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Liquid-Crystalline Properties of Dissymmetric Molecules Part 3:[1] Smectic Properties of 4-[2-(Perfluoroalkyl)ethoxy]-Substituted Nitrobenzenes and Benzonitriles

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This paper describes the thermal properties of some homologs of 4- and 3-[2-(perfluoroalkyl)ethoxy]-substituted nitrobenzenes and benzonitriles. Many of the homologs show notable smectic properties involving smectic A and B phases. The smectic structures were characterized by an X-ray diffraction examination. The smectic A phase has a partially interdigitated bilayer arrangement where the layer spacing is 1.2—1.8 times the calculated molecular length. Interestingly, some homologs show a smectic B phase with a layer spacing of 2 times the calculated molecular length. Both fluorophilic and polar interactions are supposed to play important roles for the molecular arrangements.

It is well known that liquid crystals incorporating a perfluoroalkyl group show notable smectic properties.[2—7] Some (perfluoroalkyl)alkanes have been reported to form a lamellar structure in solid states.[8,9] Some phenyl benzoate[10,11] and benzene[12—14] compounds with a perfluoroalkyl chain are known to show liquid-crystalline phases having an optically uniaxial nature, such as smectic A and B phases. Some phenyl benzoates with the perfluoroalkyl group also show a smectic C phase and a chiral one.[11] We reported that in alkyl 4-[2-(perfluoroalkyl)ethoxy]benzoates, the formation, thermal stability and molecular arrangement of the smectic A phase are strongly dependent on the relative geometrical ratio between the perfluoroalkyl group and the residual hydrocarbon moiety, and the fluorophilic and fluorophobic interactions between both groups are supposed to be of primary importance in enhancing the smectic properties.[13,14]

Our next interest is the relative importance between polar and fluorophilic interactions for the liquid-crystalline properties in nitrobenzene and benzonitrile derivatives with a perfluoroalkyl group. Generally, liquid crystals having a terminal cyano or a nitro group show interesting polymesomorphisms involving reentrant nematic and some kinds of smectic A and C phases.[15,16] In polar liquid crystals, the attractive interaction around the polar groups has been supposed to be responsible for the complex mesomorphic properties.

In this paper, we describe the thermal properties of 3- and 4-[2-(perfluoroalkyl)ethoxy]-1-nitrobenzenes (abbreviated as **3N***n* and **4N***n* *n* indicating the carbon number of the perfluoroalkyl chain) and 3- and 4-[2-(perfluoroalkyl)ethoxy]-benzonitriles (**3C***n* and **4C***n*), and the relative importance between the polar interaction around the polar groups and the fluorophilic one around the perfluoroalkyl chains concerning the mesomorphic properties (Fig. 1).

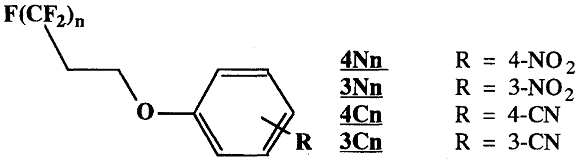


Fig. 1. Chemical structures of compounds.

Experimental

Materials: **3N***n* and **4N***n* were prepared from the corresponding 2-(perfluoroalkyl)ethanols and 3- or 4-nitrophenol according to the conventional method, as reported in our previous papers.[13,17] **3C***n* and **4C***n* were prepared similarly from the corresponding 2-(perfluoroalkyl)ethanols and 3- or 4-cyanophenol. The purity was checked by ^{1}H NMR spectroscopy and HPLC, and was also confirmed by a DSC thermogram by using a "DSCPURITY" program (Seiko-denshi Co.).

Method: The transition temperatures and latent heats were determined using a differential scanning calorimeter (DSC; Seiko SSC-5200), where indium (99.9%) was used as a calibration standard (mp 156.6 °C, 28.4 J g^{-1}). The DSC termogram was operated at a heating or cooling rate of 5 °C min^{-1}. The mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900). X-Ray diffraction experiments were performed using a Rigaku-denki RINT 2200 diffractometer with Cu $K\alpha$ (λ = 1.540 Å) as an X-ray source, where the temperature was controlled by a Rigaku PTC-20A termo-controller. The reflection angle (2θ) was calibrated by comparing both the left and right ones. A powdered sample crammed into a quartz capillary (1.5 mmϕ) was heated up to an isotropic solution, and measurements were carried during the cooling process.

