimensional ribbons of tightly fitted pyrimidine rings with CH—N hydrogen bonds are formed as –A–C–A–C– and –B–D–B–D– along the direction [1 0 1], as shown in figure 1 (*a*). The arrangement results in a large overlapping of core moieties and

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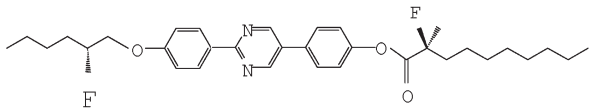
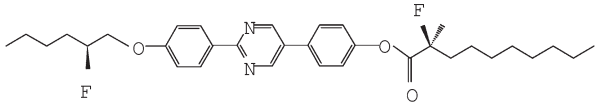
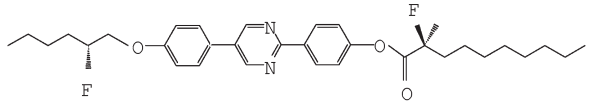
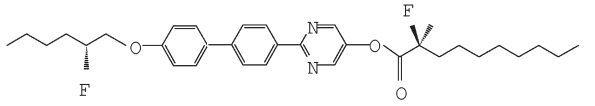
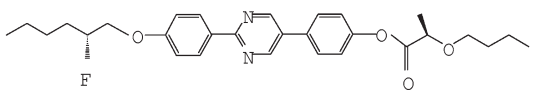
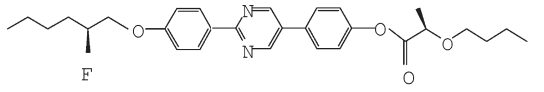
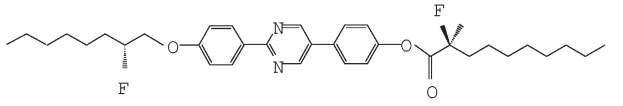
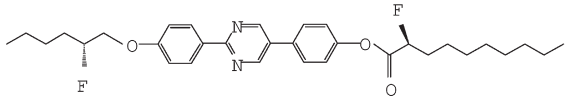
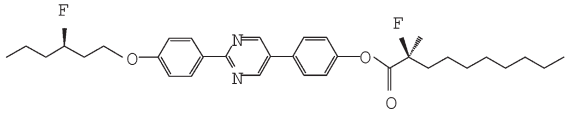
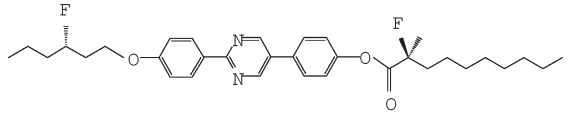
Table 1. Molecular structures and phase sequences (transition temperatures in °C). Arrows denote irreversible transitions.

1		Cr 89 SmX 99 IsoX $\xrightarrow{126}$ iso. 107↖ ↗117 Sm*C
1′		Cr 102 SmX 122 Sm*C 128 iso.
2		Cr 98 Sm*C 102 SmA 136 iso.
3		Cr 102 SmX 122 Sm*C 128 iso
4		Cr 148 (SmX 112) Sm*C 151 iso.
5		Cr 115 Sm*C 149 iso.
6		Cr 95 IsoX 127 iso.
7		Cr 129 SmX 139 SmC* 191 SmA 216 iso.
8		Cr 109 SmC* 130 iso.
9		Cr 86 SmC* 126 iso.

hence, the stereo-specific F–methyl interactions between the chiral groups of molecular pairs A–B and C–D, as shown in figure 1 (*b*). These interactions were considered to be responsible for the uniquely organized IsoX phase [2].

The appearance of the IsoX phase is strongly structure-dependent. Various modified compounds based on **1** do not show the phase, except for **6** for which only a chain was lengthened, see table 1 [3]. In order to clarify the factors responsible for the formation of the IsoX phase, crystal structures have been determined for compounds (**2–5**). Compounds **2** and **3** (*R*,*S*-5 and *R*,*S*-6, respectively, in ref. [3]) are isomers of **1** with different positions of the N-atoms. Compounds **4** and **5** have a common core moiety with **1** but different chains, and are diastereomers of each other. Synchrotron radiation was used for the small crystals of **4** and **5** as well as the diastereomer of **1** (**1′**). Unfortunately only the unit cell was determined for **1′**.

