Liquid Crystals

DOI: 10.1002/anie.200603594

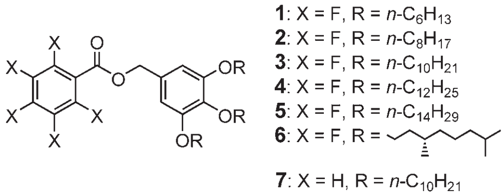
Columnar Superstructures of Non-Disc-Shaped Molecules Generated by Arene–Perfluoroarene Face-to-Face Interactions**

Keiki Kishikawa, Katsuyuki Oda, Sumihiro Aikyo, and Shigeo Kohmoto*

Arene–perfluoroarene interaction is known as a strong face-to-face interaction between perfluorinated and nonfluorinated aromatic rings.[1,2] It has been reported that the interaction was not a donor–acceptor interaction, that it originated in both dispersion and electrostatic interactions, and that the dispersion interaction was more effective than the electrostatic interaction.[3] The sum of the dispersion and electrostatic energies between benzene and hexafluorobenzene molecules was estimated to be 3.7–5.6 $\text{kcal}\,\text{mol}^{-1}$.[4] In other reports, the interactions between phenyl and fluorinated phenyl groups were estimated to be 0.5 $\text{kcal}\,\text{mol}^{-1}$ per fluorine atom from the study of the rotational barriers of 1-(fluorinated phenyl)-8-phenylnaphthalenes.[5] Further, the attractive interaction was used for crystal engineering[6] and solid-state stereoselective photoreactions.[7]

Despite the wide application of arene–perfluoroarene interaction in various areas, it is very difficult to maintain the strong interaction in liquid-crystal (LC) phases. The two different benzene rings have to be kept at a short distance to maintain the large attractive forces because the dispersion and quadrupole–quadrupole forces are proportional to r^{-6} and r^{-5}, respectively (r is the intercentroid distance between two benzene rings).

In this study, we designed and synthesized non-disk-shaped simple molecules **1**–**6** (Scheme 1) with both pentafluorophenyl and nonfluorinated phenyl groups. The compounds **2**–**5** generated a columnar superstructure in the mesophases by using intermolecular attractive interactions, such as dipole–dipole, arene–perfluoroarene, and CH–F interactions. In the superstructures, arene–perfluoroarene face-to-face interactions should be the main attractive force for the molecular stacking. Although several interactions, such as hydrogen bonding, dipole–dipole interaction, ionic bonding, charge-transfer complexation, and microsegregation, were used recently for generation of superstructures in LC phases,[8] arene–perfluoroarene interaction has hardly been utilized. This suggests that it is difficult to use the interaction for the construction of superstructures.



Scheme 1. Structures of compounds **1**–**7**.

For stabilization of a LC phase by arene–perfluoroarene interactions, only the following two examples are known. Grubbs and co-workers reported that the clearing point of the columnar phase of a liquid-crystalline triphenylene derivative was raised by the addition of an equimolar amount of perfluorotriphenylene.[9] In this case, however, it seemed that the stabilization energy did not originate only in the π–π interaction, but also in the decrease of the intermolecular steric repulsion in the column by the insertion of the small disklike (perfluorotriphenylene) molecules between the bulky disklike (hexaalkoxytriphenylene) molecules. In the other example, Marder and co-workers reported that the 1:1 complex of 1,4-di(phenylethynyl)benzene and 1,4-di(pentafluorophenylethynyl)-2,3,5,6-tetrafluorobenzene showed smectic B and nematic LC phases, despite each of them not exhibiting any LC phase.[10] In this case, the spinning of the rodlike molecules around their molecular long axes seemed to be so rapid that the arene–perfluoroarene face-to-face interaction could not be distinguished from the CH–F edge-to-edge attractive interaction.[11] Thus, in those two examples it was not clear whether the face-to-face interaction was the main intermolecular interaction in the self-organizations.

The simple molecules **1**–**6** have one pentafluorophenyl group and one nonfluorinated phenyl group linked by an ester junction. We expected the following processes in their molecular aggregation; 1) the molecules are organized into dimers in an antiparallel manner by the intermolecular dipole–dipole interaction of the central ester moieties and the edge-to-edge CH–F interaction (A→B in Figure 1); 2) the dimers are piled up by using the intermolecular arene–perfluoroarene face-to-face interaction (B→C); and 3) by doping of chiral dopant molecules, the column twists helically (C→D).