Results and Discussion

The homologs exhibit two kinds of smectic phases. The smectic phases have a strong tendency for a homeotropic alignment between two glass plates, probably due to a repulsive interaction between the perfluoroalkyl group and the glass surface. The smectic phase formed at a high-temperature region shows a typical focal conic fan texture under a homogeneous alignment, and an isotropic one under a homeotropic one, indicating the optical uniaxial nature of the molecular arrangement. The smectic phase was further characterized by an X-ray examination. As an example, the X-ray profiles of the smectic phases for **4N10** are shown in Fig. 2. The profile at 100 °C (T_{S-I} -9 °C) shows a sharp reflection at $2\theta = 2.28°$ (38.7 Å) and 4.60° (19.2 Å) arising from the d_{001} and d_{002} directions, respectively, as well as a broad one centered at $2\theta = 16.4°$ (5.4 Å) arising from the d_{100} one. From the characteristic feature, the smectic phase was assigned to the A modification (S_A) with a layer spacing of 38.7 Å. A noteworthy fact is that the lateral molecular distance within the layer was larger than those of the usual liquid crystals having aromatic rings (ca. 4.9 Å).[18] This can be associated with the longer C–F bond (1.37 Å) and larger van der Waals radius (1.39 Å) of fluorine than those of hydrocarbon derivatives. The S_A phase is formed by **4N*n***, **3N8**, **4C*n***, and **3C8**.

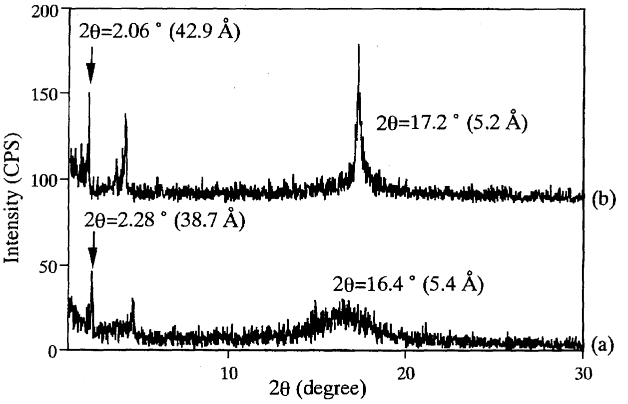


Fig. 2. X-ray profiles for **4N10** at (a); 100 °C (S_A phase), and (b); 86 °C (S_B phase).

4N10 shows another kind of a smectic phase having a broken focal conic fan texture with an optical uniaxial nature below the temperature of the S_A phase. The latent heat for the smectic-S_A transition is almost comparable with that of the S_A–I one. A similar transition behavior was observed in **4C8** and **4C10**. In Fig. 2, the profile for the smectic phase of **4N10** at 86 °C shows a sharp reflection at $2\theta = 2.06°$ (42.9 Å) and 4.12° (21.4 Å) arising from the d_{001} and d_{002} directions, respectively, and a sharp one at $2\theta = 17.2°$ (5.2 Å) arising from the d_{100} one. This feature suggests that the molecular arrangement of the smectic phase has a hexagonal order within the layer, where the lateral distance of molecules is 5.2 Å, which is shorter by 0.2 Å than that of the S_A phase. From these results, the smectic phase is assigned to the B modification (S_B). The smectic phases of **3N10** and **3C10** showed a similar X-ray profile, and were also assigned to the S_B phase.