2. Experimental

All the compounds have been synthesized previously [3]. Procedures for crystal structure analysis and final results are summarized in table 2. Data collected at room temperature gave only poor results due to large

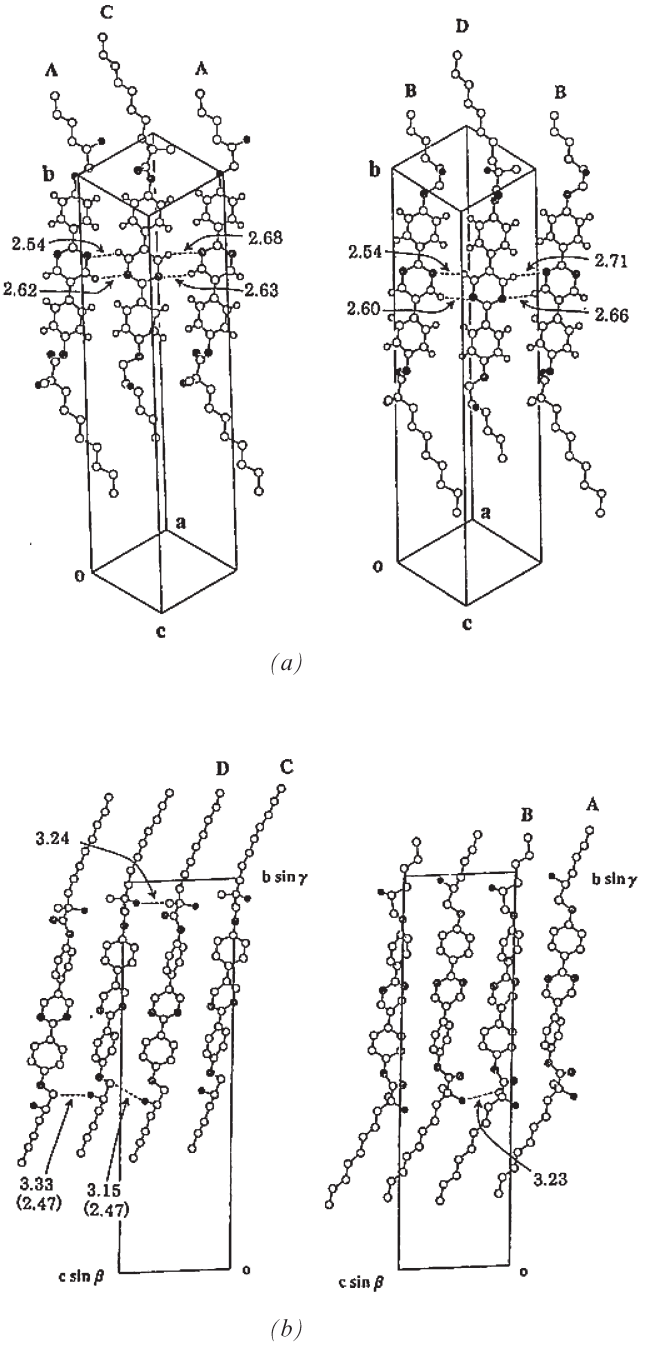


Figure 1. Crystal structure of **1**, showing (*a*) CH—N hydrogen bonds and (*b*) chiral interactions between molecular pairs, A–B and C–D. Hydrogen atoms, except for the core moiety in (*a*), are omitted for clarity. Crystal data: $T=230$ K, triclinic, $P1$, $a=10.161(3)$, $b=32.725(13)$, $c=10.021(3)$ Å, $\alpha=94.43(2)^\circ$, $\beta=110.54(3)^\circ$, $\gamma=86.29(3)^\circ$, $V=3108.8(18)$ Å^3, $Z=4$, $d_x=1.181$ Mg/m^3, $\mu=0.675$ mm^{-1}; (cited from ref. [2]).

temperature factors; data were therefore collected at low temperatures.

For compounds **4**, **5**, and **1′**, synchrotron radiation at the BL04B2 in the SPring-8 was used, because only small crystals were obtained for these compounds. In particular, **1′** gave very thin and fragile crystals. Data collection and processing were performed as previously described [4].

