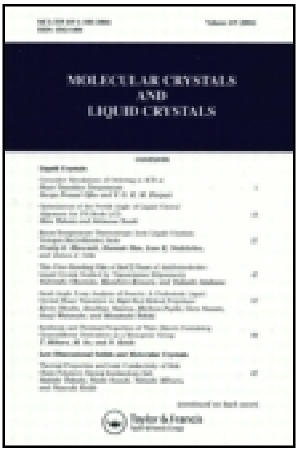

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Thermal and X-Ray Diffraction Studies of Liquid Crystals Incorporating a Perfluoroalkyl Group

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Thermal and X-Ray Diffraction Studies of Liquid Crystals Incorporating a Perfluoroalkyl Group

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Thermal properties of some liquid crystals incorporating a perfluoroalkyl group have been examined. The perfluoroalkyl group tends to enhance the smectic properties. The layer spacing in the smectic A and C phases was examined by X-ray diffraction, showing that the ratio of the layer spacing to the calculated molecular length is dependent on the entirety of molecular structures rather than the length of the perfluoroalkyl chain, and is in the range between 1.0 and 1.4. Novel perfluoroalkyl 3- or 4-substituted benzenes exhibiting smectic A phase were also prepared.

Keywords: smectic, x-ray studies, perfluoroalkyl group

INTRODUCTION

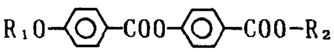
In this paper, we describe the thermal properties of some liquid crystals having a perfluoroalkyl group at the terminal position, as shown below, and the effect of the perfluoroalkyl group on mesomorphic properties has been discussed.

For compounds 1 and 2 the layer spacings of smectic A and C phases are also examined by X-ray diffraction. The effect of the perfluoroalkyl group on the mesomorphic properties is discussed.

EXPERIMENTAL

Preparation and methods have been already reported elsewhere.[1,2]

Compound



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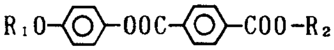

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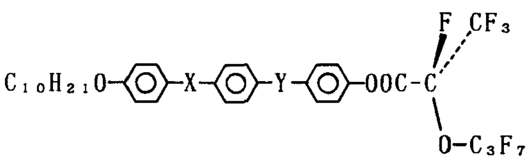
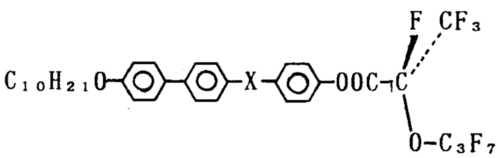


3 (X = -COO-, Y = -COO-)

4 (X = -OOC-, Y = -OOC-)

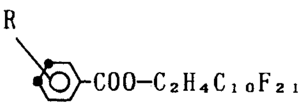
5 (X = -COO-, Y = -OOC-)

6 (X = -OOC-, Y = -COO-)



7 (X = -COO-)

8 (X = -OOC-)



9

RESULTS

Thermal Properties

Transition temperatures for compounds 1–9 are summarized in Tables I–IV, respectively.

X-ray Diffraction Study

The molecular arrangements in S_A and S_C phases were examined by X-ray diffraction.[2] The layer spacings for some derivatives of compounds 1 and 2 were obtained from the X-ray diffraction, and the results are summarized in Table V.

DISCUSSION

An introduction of a perfluoroalkyl group is known to enhance smectic properties of molecule, and increases the S_A-I transition temperature.[3,4] A similar trend can be recognized in the present compounds. For compound 1 the hydrogen derivatives (1′a and 1′b) show only S_A phase. The perfluoro derivatives (1a–1j) also show the S_A phase, where the S_A–I transition temperatures are higher than those of 1′a and 1′b. The S_C phase is also formed when the alkoxy group (R_1) is long. Compound 2 shows a similar trend, but the S_C phase is not formed even in the higher members.