The thermodynamic properties of the present compounds are summarized in Table 1. The S_A–I transition temperatures increase by 30—40 °C/tetrafluoroethylene unit, indicating that the perfluoroalkyl group effectively enhances the thermal stability. On the other hand, the S_B phase is formed by some perfluorooctyl and perfluorodecyl homologs, and the S_B–S_A transition temperature increases 62 °C/tetrafluoroethylene unit for **4C8**, suggesting that the long perfluoroalkyl chain is indispensable for forming the S_B phase. In general, a replacement of the terminal substituent to the lateral position gives rise to a reduction of anisotropy of the polarizability, a change in the molecular geometry, and is very unfavorable for the mesomorphic properties. Certainly, a replacement of the nitro group at the 4 position to the 3 one (**4N8** to **3N8**) reduces the S_A–I transition temperature by 37 °C. Interestingly, the effects of such a substitution on the S_B–S_A (I) transition temperatures are 1 and 17 °C for **N10** and **C10** homologs,

Table 1. Thermodynamic Properties of Compounds

Compounds			Transition temperatures (T/°C)							Latent heats (kJ mol^{-1})		
	n	R	C		S_B		S_A		I	ΔH_{mp}	$\Delta H_{SB-SA(I)}$	ΔH_{SA-I}
4N6	6	4-NO$_2$	·	22	—		·	41	·	13.3		2.1
4N8	8		·	49	—		·	78	·	25.4		3.0
4N10	10		·	82	·	86	·	109	·	16.2	5.1	4.7
3N6	6	3-NO$_2$	·	20	—		—		·	26.5		
3N8	8		·	55	—	(	·	41)	·	34.5		*1
3N10	10		·	69	·	85	—		·	16.1	16.3	
4C6	6	4-CN	·	40	—		·	45	·	17.0		3.4
4C8	8		·	56 (	·	42)	·	81	·	12.1	3.0	4.0
4C10	10		·	83	·	104	·	112	·	12.2	6.7	7.1
3C6	6	3-CN	·	49	—		—		·	38.2		
3C8	8		·	65	—	(	·	42)	·	25.3		*1
3C10	10		·	79	·	87	—		·	16.3	13.8	

C, S_B, S_A, and I indicate crystal, smectic B, smectic A, and isotropic phases, respectively. Parentheses indicate a monotropic transition. *1 The latent heat was not determined because of recrystallization.

respectively. A similar trend was observed for the cyano compounds. The effect of the substitution on the S_A and S_B thermal stabilities might concern molecular arrangements of these phases, as mentioned in a later part. In our earlier paper, we described that for the homologous series of alkyl 4-[2-(perfluorooctyl)ethoxy]benzoates, the methyl homolog has the S_A–I transition temperature at 84 °C.[13] 4-[2-(Perfluoroalkyl)ethoxy]phenols have a similar mesophase thermal stability.[19] Taking these results into consideration, it can be suggested that the terminal nitro and cyano substitutions are one of the important factors, but are not indispensable for displaying the mesomorphic properties.

The structures of the smectic phases were examined by X-ray diffraction, for example, as shown in Fig. 2; the results are summarized in Table 2. As shown in the table, the positions of the d_{001}, d_{002}, and d_{100} reflections are strongly dependent on the perfluoroalkyl chain length and, especially, on the position of the polar substituent. In order to analyze these results, the molecular lengths for the most stable conformation of the compounds under investigation were estimated by molecular-orbital calculations with the AM1 method (MOPAC, Ver. 6.0); the results are also summarized in Table 2. In the calculation, the C–C and C–F bond lengths for the fluoroalkyl chain were 1.610 and 1.368 Å, respectively. The rotational barriers for the $-CF_2-CF_2-$ and $-CH_2-CH_2-$ bonds for the butane skeleton were calculated to be 19.3 and 13.8 kJ mol^{-1}, respectively; thus, the carbon chain of the former is assumed to be more rigid than the latter. The perfluoroalkyl chain has a zigzag conformation with a torsional angle of ca. 13°, due to a steric hindrance between the fluorine atoms, resulting in a helical structure with a pitch of 27 methylene units. It is assumed that the fluoromethylene compounds consist of a racemic mixture of the P and M helices in the solid phase. As shown in the table, the layer spacing for the S_A phase increases by 4.0—4.7 Å/tetrafluoroethylene unit, and those for **4N6**, **4N8**, and **4N10** correspond to 1.72, 1.68, and 1.73 times the calculated molecular lengths, respectively. These results indicate that the S_A phase has a so-called "partially bilayer (S_{Ad})" arrangement. Considering the fact that in many polar liquid crystals the layer spacings of the S_{Ad} phase lie in the range between 1.0 and 1.2 or 1.4 and 1.5 times the molecular length,[15,16] the present values of ca. 1.7 times are rather rare cases. This is probably concerned with the fact that the present compounds have a single benzene ring as the liquid crystalline core, whilst the usual polar liquid crystals consist of a two or a three ring system, so that the overlap of the liquid crystalline core in the S_{Ad} phase for the present compounds is shorter than that for the usual one.

