Thermal Properties of Novel Liquid Crystals having a Single Benzene Unit

Shunsuke Takenaka

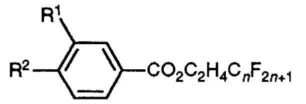
Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai 2557, Ube, Yamaguchi 755, Japan

Some derivatives of 2-(n-perfluoroalkyl)ethyl 3- and/or 4-substituted-benzoates show smectic phases having an orthogonal nature; the substituent at position 3 is indispensable for them to display liquid crystalline properties.

The development of liquid crystals having a single benzene ring as the liquid crystal core is of importance and current interest. Single-benzene ring compounds would be expected to have low molecular anisotropy and would not readily display liquid crystalline properties, with the exception of special examples such as 4-substituted benzoic acids,[1] and benzene hexaalkanoates.[2] We have already reported that a perfluoroalkyl group tends to enhance the thermal stability of smectic A and C phases owing to the increased rigidity around the perfluoroalkyl moiety and the fluorophobic effect.[3]

We now describe the mesomorphic properties of 2-(n-perfluoroalkyl)ethyl 3- and/or 4-substituted benzoates, in which the liquid crystal core[2] consists of a single benzene ring.

Table 1 Transition temperatures for substituted benzenes **1–18**



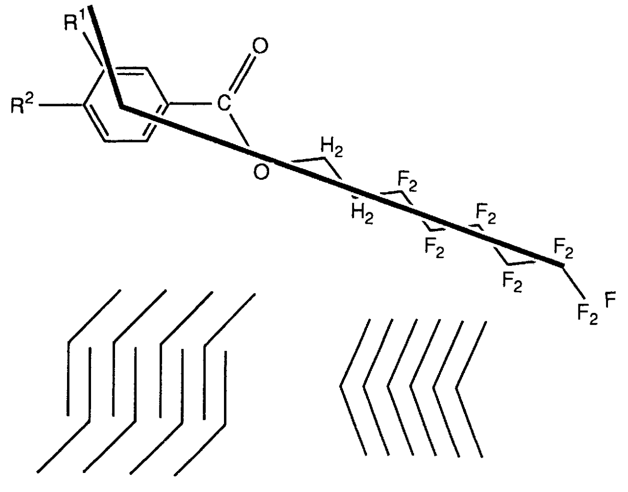
				Transition temperatures (*T*/°C)						
	R^1	R^2	*n*	C		S		S_A		I
1	H	OMe	10	·	66	—		—		·
2	H	$C_{10}H_{21}O$	10	·	77	—		—		·
3	H	F	10	·	74	—		—		·
4	H	CN	10	·	118	—		—		·
5	H	CF_3	10	·	60	—		—		·
6	NO_2	H	10	·	62	·	92	—		·
7	CN	H	10	·	77	·	90	—		·
8	Me	H	10	·	60	(·	54)	—		·
9	F	H	10	·	63	(·	60)	—		·
10	H	CN	8	·	98	—		—		·
11	H	C_4H_9	8	·	32	—		—		·
12	NO_2	H	8	·	65	(·	44	·	53)	·
13	CN	H	8	·	70	(·	41	·	48)	·
14	F	H	8	·	27	(·	3	·	7)	·
15	NO_2	OC_6H_{13}	8	·	44	(·	49	·	51)	·
16	Br	OC_6H_{13}	8	·	[a]	(·	30	·	30)	·
17	NO_2	H	6	·	44	—		(·	2)	·
18	CN	H	6	·	19	—		(·	−6)	·

[a] The crystalline phase could not be obtained. Parentheses indicate a monotropic transition.

The transition temperatures for compounds **1–18** are summarized in Table 1. The *para*-substituted esters **1–5** with $n = 10$ have high m.p.s and do not show any mesophase even in the monotropic process. The *meta*-substituted derivatives **6** and **7** show enantiotropically a smectic phase with a fan or a mosaic texture. A similar phase transition is observed monotropically in the methyl and fluoro compounds **8** and **9**. The latent heats for the smectic–isotropic transition are *ca.* 15 mJ mg^{-1}, indicating that the smectic phase has a high order of molecular arrangement. The formation of a liquid crystalline phase is more apparent in the *meta*-substituted compounds with $n = 8$. The nitro, cyano and fluoro compounds **12–14** show two kinds of smectic phase. That in the high temperature region has a fan texture, and is miscible with the smectic A phase of perfluoroalkoxybenzoyl 4-alkoxybenzoates.[3] The other smectic phase in the low temperature region shows a fan or a mosaic texture with an orthogonal nature. Interestingly a long alkoxy group at position 4 appears to be fundamentally irrelevant for mesomorphic properties (compounds **15** and **16**). Compounds **10** and **11** having a substituent at position 4 and with $n = 8$ show no mesophase even in the cooling stage, while their melting points are not high. Although the cyano **17** and nitro **18** compounds with $n = 6$ also show one smectic phase on the cooling stage of the isotropic solution, the smectic–isotropic transition temperatures are low.

These results indicate that in order to show smectic phases in the present system, the molecules must have a long perfluoroalkyl group; a lateral substituent is indispensable and a dipole within the substituent is desirable.

It is known that perfluoroalkyl groups are more rigid and more linear than the corresponding alkyl group owing to steric hindrance between the fluorine atoms.[4] We can conclude that the rigidity and linearity associated with the perfluoroalkyl group is of primary importance for the formation of the smectic phases. In this connection, a tetrafluoroethylene group increases the clearing point by *ca.* 40–50 °C. As Table 1 shows, compounds having no lateral substituent do not show any smectic phases, and, interestingly, a long alkoxy group at position 4 is not crucial for mesomorphic properties. These results indicate that the substituent at position 3 rather than 4 plays an important role for compounds to display smectic phases. The lateral substituent apparently reduces the linear-



(*A*) (*B*)

Fig. 1 Structure of the liquid crystalline materials prepared

ity of the whole molecule. As is evident from Fig. 1, the molecules have a bent structure. In an earlier paper, we emphasized that a bent structure is preferable for a layered arrangement of molecules, owing to the packing effect of the molecules (*e.g.* Fig. 1, *A* and/or *B*).[5] In the present system, the closed packing should also allow the formation of smectic phases, although the bent structure may be very unfavourable for the formation of the nematic phase. In fact, the present compounds and related ones are very poor in nematic properties.[6]

Received, 25th August 1992; Com. 2/04579F

References

1 D. Demus and H. Demus, *Flüssig Kristalle in Tabellen*, VEB Deutscher Verlag für Grundstoff Industrie, Leipzig, 1974.

2 S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, 1977, **9**, 471.

3 T. Doi, Y. Sakurai, A. Tamatani, S. Takenaka, S. Kusabayashi, Y. Nishihata and H. Terauchi, *J. Mater. Chem.*, 1991, **1**, 169.

4 M. Koden, T. Kuratate, T. Shinomiya, K. Nakagawa and F. Funada, personal communication.

5 Y. Sakurai, S. Takenaka, H. Miyake, H. Morita and T. Ikemoto, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1199.

6 S. Takenaka, to be published.