TABLE I

Transition temperatures (T/°C) and latent heats (kJ/mol) for compound 1

Compounds	R_1	R_2	C		S_C (S_C^*)		S_A		I	ΔH_{SC-SA}	ΔH_{SA-I}
1a	C_4H_9	$CH_2C_6F_{13}$	.	81	-		.	147	.	-	7.4
1b		$C_2H_4C_4F_9$	.	94	-		.	133	.	-	4.8
1c		$C_2H_4C_6F_{13}$	.	104	-		.	151	.	-	7.7
1d		$C_2H_4C_8F_{17}$	.	117	-		.	168	.	-	9.1
1e		$C_2H_4C_{10}F_{21}$	.	130	-		.	175	.	-	10.7
1f	C_8H_{17}	$CH_2C_6F_{13}$	.	71	.	107	.	120	.	0.2	8.5
1g		$C_2H_4C_4F_9$	.	71	.	109	.	111	.	0.25	6.4
1h		$C_2H_4C_6F_{13}$	.	88	.	122	.	129	.	0.2	8.2
1i		$C_2H_4C_8F_{17}$	.	101	.	131	.	145	.	0.2	8.5
1j		$C_2H_4C_{10}F_{21}$	.	109	.	136	.	158	.	0.2	7.9
1k	$C_2H_5CH(CH_3)$ *1	$C_2H_4C_4F_9$	.	85	-		-		.		
1l	$C_2H_5CH(CH_3)C_3H_6$ *1	$C_2H_4C_8F_{17}$	.	105	(.	104)	.	136	.	0.2	6.8
1'a	C_8H_{17}	C_6H_{13}	.	51	-		.	69	.	-	6.3
1'b		$C_{10}H_{21}$	.	54	-		.	67	.	-	8.6

*1 S-configuration.
Parentheses indicate a monotropic transition.

TABLE II

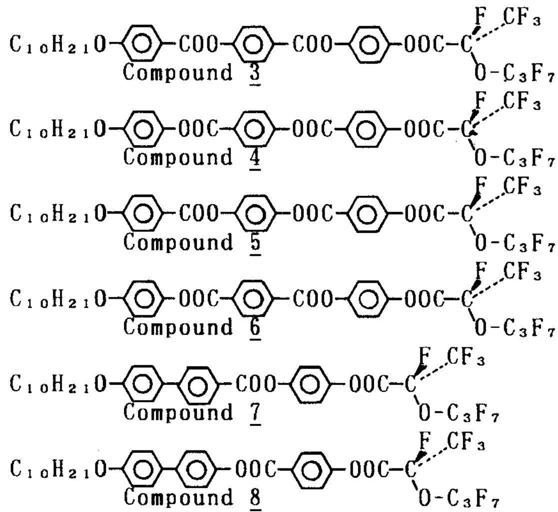
Transition temperatures (T/°C) and latent heats (kJ/mol) for compound 2

Compounds	R_1	R_2	C		S_A		I	ΔH_{SA-I}
2a	CH_3	$C_2H_4C_4F_9$	.	75	.	106	.	6.5
2b	C_2H_5	$C_2H_4C_4F_9$	.	84	.	117	.	6.4
2c	C_4H_9	$C_2H_4C_4F_9$	.	78	.	107	.	5.3
2d	C_8H_{17}	$C_2H_4C_4F_9$	.	87	.	96	.	6.9
2e		$C_2H_4C_6F_{13}$	.	98	.	118	.	6.8
2f		$C_2H_4C_8F_{17}$	.	116	.	136	.	8.0
2g		$C_2H_4C_{10}F_{21}$	.	128	.	149	.	8.0
2h	$C_2H_5CH(CH_3)$	$C_2H_4C_6F_{13}$	.	97	.	97	.	-
2i	$C_2H_5CH(CH_3)C_3H_6$	$C_2H_4C_8F_{17}$	.	112	.	119	.	6.6
2'a	C_8H_{17}	C_6H_{13}	.	57	-		.	-

In Table V, the molecular lengths were estimated from the molecular models where conformation around the ester, ether, and alkyl chains was supposed to be trans.[1] The layer spacing in the S_A phase of compound 1e is larger than the calculated molecular length, while that of 1i agrees with the calculated value. Furthermore, the layer spacings in the S_A and S_C phase of 1l are also larger than the calculated molecular lengths. These facts indicate that the feature of the alkyl group (R_1) is very important in determining the molecular arrangement in the smectic phases. On the other hand, the layer spacing of the S_A phase of compound 2f is apparently larger than the molecular length, though R_1 is long.