Structures were solved by applying programs SHELXS86 [5] (**2** and **5**), SIR88 [6] (**3**), and SHELXS97 [7] (**4**) and refined using SHELXL97 [8]. When the refinement of **2** converged to $R1$ (for obs. refl.) = 0.084 and Rw2 (for all) = 0.3132, displacement parameters of the atoms of one of the phenyl rings and the pyrimidine ring in one of the two crystallographically independent molecules were elongated perpendicular to the planes. In addition, several peaks up to 0.8 e Å^{-3} clearly showed another geometry of the rings and the ester linkage. These peaks were treated as disordered atoms (occupation factor: 0.4) and refined isotropically with loose restraints for several bonds, resulting in the final $R1$ (for 3 854 obs. refl.) = 0.0550 and Rw2 (for all) = 0.1928.

For compound **3**, displacement parameters of the terminal atoms in the chains were very large. Terminal atoms C35 and C36 of molecule A were isotropically refined and fixed, while C34, C35, and C36 of molecule B were disordered and refined isotropically, still giving large displacement parameters, several of which were also fixed. The final R-values are relatively high, partly due to the disorder and partly due to the poor crystallinity despite repeated attempts at crystallization. For **4** also, displacement parameters of atoms in the chains became large; in particular those of C(20) of both of the two crystallographically independent molecules were extremely prolate. For compound **5**, one of the terminal atoms, C(36), was disordered and the other, C(27), had a prolate displacement ellipsoid.

For **1′**, all attempts at structure analysis were unsuccessful, because of the small $I/\sigma(I)$, in particular at higher angles, despite the data collection being at 100 K. Crystal data: $a=32.569$, $b=8.927$, $c=5.368$ Å, $\alpha=90.708^\circ$, $\beta=91.433^\circ$, $\gamma=90.271^\circ$, $V=1560.1$ Å^3, $Z=2$, $d_X=1.18$ g cm^{-3}, space group $P1$.

Final atomic coordinates and related materials for **2**–**5** have been deposited in Cambridge Structural Database (No. 221144–221147).

3. Results

3.1. *Molecular structures*

Molecular structures are shown in figure 2. Bond lengths and angles are normal within experimental error. There are two crystallographically independent molecules, A and B, in compounds **2**, **3** and **4**. Dihedral angles between the rings and torsion angles of chains are summarized in table 3.

In **2**, two rings in the core moiety of molecule B are

Table 2. Experimental details and final results of refinements.

Parameter	**2**	**3**	**4**	**5**
T/K	230		170	
Formula	$C_{33}H_{42}O_3F_2N_2$		$C_{29}H_{35}O_4FN_2$	
F.W.	552.69		494.59	
Source	Cu K_α ($\lambda = 1.5418$ Å)		SR ($\lambda = 0.3282$ Å)	
Apparatus	AFC-7R		Weissenberg camera	
Crystal shape	plate	plate	plate	needle
Crystal size/mm	0.3, 0.3, 0.02	0.3, 0.3, 0.02	0.2, 0.2, 0.03	0.3, 0.06, 0.06
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P1$	$P2_1$	$P1$	$C2$
a/Å	10.6506(16)	9.818(8)	9.4970(10)	18.167(3)
b/Å	27.199(3)	56.06(3)	23.991(2)	6.3040(6)
c/Å	5.4920(7)	5.715(4)	6.2170(4)	23.259(3)
α/°	91.132(10)	90	90.019(4)	90
β/°	102.315(11)	102.75(5)	109.085(4)	96.264(2)
γ/°	83.159(11)	90	85.103(2)	90
V/Å^3	1543.2(4)	3068(4)	1333.2(2)	2647.8(6)
Z	2	4	2	4
d_X/Mg m^{-3}	1.189	1.197	1.232	1.246
$\sin\theta/\lambda$	0.6010	0.6014	0.6252	0.7113
μ/mm^{-1}	0.680	0.684	0.054	0.055
T_{min}/T_{max}	0.920	0.675	—	—
measured refl.	6879	7074	12570	10497
refl. used for l. s.	5577	5609	9018	6106
R(int)	0.034	0.199[a]	0.049	0.028
obs. refl. ($I > 2\sigma(I)$)	3854	2845	8103	5587
R1 (for obs. Refl.)	0.0550	0.1053	0.0739	0.0609
Rw2 (for all)	0.1928	0.3668	0.2093	0.1873
S	1.015	1.269	1.046	1.031
Δ/σ	0.012	0.243	0.173	0.019
$\Delta\rho$/e Å^{-3}	0.204, −0.224	0.435, −0.522	0.384, −0.302	0.369, −0.458

