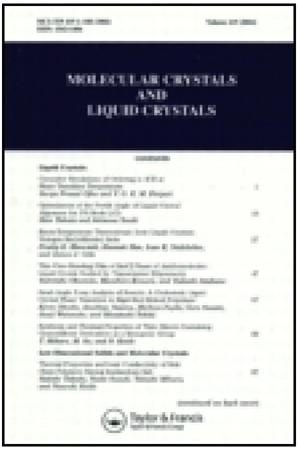

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

X-ray diffraction study of some liquid crystalline 2,5-disubstituted 1, 3, 2-dioxaborinane derivatives

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X-ray diffraction study of some liquid crystalline 2,5-disubstituted 1,3,2-dioxaborinane derivatives

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X-ray diffraction study of some liquid crystalline 2,5-disubstituted 1,3,2-dioxaborinane derivatives reveals the existence of a partially bilayered smectic Ad phase in the terminally CF_3 and OCF_3 substituted derivatives, with the higher level of molecular overlapping in the formation of the dimer observed for the latter compound; and the dimeric density wave fluctuations in the nematic phase of CN substituted derivative.

Keywords: X-ray diffraction; 1,3,2-dioxaborinane; terminal substitution

1. INTRODUCTION

It has been shown that the terminal substitution of liquid crystals strongly affects their mesomorphic and physical properties in the different degrees depending on the nature of terminal substituents.[1–8] As the mesophase stability is influenced by molecular packing[9], the investigation of intermolecular interactions, association phenomena, dipole-dipole correlations affecting the molecular packing could lead to a better understanding of liquid crystal properties. It has been demonstrated that X-ray diffraction of the mesophases is one of the useful methods to study the association phenomena in the liquid crystals.[3,4,10–18] It is well-known that the terminally substituted liquid crystalline cyano and nitro derivatives may exhibit a number of lamellar packings.[11–13, 15–21] Apart from the ordinary smec-

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tic A_1 phase with a period, d, approximately equal to the molecular length, L, there are bilayered smectics A_2 with the period $d \approx 2L$ and intermediate (partially bilayered) smectics A_d having the period d which is $L < d < 2L$. These phenomena are due to the specific nature of intermolecular interactions in polar liquid crystals, resulting in various effects of molecular association. Anti-parallel correlations between permanent and induced molecular dipoles influence the subtle balance between the attractive dispersion forces and the repulsive steric ones, and give rise to the structural packing of the S_{A1}, S_{A2} or S_{Ad} types. [22]

In the nematic phase small-angle X-ray scattering is concentrated near vectors $q_i = 2\pi / d_i$ in reciprocal space. Here d_i is the length of the structural unit of the medium which may often be referred to as a molecular associate (dimer). [12,14,23–26]

The intensity of X-ray scattering from the nematic phase includes two additional contributions against the isotropic background. The first, pure nematic, results from the orientational correlations of the long molecular axes, the second is due to the scattering by smectic fluctuations in the nematic phase. The latter contribution to intensity increases sufficiently near the transition into the smectic A phase. Indeed, a variety of smectic phases influences the fluctuational behaviour in the nematic phase. It means that X-ray diffraction allows the nucleation of different smectic phases in the nematic phase to be studied at the level of fluctuations, revealing for some cyano derivatives the simultaneous existence of two fluctuation-layer structures with incommensurate periods d_1 and d_2, where $d_1 < L$ and $L < d_2 < 2L$.[12, 14, 15] The detailed theoretical description of X-ray scattering from nematic liquid crystals is presented in reference 12.