According to these results, the possible model arrangements of the molecules for **4N10** are illustrated in Fig. 3. The overlap of the molecules within the smectic layer for **4N10** was calculated to be 5.9 Å, which is close to the longitudinal length of a nitrobenzene core or a perfluoropentamethylene unit. For the S_A phase, two molecular arrangements (illustrated in models **a** and **b** in Fig. 3) are possible. In model **a**, the aromatic groups involving the nitro group meet around the center of the smectic layer, and are piled up side by side, where the polar interaction of the nitrobenzene moieties and the fluorophilic one around the layer boundary might effectively stabilize the layer structure. In model **b**, on the other hand, the aromatic groups meet around the boundary of the smectic layer, and the terminals of the perfluorooctyl moieties meet around the center of the smectic. In such an arrangement, both the polar interaction around the layer boundary and the fluorophilic one inside of the layer might stabilize the layer structure. In these models, the lateral molecular distance within the layer is 5.4 Å on the

Table 2. X-Ray Results of Compounds

Compounds	X-ray results for d_{001} and d_{002}(up), d_{100} (down), 2θ (Å)					Calcd Mol. length
	S_B		S_A		I	
4N6	·		·	2.94 (30.0) 16.6 (5.3)	·	17.4
4N8	·		·	2.60 (34.0) 16.4 (5.4)	·	20.2
4N10	·	2.06 (42.9),4.14 (21.3) 17.2 (5.2)	·	2.28 (38.7) 16.4 (5.4)	·	22.3
3N8	·		·	3.76 (23.5)[a)]	·	19.9
3N10	·	2.02 (43.7), 4.04 (21.9) 17.4 (5.1)	·		·	22.4
4C6	·		·	2.76 (31.9)[b)]	·	17.8
4C8	·	c)	·	2.48 (35.6)	·	20.4
4C10	·	1.98 (44.1), 4.00 (22.1) 17.2 (5.2)	·	d)	·	23.0
3C10	·	1.90 (44.6), 4.00 (22.1) 17.2 (5.2)	·		·	22.2

The X-ray data were taken at T_{SA-I} −10 °C or $T_{SB-SA(I)}$ −10 °C. a) The X-ray data were obtained at 39 °C. b) The X-ray data were obtained at 40 °C. c) X-ray data were not obtained due to recrystallization. d) The reflection maxima were not evaluated because of the weak intensity.