Esters **1**–**6** were prepared from pentafluorobenzoic acid and the corresponding 3,4,5-trialkoxybenzyl alcohol. The nonfluorinated homologue **7** was also synthesized, and its behavior was compared with that of fluorinated compound **3** to clarify the influence of the pentafluorophenyl group (Scheme 1). The transition temperatures and enthalpies of

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[*] Prof. K. Kishikawa, K. Oda, S. Aikyo, Prof. S. Kohmoto
Department of Applied Chemistry and Biotechnology
Faculty of Engineering
Chiba University
1-33 Yayoi-cho, Inage-ku, Chiba 263-8522 (Japan)
Fax: (+81) 43-290-3422
E-mail: kishikawa@faculty.chiba-u.jp

[**] This work was supported by the Ministry of Education, Science, Sports, and Culture, Grant-in-Aid for Scientific Research (B), 2003, 53501081 and Exploratory Research, 2004, 16655090.

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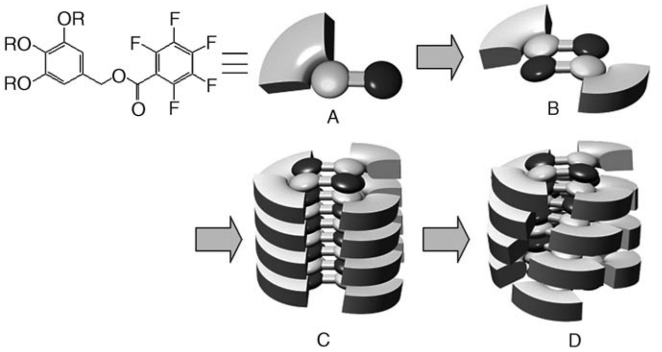

Figure 1. Schematic representation of the generation of the columnar structure. A: monomer; B: dimer; C: columnar aggregate; D: helically twisted columnar aggregate. (light-gray disk: nonfluorinated benzene ring; dark-gray disk: perfluorinated benzene ring; gray block: trialkoxy groups).

these compounds were investigated by differential scanning calorimetery (DSC) and their phases were identified by polarized optical microscopy (POM). Compounds **2**–**4** showed enantiotropic columnar phases at room temperature (Table 1). Compound **5** showed a monotropic columnar phase. At the transition from the isotropic to columnar phase, the ribbonlike textures (or peeled apple skins) appeared from the isotropic liquid (Figure 2 a) and coalesced to focal conic textures (Figure 2 b). Even with a slow cooling rate (0.1 °C min^{-1}), the ribbons were mainly observed at the transition. The generation of the ribbonlike textures suggests that the growth of the column in the direction of the column axis is much faster than that in the perpendicular direction to the column axis.[12] Accordingly, it is assumed that the stacking interactions between the molecules in these columnar phases are much stronger than those in general columnar phases. The transition enthalpies (5.4–5.8 kcal mol^{-1}) of the ordered hexagonal columnar–isotropic (Col$_{\text{ho}}$–Iso) phase transitions of **2**–**4** were larger than those of other columnar liquid-crystalline compounds with a similar molecular weight.[13,14] The nonfluorinated benzoate **7** (X = H, R = n-$C_{10}H_{21}$) was a clear oil even at room temperature and did not show any LC phase. These results strongly suggest that the driving force for the self-organization of the molecules into the columnar superstructures is the intermolecular interaction between the pentafluorophenyl and trialkoxyphenyl groups.

Table 1: Phase-transition behavior of **1**–**7**.[a]

Compound	Phase-transition behavior	T [°C] (ΔH [kcal mol^{-1}])
1	cryst–Iso	51 (6.3)
2	Col$_{\text{ro}}$–Col$_{\text{ho}}$–Iso	29 ([b]), 46 (5.4)
3	Col$_{\text{ho}}$–Iso	42 (5.8)
4	Col$_{\text{ho}}$–Iso	40 (5.7)
5	cryst–(Col$_{\text{ho}}$)–Iso	62 (7.6), 37 (1.8)
6	cryst–Iso	23 (4.2)
7	Iso < RT	n.a.

[a] Cryst, Col$_{\text{ro}}$, Col$_{\text{ho}}$, and Iso indicate crystal, ordered rectangular columnar, ordered hexagonal columnar, and isotropic phases, respectively. [b] The transition enthalpy was too small to be measured, n.a.: not applicable.