The present boom in the development of liquid crystal displays for multimedia is closely connected with the progress made in the synthesis of liquid crystals with fluorinated terminal substituents (F, CF_3, OCF_3, etc.).[5–8, 18, 27]

Recent X-ray diffraction studies of some two-ring liquid crystalline derivatives have revealed that in contrast to the corresponding CN derivatives, terminally CF_3 and OCF_3 substituted compounds form only a monolayer smectic A_1 phase[18,28] which may be caused by purely steric factors.[18] While increasing the length of the perfluorinated chain and / or molecular core may lead to the formation of the Ad phase depending on its length and its molecular core structure.[3,4,18, 29–31]

Here we present the results of X-ray diffraction study of some terminally CN, $OCF_3$and CF_3 substituted liquid crystalline 1,3,2-dioxaborinane-2,5-diy derivatives. The experimental results will be discussed in terms of influence of terminal substitution of liquid crystals on the structure of their mesophases The synthesis, mesomorphic, physical and electro-optical properties of these compounds have been reported earlier.[6,8]

2. EXPERIMENTAL TECHNIQUE

X-ray diffraction experiments were performed with a Rigaku-Denki RINT 2200 diffractometer, fitted with a Rigaku PTC-20A thermal controller, where CuKα ($\lambda = 1.540$ Å) was used as the X-ray source. The reflection angle was calibrated by the examination of both left and right angles. Samples filled in the quartz capillaries (d = 1 mm) were oriented by a constant magnetic field (480 G). The samples were placed along the goniometer axis so that the counter movement in the recording plane allowed us to scan the nematic and smectic A reciprocal lattice mode along q ($q = 2\pi /d$ is the reciprocal space vector), i.e. in the direction parallel to the director **n**.

3. EXPERIMENTAL RESULTS AND INTERPRETATION

The phase transition temperatures and enthalpies of compounds **1–4**[6,8]; their molecular lengths L calculated by MOPAC AM1 method[33]; the layer spacing of the smectic A phase and a period of the fluctuation density wave d in the nematic phase obtained from X-ray diffraction profiles; the intensity of X-ray scattering I and corresponding correlation length ζ {calculated from the angular width of the intensity profile at half-height $\Delta(2\Theta)$[12]}; and the ratios d / L are presented in table I. The values of ratios d / L >1 indicate the formation of a partially bilayered smectic A phase – A_d in compounds **1, 2, 4** and the existence of the fluctuation dimeric density wave in the nematic phase of compound **3**.

Based on these results, the antiparallel molecular arrangements supported by the theoretical models[18] can be proposed for these liquid crystals.

The presence of the 1,3,2-dioxaborinane-2,5-diyl fragment with its electron-deficient boron atoms having vacant p-orbitals may affect the intra- and intermolecular interactions between the p-orbitals and aromatic π–electron systems[34] in compounds **1–4**, leading to their molecular arrangenents and results in the lower value of ratio d / L recorded for compound **3** in comparison with that of other liquid crystalline three-ring cyano derivatives.[15]

The similar antiparallel molecular arrangement was proposed for another liquid crystalline 2,5-disubstituted 1,3,2-dioxaborinane derivative: 2-(4-cyanophenyl)-5-(4-butylphenyl)-1,3,2-dioxaborinane.[35]

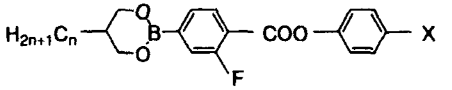
It is convenient to express the influence of terminal substitution x of the system (I) on their ratio d / L and correlation length ζ by the following orders (table I) :

$$n=5$$

$$d/L \rightarrow X:\ OCF_3 < CF_3 \tag{1}$$

$$\zeta \rightarrow X:\ CF_3 < OCF_3 \tag{2}$$

TABLE I Physico-chemical properties of some liquid crystals:



(I)

No.	*n*	*X*	*Phase transitions, °C (Phase transition enthalpies, cal mol^{-1})*	*Abbrev.*	*L, Å*	*d^a, Å*	*d/L*	*I^a, count*	*ζ^a Å*
1	5	CF_3	Cr 74.4 (4540) S_{Ad} 102.8 (440) I	$C_5BF\text{-}CF_3$	22.49	24.80	1.103	216	865
2	5	OCF_3	Cr 48.4 (7410) S_{Ad} 111 (510) N 113.9 (385) I	$C_5BF\text{-}OCF_3$	23.62	25.08	1.062	690	1220
3	5	CN	Cr 94 N 167 I	$C_5BF\text{-}CN$	22.84	23.73^b	1.039	70^b	26^b
4	3	OCF_3	Cr 68.8 (4370) S_{Ad} 77.5 (40) N 108.4 (150) I	$C_3BF\text{-}OCF_3$	21.24	22.87^c	1.077	140^c	320^c

a. $T_{meas} = T_{cl} - 20$ °C
b. $T_{meas} = T_{cl} - 50$ °C
c. $T_{meas} = T_{cl} - 31.4$ °C