[a]Absorption correction was done based on ψ-scan.
[b]0.095 for $I > \sigma(I)$

disordered, as was mentioned in § 2. The dihedral angles between the two disordered rings are 75.1(11)° and 58.8(16)° for the pyrimidine and benzene rings, respectively. In the chains, the shorter chain (O3–C36) has an all-*trans*-conformation, while the longer chain is twisted at the root of the chain (C21–C24) with the remaining (C22–C30) in an all-*trans*-conformation, resulting in an L-shaped molecule.

For **3**, both molecules, A and B, have almost planar core moieties. A difference is found in the conformations of C21–C24 and O3–C33: twisted for A and *trans* for B. The molecules are more extended than in **2**.

The molecular shapes of **4** and **5** are characterized by the twisted core moieties and twisted chain conformations in C21–C24, O4–C26 and O3–C33.

3.2. *Packing modes*

Figure 3 shows the crystal structure of **2**. The core moieties are almost parallel, giving a smectic-like layer structure, while the long chains perpendicular to the core moieties are associated between layers. This type of packing has been observed in crystals of 4-[(*S*)-1-methylheptyloxycarbonyl]phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC) [9] and related antiferroelectric mesogens [10, 11].

Figure 4 shows the crystal structure of **3**. In this crystal, the core moieties are almost parallel to each other with a regular herringbone arrangement of aromatic rings, while the chains are crossed between A and B molecules. However, the most striking feature of the crystal is that projections of all the molecules are in the same orientation along the b axis in a polar structure of stacked monolayers of parallel molecules.

Figure 5 shows that in the crystal structure of **4**, the core moieties of molecule A and B are not parallel but make a large angle. Similarly, figure 6 shows that in the crystal of **5**, alternate molecules related with symmetry elements are not parallel but crossed. Therefore, the packing modes of **4** and **5** are very similar despite the different space groups.

4. Discussion

4.1. *Intermolecular interactions in crystals*

Figure 7 shows that the pyrimidine rings are closely arranged between neighbouring molecules. The core