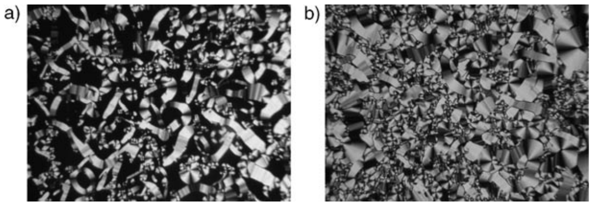

Figure 2. Polarized optical micrographs of **2** at 46 °C. a) Ribbonlike textures and b) focal conic textures.

To investigate the molecular-packing structures, the X-ray diffraction (XRD) profiles of **2**–**4** in liquid-crystalline states were measured (Table 2). In the cases of **3** and **4**, the ratios of the d spacings (100), (110), (200), (210), and (300) were 1, $1/\sqrt{3}$, 1/2, $1/\sqrt{7}$, and 1/3, respectively, which was indicative of a hexagonal columnar structure. A sharp peak observed at 3.7 Å corresponds to the repeat distance of the stacked aromatic rings and indicates that the phases have a Col$_{\text{ho}}$ structure.

Table 2: XRD results for **2**, **3**, and **4**.[a]

Compound	Phase	d_{obs} [Å]	d_{calcd} [Å]	Miller index	z
2	Col$_{\text{ho}}$	22.2	22.2	100	1.8
	a = 25.7 Å	12.9	12.8	110	
	c = 3.7 Å	11.2	11.1	200	
	T = 35 °C	8.5	8.4	210	
		7.5	7.4	300	
		5.6	5.6	400	
		4.5	4.4	500	
		3.7	–	001	
	Col$_{\text{ro}}$	22.4	22.4	200	3.7
	a = 44.8 Å	22.1	22.1	110	
	b = 25.4 Å	12.9	12.9	310	
	c = 3.7 Å	12.7	12.7	020	
	T = 20 °C	11.2	11.2	400	
		11.0	11.0	220	
		8.6	8.4	420	
		8.3	8.3	130	
		7.3	7.2	330/600	
		5.7	5.8	800	
		5.5	5.5	440	
		4.5	–	–	
		3.7	–	001	
		3.6	–	–	
3	Col$_{\text{ho}}$	24.0	24.0	100	1.9
	a = 27.7 Å	13.9	13.9	110	
	c = 3.6 Å	12.0	12.0	200	
	T = 20 °C	9.1	9.1	210	
		8.0	8.0	300	
		3.6	–	001	
4	Col$_{\text{ho}}$	25.4	25.4	100	1.9
	a = 29.3 Å	14.7	14.7	110	
	c = 3.6 Å	12.8	12.7	200	
	T = 20 °C	9.7	9.7	210	
		8.5	8.5	300	
		3.6	–	001	

[a] a, b, and c: cell parameters, T: temperature, z: number of molecules in the unit cell (calculated as the specific gravity was 1.0), d_{obs} and d_{calcd}: observed and calculated layer spacings.

On the other hand, compound **2** exhibited an ordered rectangular columnar phase (Col$_{\mathrm{ro}}$ phase, Figure 3 a) and a Col$_{\mathrm{ho}}$ phase (Figure 3 b). The Col$_{\mathrm{ro}}$ phase showed two peaks for the stacking distance at 3.68 Å and 3.63 Å. Such double stacking distances were only observed in the cases of pseudohexagonal columnar phases of disk-shaped metallomesogens[15,16] in which a rare-earth-metal atom was sandwiched by two phthalocyanine molecules. In those cases, the double stacking peak was explained by different tilt angles of the adjacent columns that had $P2_1/a$ as the space group. In our case, the space group was $C2/m$ from its XRD peak pattern, and the phase also may belong to a pseudohexagonal columnar phase based on $a \approx b\sqrt{3}$. The Col$_{\mathrm{ro}}$–Col$_{\mathrm{ho}}$ transition of **2** was not observed by DSC and POM because the enthalpy was too small to be measured. Therefore, it suggests that the superstructure of the Col$_{\mathrm{ro}}$ phase is almost similar to that of the Col$_{\mathrm{ho}}$ phase. In all the columnar phases, halos were observed at $2\theta = 12°$ (7.4 Å) and $2\theta = 20°$ (4.5 Å), which corresponds to twice the thickness of a benzene ring and the diameter of a molten alkyl chain, respectively.