These results and the data presented in table I reveal that terminal OCF_3 substitution of the system (I) gives the liquid crystals exhibiting the smectic Ad phase with lower ratio d /L (higher level of molecular overlapping in the formation of the dimer) and higher correlation length in comparison with those of the corresponding CF_3 substituted derivative, while decreasing the alkyl chain length of the OCF_3 substituted derivative from pentyl group to propyl group (compounds **2** and **4**, table I) results in increasing the ratio d/L (decreasing the level of molecular overlapping in the formation of the dimer).

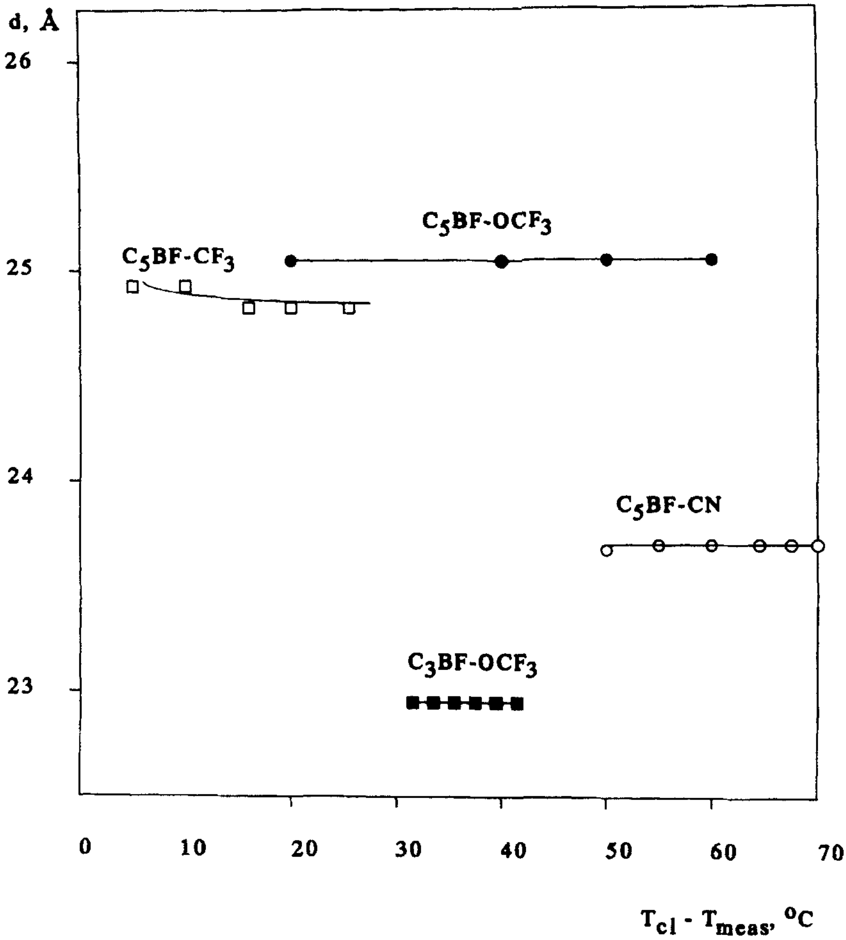


FIGURE 1 Temperature dependences of the layer spacing d for C_5BF-OCF_3(●), C_5BF-CF_3 (☐), C_3BF-OCF_3 (■), and the period d of the fluctuation density wave for C_5BF-CN (○). The lines are guides for the eye

As can be seen from table I, the terminal CN substitution of the system (I) produces the liquid crystals exhibiting only nematic phase (compound **3**) with the lowest values of the intensity of X-ray scattering and correlation length (as expected).