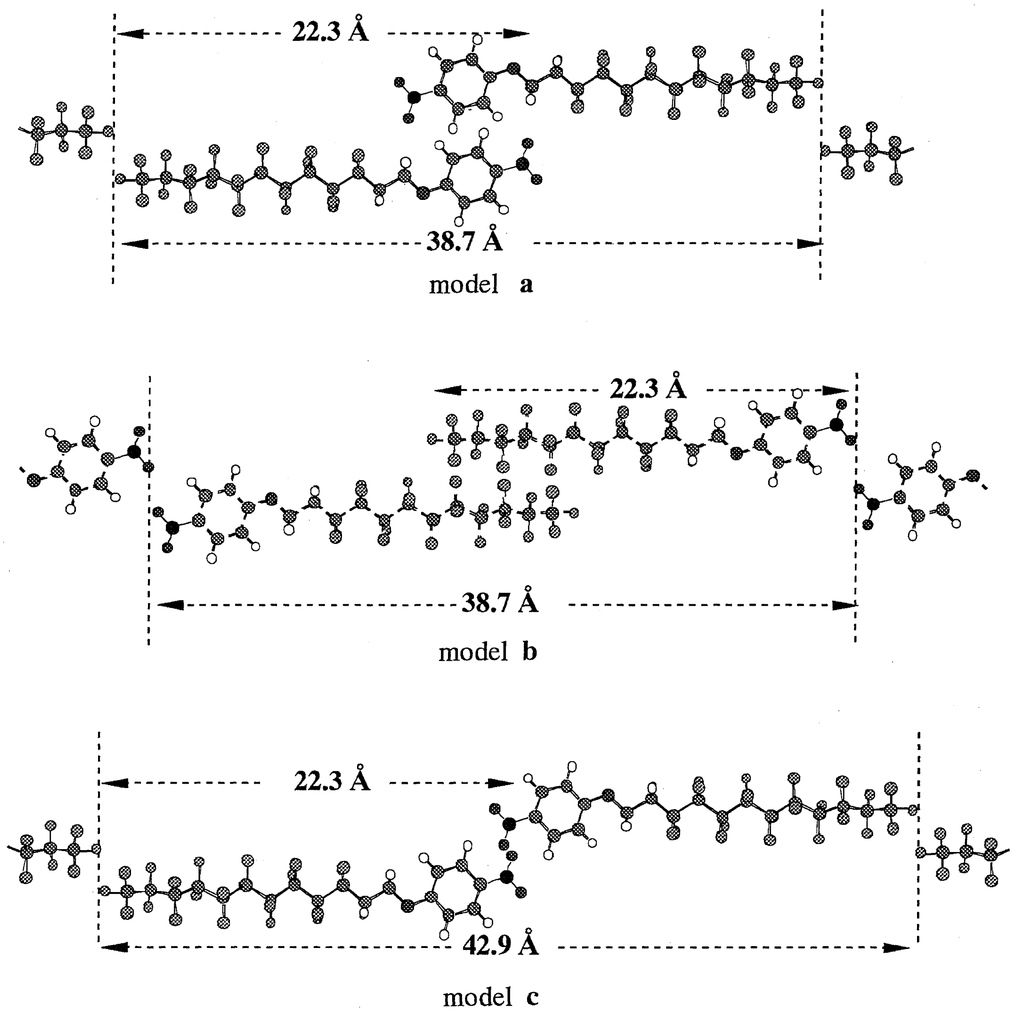


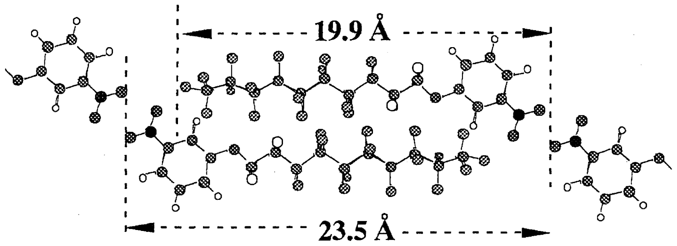
Fig. 3. Possible molecular arrangements for the S_A (models **a** and **b**) and S_B (model **c**) phases of **4N10**.

average. In model **b**, however, there would be no necessity that only the terminal C_5F_{11} moieties of the C_6F_{13} (**4N6**), C_8F_{17} (**4N8**), and $C_{10}F_{21}$ (**4N10**) chains are interdigitated. Therefore, we assume that model **a** is more suitable for the S_A phase, and, in addition, the partially bilayer arrangement might smoothly shift to the bilayer one shown in model **c** with the S_A–S_B transition. The S_A phase of **4N6** and **4N8** are assumed to have a similar molecular arrangement to that of model **a**, where the overlaps of the molecules within the smectic layer are 4.8 and 6.4 Å, which almost agree with the longitudinal length of the nitrobenzene, respectively. The layer spacing of 42.9 Å for the S_B phase of **4N10** is shorter by 1.7 Å than 2 times the calculated molecular length, and the differences almost agrees with the longitudinal length of the nitro group. These facts indicate that the smectic layer is formed by an antiparallel arrangement of two molecules, where only the nitro groups are arranged just like model **c** in Fig. 3. In the model, all molecules are arranged side by side, where the lateral molecular distance within the layer is 5.2 Å on the average, and the strong lateral fluorophilic interaction might facilitate the layer arrangement of the molecules.