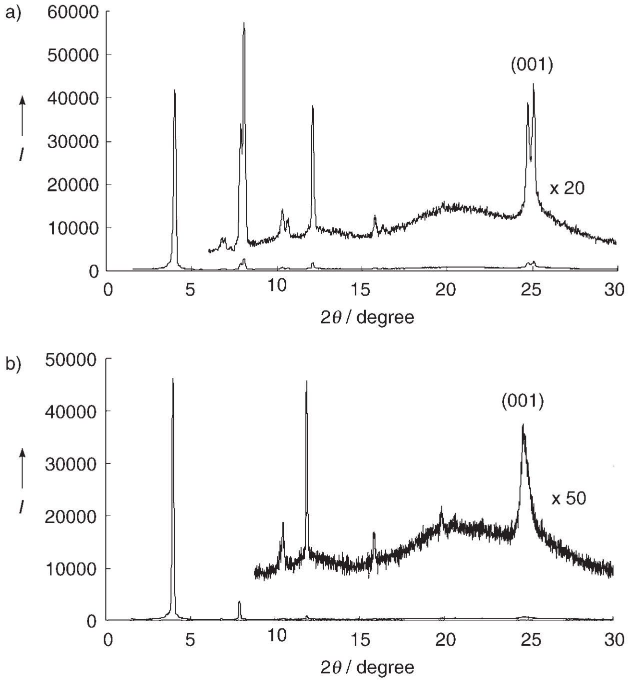

Figure 3. XRD charts of **2** at a) 20 °C and b) 35 °C. *I* = intensity measured in counts per second.

Figure 4 shows the 2D XRD profile of **2** in the Col$_{\mathrm{ro}}$ phase. The sample on a polyimide film was sheared in the direction indicated by the arrow. The sets of bright arcs at the small-angle region are the peaks of d_{110} and d_{200}, and the arcs of d_{220}, d_{400}, d_{420}, d_{130}, d_{330}, and d_{600} are also located on the meridian. One set of arcs (d_{001}) on the equator is observed as the wide-angle scattering, which indicates the stacking distance in the column and is not observed as double lines because of the low resolution.

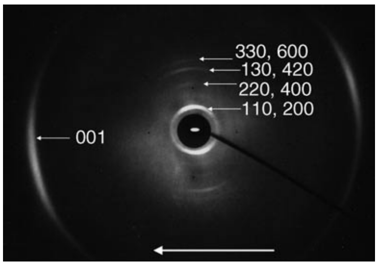

Figure 4. 2D XRD image of **2** in the Col$_{\mathrm{ro}}$ phase at 20 °C. The sample on a polyimide film was sheared in the direction indicated by the arrow.

In all of the columnar phases, each of the XRD peaks were very sharp, which suggests that these columnar phases have well-defined molecular-packing structures. In general, the sharp scattering peak (d_{001}) at the wide-angle region is observed in the mesophases of large conjugated π systems, such as triphenylenes,[17] perylenes,[18] truxenes,[19] phtharocyanines,[20] and hexabenzocoronenes,[21] all of which have strong attractive π–π interactions as their stacking forces. Accordingly, the sharp scattering peaks in the columnar phases of **2**–**4** suggest that their stacking interactions are strong. It is a great surprise to have such strong interactions even though each of the molecules only has two benzene rings that are not conjugated. The distances between the rings of 3.6–3.7 Å are as short as those in the 1:1 cocrystals of perfluorinated benzene and benzene derivatives.[6,7] The short distance showed that the two kinds of benzene rings have face-to-face stacking in the direction of the column axis. In the hexagonal mesophases of **2**, **3**, and **4**, the z values (the number of the molecules in the unit cell) were 1.8, 1.9, and 1.9, respectively. Usually, the z values of disk-shaped mesogens in hexagonal columnar phases are around 1.0. Accordingly, it can be assumed that association of the two molecules with an antiparallel manner generates a full disk shape to cancel out their dipoles (B in Figure 1 and Figure 5 a).[13] The electrostatic attractive CH–F interaction also interacts between the two benzene molecules.[11] These results support the self-organization postulated in Figure 1. The dimer stacks on another dimer and changes the positions of the perfluorinated and nonfluorinated benzene rings alternately as shown in B → C in Figure 1. This is also suggested by the repeat distances (7.4 Å) observed as the halos in XRD analysis (Figure 3).