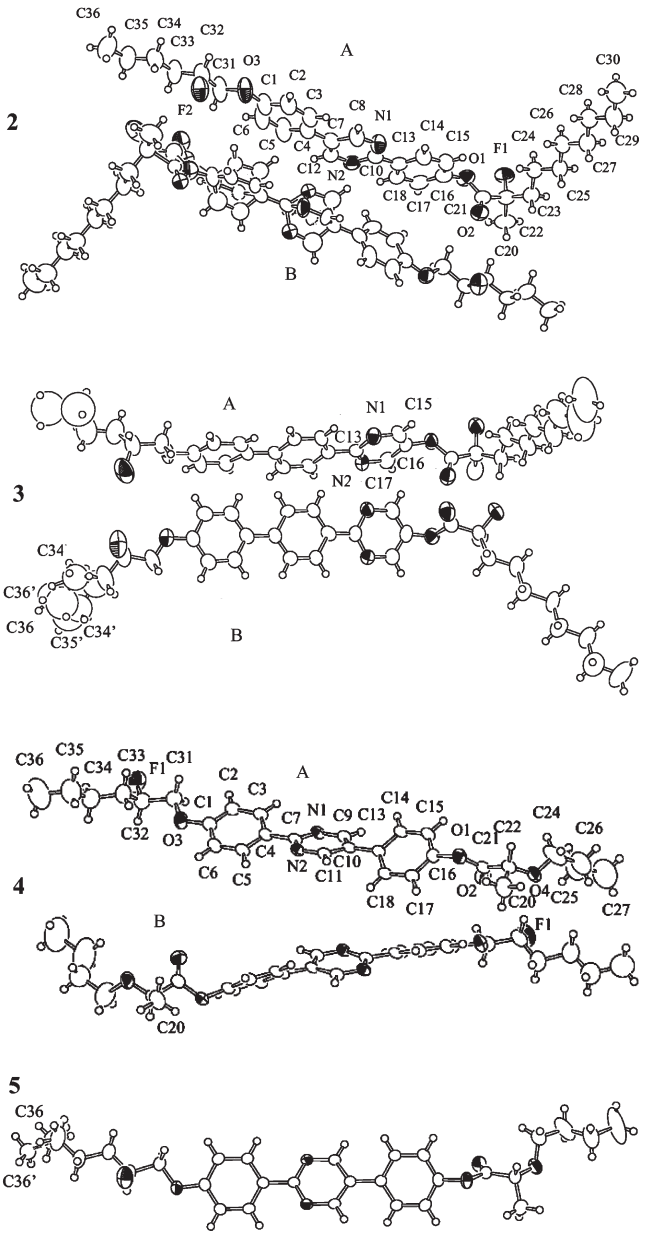


Figure 2. Molecular structures of **2**–**5**. The same scheme of numbering is applied to each molecule. Displacement ellipsoids are shown at 50% probability level.

moieties are arranged in a parallel fashion to a greater or lesser degree in **2** and **3**, with the direction of the core axes antiparallel and parallel, respectively. On the other hand, in **4** and **5**, the cores are crossed at the pyrimidine ring as the pivot with an angle of about 45°. Interatomic C–N distances are shown in table 4, and are as short as 3.3 Å, except for **3** for which the C–N distances are a little longer (> 3.47 Å). In **2**, both the disordered pyrimidine rings participate in the close arrangements. These facts show that special interactions such as an electrostatic interaction and/or dipole–dipole interactions between the pyrimidine rings are crucial in the crystals. In the extreme case of **1**, hydrogen bonds are formed between pyrimidine rings. In **3**, the pyrimidine ring is located near the end position of the core. If the molecules had an antiparallel arrangement with the pyrimidine rings close, overlapping of the core moieties would be small: a parallel arrangement of the cores with the pyrimidine rings close favours the large overlapping of cores. Thus, special interactions between pyrimidine rings, as well as the requirement of maximum overlapping of cores, lead to the very different crystal structures of **1**, **2**, and **3** due to the different positions of N-atoms. Packing efficiencies of **1**, **2**, and **3** are estimated approximately in table 5. It is noteworthy that the volume of the core is largest for **1**, despite the tightly fitted structures with infinite hydrogen bonds between pyrimidine rings.

Table 6 summarizes interatomic distances involving the chiral centres and polar groups. In contrast to the structure seen for **1**, there are few interactions between the chiral centres in **2** and **3**: in **2** a short distance is only found between C20A and F2B. It is, however, reasonable that the protruding chiral moieties tend to avoid facing each other in a crystal lattice. In other words, this confirms that the chiral interactions dominant in **1** are introduced by the very unique crystal packing of **1**.

On the other hand, crystals **4** and **5** have quite different structures from **1**, despite having the same core moieties as **1**. However, they are similar to each other with crossed core moieties. This may be interpreted in terms of the existence of the O4 atom adjacent to the bulky methyl group introducing an irregularity in the chain, i.e. chain twist as was described in the previous section, the molecules are then forced to cross each other to avoid steric hindrance caused by the chain twist.

4.2. *Relations between crystal structures and mesophase behaviour*

Let us now discuss the intermolecular interactions responsible for the appearance of the IsoX phase based on the crystal structures. The diversity in packing modes of the dichiral compounds is consistent with the structure–property correlations for the appearance of the IsoX phase, indicating that the unique packing mode of compound **1** reflects the molecular organization of the IsoX phase. In a smectic-like layer structure, strong interactions due to the CH—N hydrogen bonds exist between pyrimidine rings of antiparallel molecules, leading to the large overlapping of the core moieties and strong interactions between chiral groups. As

Table 3. Dihedral angles (°) between rings and torsion angles (°) of chains. Rings are denoted as I, II and III, for C(1)–C(6), (C7)–C(12) or–N(2), and C(13)–C(18), respectively. Geometries concerning disordered structures are shown in two columns.