TABLE III

Transition temperatures (T/°C) and latent heats (kJ/mol) for compounds 3–8



Compound		
Compound 3	mp. 94 °C	Non-mesogenic
Compound 4	mp. 96 °C	Non-mesogenic
Compound 5	mp. 153°C	Non-mesogenic
Compound 6	mp. 94 °C	Non-mesogenic
Compound 7	mp. 90 °C	Non-mesogenic
Compound 8	mp. 93 °C	Non-mesogenic

TABLE IV

Transition temperatures (T/°C) and latent heats (kJ/mol) for compound 9

Compounds	R	C		S_A		I	ΔH_{mp}	ΔH_{SA-I}
9a	p-CH_3	.	66	-		.	34.7	-
9b	F	.	74	[.	30]	.	37.1	-
9c	CF_3	.	62	(.	41)	.	33.1	*1
9d	CN	.	118	-		.	35.6	-
9e	$C_{10}H_{21}O$	.	77	-		.	55.7	-
9f	m-CH_3	.	60	-		.	15.4	-
9g	F	.	63	-		.	19.4	-
9h	CN	.	77	.	90	.	17.3	18.9
9i	NO_2	.	62	.	92	.	17.9	18.9

*1 The transition was impossible to detect by DSC because of recrystallization.
Parentheses indicate a monotropic transition. Brackets indicate a virtual transition, and the temperature was extrapolated from the binary phase diagram for the mixture of 9b and 1f.

These results suggest that the molecular arrangement in S_A phase is determined by the entirety of the molecular structure rather than "fluorophobic" interaction,[5,6] since the perfluoroalkyl group is harder and more linear than the corresponding alkyl one.[7] An interesting fact is that the S_C phase of compound 1i has the same layer spacing as that of the S_A one, while the tilt angle calculated from the Laue picture is 15°. A possible explanation is that in the S_A phase the rotational axis of the aromatic portion is orthogonal to the layer, while the average rotational axis of the aromatic and the hard perfluoroalkyl portions is orthogonal to the layer.

Compounds 3–8 have a chiral long chain. Interestingly, these compounds do not

TABLE V

Layer spacing and molecular length of compounds

Compounds	R_1	R_2	Molecular length (M) *1 (Å)	Layer spacing (L) (Å)	L/M	Temperature (°C)	Phase
1i	C_8H_{17}	$C_2H_4C_8F_{17}$	37.5	38.1	1.01	80	S_C
				37.8	1.01	90	S_C
				37.5	1.00	100	S_C
				38.3	1.02	105	S_C
				37.7	1.00	120	S_C
				38.0	1.01	125	S_C
				37.4	1.00	137	S_A
1e	C_4H_9	$C_2H_4C_{10}F_{21}$	34.4	42.4	1.23	140	S_A
				41.5	1.20	150	S_A
2f	C_8H_{17}	$C_2H_4C_8F_{17}$	38.1	41.8	1.10	110	S_A
				42.0	1.10	125	S_A
11	$C_2H_5CH(CH_3)C_3H_6$	$C_2H_4C_8F_{17}$	34.9	43.5	1.25	95	S_C^*
				47.7	1.37	120	S_A

*1 See text.

show any mesophase, while these would have long molecular structures. A possible reason is that the heptafluoropropyl group extends to the lateral direction due to steric hindrance between trifluoromethyl and heptafluoropropyl groups.

Based on the results in Tables I and II, we prepared mono-benzene ring compounds having a perfluoroalkyl chain, and transition temperatures are summarized in Table IV. Only trifluoromethyl derivative 9c in para-substituted benzenes shows a monotropic S_A phase. Although the fluoro derivative (9b) is non-mesogenic, the virtual S_A-N transition temperature is not so low. The virtual transition temperature for 9a was too low to estimate.

In meta-substituted benzenes, compounds 9h and 9i show the S_A phase. These S_A phases are miscible with the S_A phase of compound 1, where the S_A-I transition temperature shows a linear correlation against the molar concentration of each component.

For the effect of the substituent at para-position on the mesomorphic properties we can assume that the electron-withdrawing nature of fluorine atom and the trifluoromethyl group reduces the dipole moment of the ester group.[8]

CONCLUSION

A perfluoroalkyl group facilitates the layer arrangement of molecules, and enhances the S_A-I transition temperature. The rigidity of the perfluoroalkyl group is assumed to be more important than the fluorophobic interaction for the enhancement of the smectic properties. The molecular arrangements in the S_A and S_C phases are determined by the entirety of the molecular structure.

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