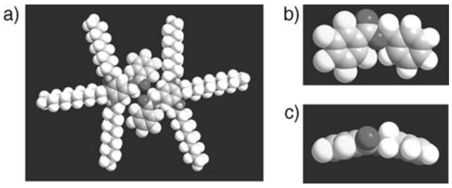

Figure 5. Molecular models for a) disk-shaped dimer of **3** (R = *n*-$C_{10}H_{21}$) and the most stable conformer of phenylmethyl pentafluorobenzoate shown from the front (b) and side (c) views (calculated by AM1).

To estimate the conformation of molecules **2**–**4**, an AM1 calculation[22] of phenylmethyl pentafluorobenzoate was carried out to give a bent-shaped conformer as the most stable form (Figure 5b,c). The stacking distances in the mesophases can be explained by using the bent-shaped molecular model as follows. In the $\mathrm{Col_{ho}}$ phase of **2**, the bent-shaped molecules are not tilted in the column (Figure 6a) and this packing model gives one repeat distance ($d = 3.67$ Å). On the other hand, in the $\mathrm{Col_{ro}}$ phase of **2**, each of the molecules slightly tilts in the column (Figure 6b), which generates the two repeat distances, d' (3.63 Å) and d'' (3.68 Å). This packing model is not consistent with the *C*2/*m* symmetry of the rectangular columnar phase in which the tilt directions and tilt angles of the columns are uniform.

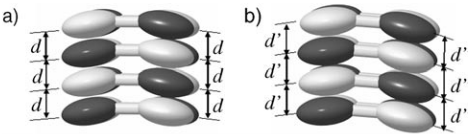

Figure 6. The molecular-packing structures in the core parts of the columns of a) $\mathrm{Col_{oh}}$ and b) $\mathrm{Col_{or}}$ phases (dark gray: pentafluorobenzene ring; light gray: nonfluorinated benzene ring).

The circular dichroism (CD) spectra of **2** in the $\mathrm{Col_{ro}}$ phase were measured. Although no CD signal was observed in the case of pure **2**, doping with 5 mol% of chiral dopant **6** induced a large negative CD signal at 306 nm (solid line in Figure 7).

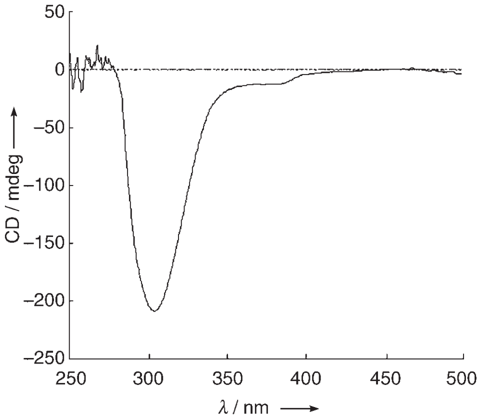

Figure 7. CD spectra of **2** doped with 5% of **6** in the LC state (solid line; quartz plate, cell gap: 5 μm, 23 °C) and a chloroform solution of **2** doped with 5% of **6** (broken line; 9.2×10^{-5} M, quartz cell, cell length: 1 cm, 23 °C).

On the other hand, a chloroform solution of **2** doped with 5% of **6** (9.2×10^{-5} M) did not show any CD signal (dashed line). This means that the CD signal observed in the mesophase originates not in each of the molecules but in the aggregate. It is assumed that the helically twisted columnar structure D (as shown in Figure 1) is generated in the mesophase.

We demonstrated that the molecules that possess both pentafluorophenyl and nonfluorinated phenyl groups were self-organized into rigid columnar superstructures in the mesophases by the strong arene–perfluoroarene face-to-face interaction. In this study, it has been clarified that the attractive stacking interaction in the columns mainly originates not in the CH–F interaction or volume effect but in the arene–perfluoroarene face-to-face interaction as 1) the pentafluorophenyl and trialkoxyphenyl groups strongly stacked in the column can not rotate around the molecular long axis, and the edge-to-edge (CH–F) interaction only takes place in the perpendicular direction to the column axis and 2) the replacement of phenyl with pentafluorophenyl group (**7**→**3**) induces the liquid crystallinity, whereas the replacement hardly changes the molecular shape or volume. Control of the interaction is still difficult and it is highly sensitive to the intermolecular distance between perfluorinated and nonfluorinated phenyl groups. Further study on the effective arrangement of these benzene rings in the molecular design is now in progress.

Received: September 2, 2006
Revised: October 13, 2006
Published online: December 13, 2006

Keywords: aromatic interactions · columnar superstructures · liquid crystals · self-assembly · supramolecular chemistry

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