	2		**3**		**4**		**5**
Angle	A	B	A	B	A	B	
I–II	14.3(7)	45(1) 60.4(6)	12.0(7)	3.8(7)	24.72(17)	24.76(14)	22.54(9)
II–III	5.8(5)	6(2) 10.5(10)	4.8(8)	4.1(6)	34.33(14)	34.36(13)	34.83(8)
C21–C22–C23(O4)–C24	−62.1(6)	−47.7(8) −79.4(9)	−70.2(13)	−172.5(12)	−120.4(10)	−125.9(8)	−80.2(3)
C22–C23(O4)–C24–C25	−179.5(5)	−177.1(5)	169.0(9)	−175.1(13)	178.2(11)	176.3(10)	−167.6(3)
C23(O4)–C24–C25–C26	−175.6(5)	170.6(6)	179.9(11)	177.8(14)	−63.6(19)	−62.7(17)	73.0(5)
C24–C25–C26–C27	179.1 (5)	178.2(6)	178.8(14)	−176.5(17)	−178.1(10)	179.2(11)	175.9(5)
C25–C26–C27–C28	−179.4(5)	173.9(6)	−178.4(17)	176.7(18)			
C26–C27–C28–C29	178.6(6)	179.7(6)	−175(3)	−180(2)			
C27–C28–C29–C30	178.2(7)	177.0(7)	179(3)	−177(3)			
O3–C31–C32–C33	178.3(7)	177.5(4)	−53(3)	−167.4(15)	−66.8(6)	−66.7(6)	161.4(3)
C31–C32–C33–C34	175.5(8)	176.1(5)	−172(3)	−89(4) −173(3)	176.2(5)	176.0(5)	171.2(3)
C32–C33–C34–C35	−176.4(8)	179.6(5)	78(5)	−176(4) −176(4)	178.1(8)	179.7(7)	−177.6(5)
C33–C34–C35–C36	174.9(9)	−178.6(5)	162(4)	90(7) −73(6)	−175.0(10)	−178.2(11)	−74.4(7) −143.6(9)

mentioned in the previous section, the cores are rather loosely packed with locally strong interactions due to the hydrogen bonds. The coupling between the core–core interactions and the overlapping of the chiral moieties are thought to be the origin of the chiral recognition.

The effect of molecular structure on the phase sequences for the dichiral derivatives [3, 12], see table 1, may be understood in terms of the crystal structures. The IsoX phase disappeared with the modification of the core structures in **2** and **3** and chain structures in **4** and **5**, because of the quite

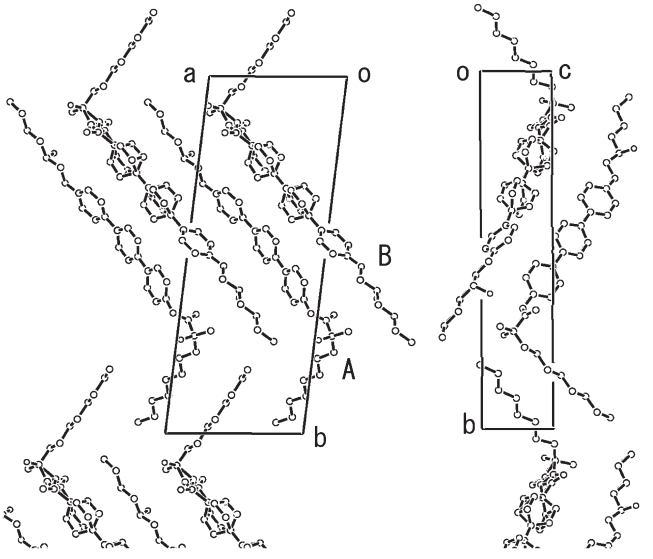


Figure 3. Crystal structure of **2** viewed along the *c* (left) and *a* (right) axes.