The temperature dependences of the layer spacing d in the smectic A phases of compounds **1**, **2**, **4**; and of the period of the fluctuation density wave for compound **3** are shown in figure 1. For the OCF_3 substituted derivatives (compounds **2**, **4**) and CN substituted compound **3** d is almost independent of the temperature, while for the CF_3 substituted derivative (compound **1**) d slightly decreases with decreasing the temperature. This difference in the temperature behaviour of the layer spacing of compounds **1** and **2** is probably due to the different role of molecular dimers in the formation of layers.[12]

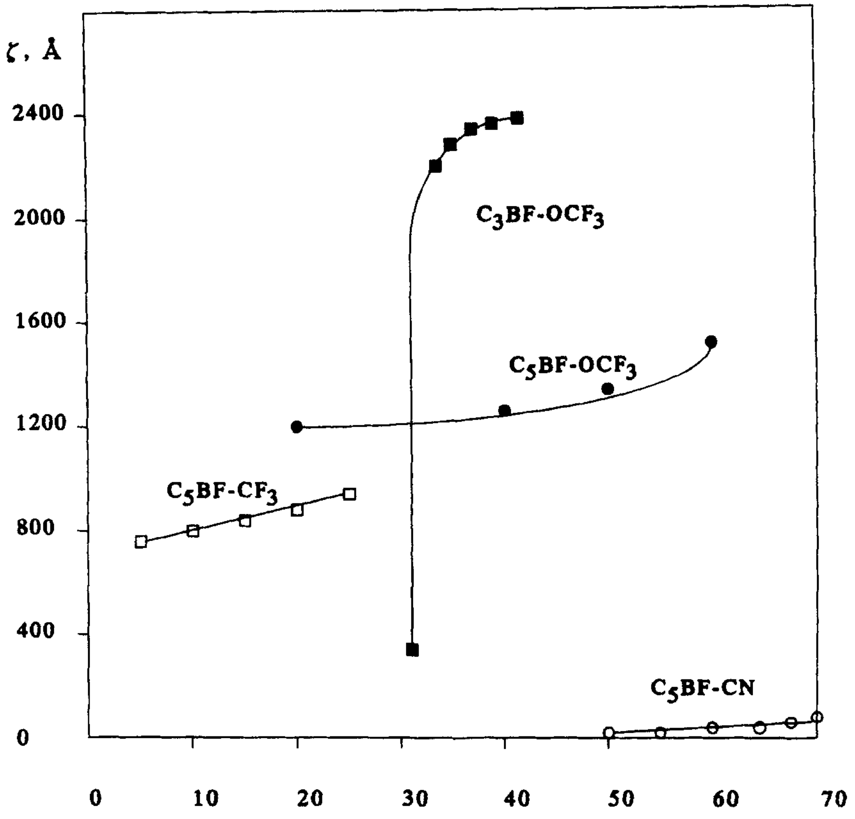


FIGURE 2 Temperature dependences of the correlation length ζ for $C_5BF\text{-}OCF_3$ (●), $C_5BF\text{-}CF_3$ (□), $C_3BF\text{-}OCF_3$ (■) and $C_5BF\text{-}CN$ (○). The lines are guides for the eye

The temperature dependences of the correlation length for compounds **1–4** presented in figure 2 show the usual increasing behaviour with decreasing the temperature, with the highest rate and value recorded for compound **4** in the smectic A phase and lowest value observed for nematic compound **3** (as expected). The different rates of increasing the correlation length observed for compounds **2** and **4** reveal the influence of the alkyl chain flexibility in the stabilization of the smectic A phase.[36]

The presented results of X-ray diffraction of some liquid crystalline 2,5-disubstituted 1,3,2-dioxaborinane derivatives show the strong effect of the structure of their terminal substituents of on the structure of their mesophases. The similar resuts have been found for other liquid crystalline derivatives.[3, 4, 14, 16–18, 28–31]

4. CONCLUSION

The results of X-ray diffraction study of some liquid crystalline 2,5-disubstituted 1,3,2-dioxaborinane derivatives reveal the strong influence of their terminal substitution on the structure of their mesophases resulting in the formation of a partially bilayered smectic Ad phase in the terminally CF_3 and OCF_3 substituted derivatives, with the lower level of molecular overlapping in the formation of the dimer recorded for the former compound; and the dimeric density wave fluctuations in the nematic phase of CN substituted derivative.

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