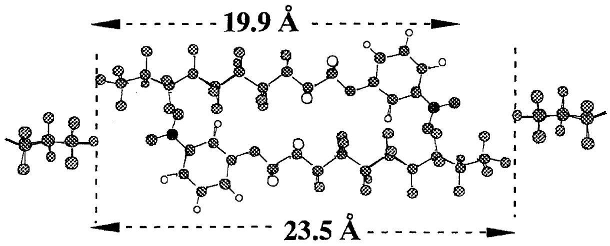
For the **3N*n*** derivatives, **3N8** shows a monotropic S_A phase with a layer spacing of 23.5 Å, which is 1.2 times the calculated molecular length, suggesting that most of the molecules were interdigitated. For the S_A phase, two possible arrangements are illustrated in Fig. 4. In model **d**, the nitrobenzene moieties meet around the layer boundary and have a polar interaction between the interlayer moieties. In model **e**, on the other hand, the nitrobenzene moieties are surrounded by perfluoroalkyl chains, and the polar interactions may be less than those in model **d**. Therefore, model **d** is more reasonable for the molecular arrangement in the S_A phase of the 3-nitro compounds.

3N10 shows only S_B phase with a layer spacing of 1.95 times the calculated molecular length. In the molecular arrangement, only the terminals of the nitrobenzene moiety are supposed to be arranged, as shown in model **f** in Fig. 4. The model structure very much resembles model **c** for **4N10**. As can be seen from Table 1, the S_B–I transition temperatures for **4N10** and **3N10** are quite similar, in spite of the difference in the substitution position. The similar thermodynamic properties must be related to the structural similarity of both S_B phases.

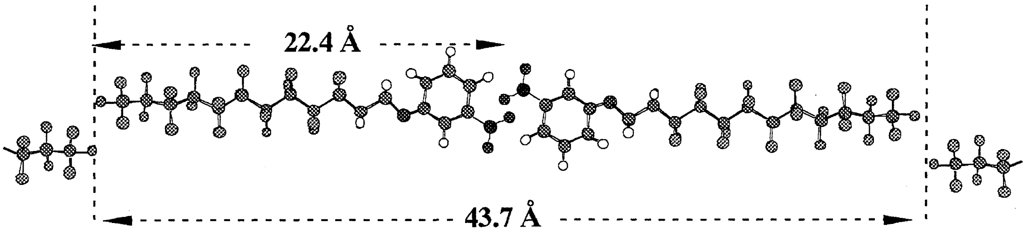
4C6 and **4C8** show the S_A phase with a layer spacing of 1.79 and 1.74 times the calculated molecular lengths. Although the ratios are slightly larger than those for **4N6** and



model **d**



model **e**



model **f**

Fig. 4. Possible molecular arrangements for the S_A phase of **3N8** (models **d** and **e**) and the S_B phase of **3N10** (model **f**).

4N8, the molecular arrangement of the S_A phase should be fundamentally similar to model **a** in Fig. 3. The reflection intensity for the S_A phase of **4C10** was so weak that the reflection maximum could not be evaluated, while intense reflection could be observed in the S_B phase.

The S_B phase for **4C10** has a layer structure of the spacing of 1.92 times the calculated molecular lengths. Therefore, the S_B phase is assumed to have the layer structure of model **f**, similar to **4N10**. Although in the cyano series the ratios of the layer spacing to the molecular length are slightly different from those for the nitro series, the molecular arrangement in the S_B phase should be fundamentally similar to model **c** in Fig. 4, where the interlayer polar interaction around the terminal position facilitates the bilayer arrangement.

Conclusion

In our earlier paper, we described that in alkyl 4-(2-perfluoroalkylethoxy)benzoate system the S_A thermal stability and the layer structure are determined by the subtle counterbalance between the fluorophilic and fluorophobic interactions around the alkyl and perfluoroalkyl groups.[14] In the present polar system, the fluorophilic interaction around the perfluoroalkyl groups is responsible for the enhanced thermal stabilities of the S_A and S_B phases, and the attractive polar interaction around the nitro or the cyano groups plays a very important role in determining the molecular arrangements within these phases.

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