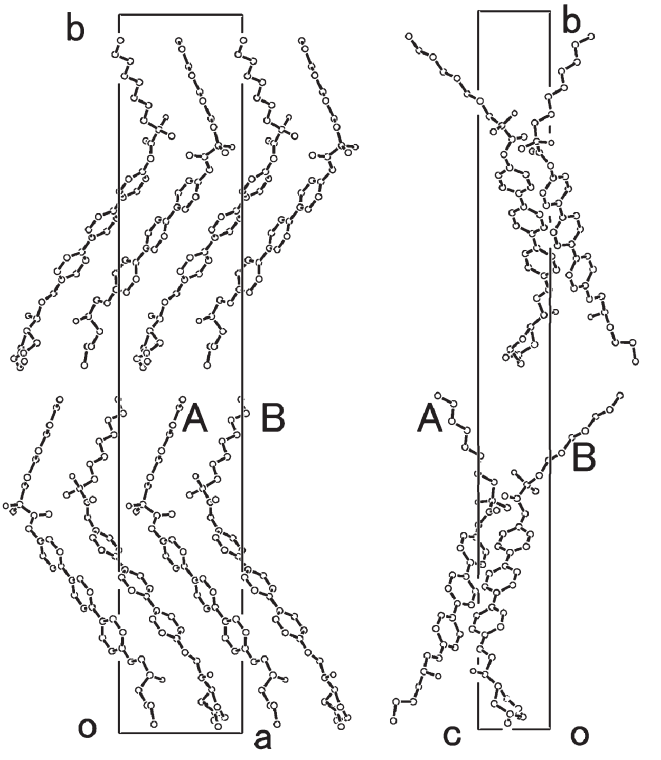


Figure 4. Crystal structure of **3** viewed along the *c* (left) and *a* (right) axes.

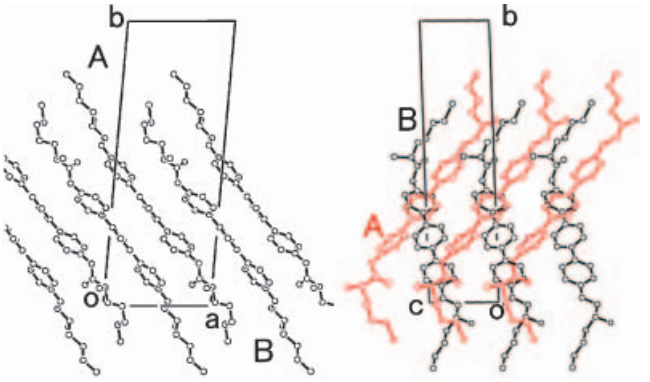


Figure 5. Crystal structure of **4** viewed along the *c* (left) and *a* (right) axes.

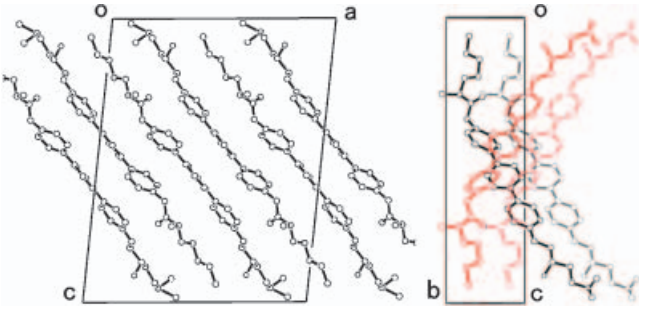


Figure 6. Crystal structure of **5** viewed along the *b* (left) and *a* (right) axes. In the right, molecules at different depths are distinguished by light and shade. All the molecules are equivalent. Both of the disordered atoms in the terminal chain are shown.

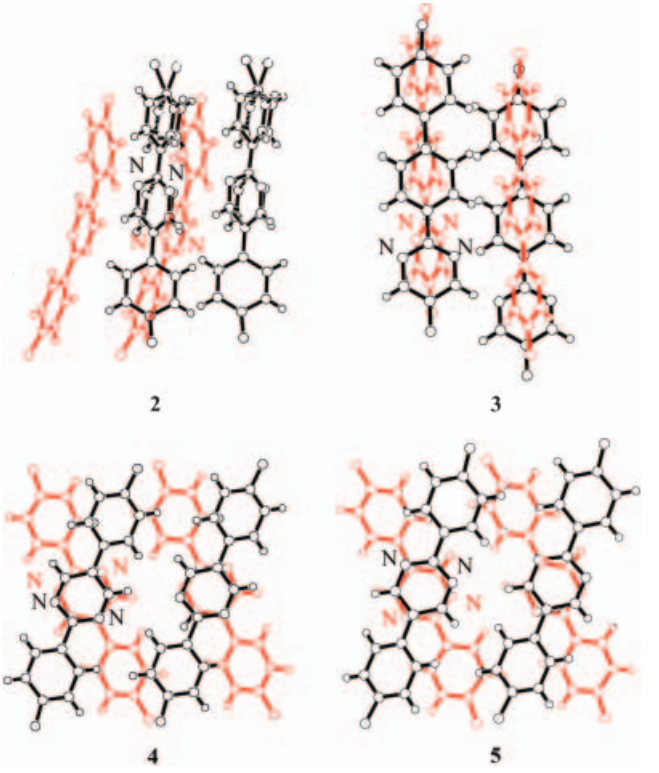


Figure 7. Arrangements of the core moieties of **2**–**5**.

different packing scheme. The effects of deleting a methyl group (**7**) and shifting the F position and chirality (**8** and **9**) would change the interaction between chiral groups, if the unique structure of core moieties remains. On the other hand, on increasing the chain length in **6**, the SmC* phase disappeared but the stability of the IsoX phase increased. The SmC* to IsoX transition for **1** is thought to originate from a competition between interlayer and intralayer chiral interactions [13]. Increasing the chain length would not

Table 5. Packing volumes (Å^3).

Compound	Core	Chain	Total *V*/*Z*
1	300	477	777
2	285	487	771
3	287	480	767

Table 4. Interatomic C—N distances (Å) between pyrimidine rings (<4.0 Å).

2		**3**		**4**		**5**	
C8B–N2B($z+1$)	3.176	N2B–C15B($z+1$)	3.474	N1A–C9B($z-1$)	3.322	N2–C11($-x$, $-z+1$)	3.330
N2A–C12B′	3.261	N1A–C17A($z+1$)	3.632	N2B–C9A($z+1$)	3.333	N2–C9($y-1$)	3.604
N2A–C12B	3.337	N1A–C17B	3.953	N2B–C11B($z-1$)	3.546	N1–C11($-x$, $-z+1$)	3.822
C12A–N2B′($z-1$)	3.390			N1A–C11($z-1$)	3.547	N1–C9($-x$, $-z+1$)	3.874
C12A–N2B′	3.549			N1B–C9A($z+1$)	3.820		
C8A–N2A($z-1$)	3.613			N2A–C9B($z-1$)	3.823		
C12A–N1B($z-1$)	3.711			N1B–C11A($z+1$)	3.871		
C8A–N2B′($z-1$)	3.827			N2A–C11B($z-1$)	3.879		
N2A–C8B($z-1$)	3.844						
N1B–C12B($z+1$)	3.863						
N1A–C12B′($z-1$)	3.864						

Table 6. Intermolecular distances (Å) involving the chiral moieties and polar groups (< 3.6 Å).

2		**3**		**4**		**5**	
F1A–O2A($z+1$)	3.57	O1A–C20B($x-1$)	3.59	O3A–O2B($z+2$)	3.23	O3–O2($y+1$,$z+1$)	3.40
F2A–C20B($z-1$)	3.52	O1A–O2B($z+1$)	3.42	O3B–O2A	3.24	O2–C20($y+1$)	3.27
F2A–O2B($z-1$)	3.54	O2A–F1($z+1$)	3.57	O3B–C20A	3.60		
C20A–F2B	3.28	O2A–F1B($x-1$,$z+1$)	3.59	O2B–C20B($z+1$)	3.31		
		F1A–O2B($z+1$)	3.44	O3B–C21A	3.50		
		C21A–O2B($z+1$)	3.32				

affect the structure of the largely overlapping core moieties but would enhance microphase separation in the ring-containing and chain-containing microphases. Thus favourable intralayer interactions can stabilize the IsoX phase.

5. Conclusions

The crystal structures of **2**–**5** differ according to the chemical constituents of the core moieties and chains. Electrostatic or dipole–dipole interactions between pyrimidine rings are crucial in the crystals. In addition, maximizing the overlap of the core moieties, and the bulkiness of the chains compete to produce the diversity of crystal structures found. However, chiral interactions are not dominant in these crystals in strong contrast with **1**. Thus, the previously determined structure of **1**, in which one-dimensional ribbons of tightly fitted pyrimidine rings with N—H hydrogen bonds lead to the dominant chiral interactions, is proved to be unique.

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