Synthesis and Thermal Properties of New Ferroelectric Liquid Crystalline Materials containing Boron Atoms

K. Seto,[a] H. Matsubara,[a] S. Takahashi,*[a] T. Tahara,[b] M. Murakami[c], S. Miyake,[c] T. Masumi,[c] T. Ando,[c] and A. Fukami[c]

[a] *The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan*
[b] *Research & Development Division, Nitto Kasei Co., Ltd., 3 Nishiawaji, Higashiyodogawa, Osaka 533, Japan*
[c] *Materials and Electronic Devices Lab., Mitsubishi Electric Corp., Amagasaki, Hyogo 661, Japan*

Chiral dioxaborinane derivatives form chiral smectic C phases which exhibit ferroelectric properties with large spontaneous polarizations.

Recent research interest in functional materials has been focused on ferroelectric liquid crystals.[1] We reported previously[2] that dioxaborinane derivatives are new liquid crystalline materials which give wide nematic ranges. Here we report that compounds (**1**) and (**2**), which contain boron atoms, form a chiral smectic C phase exhibiting ferroelectric properties; we describe the syntheses of the new compounds as well as their thermal properties.

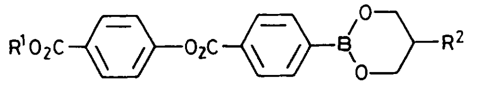
Thus, 4-carboxyphenylboronic acid was condensed with 2-dodecylpropane-1,3-diol to form the dioxaborinane derivatives (**5**). The preliminary *X*-ray structural analysis[3] of an analogous compound, 2-(4-cyanophenyl)-5-(4-butylphenyl)-1,3-dioxaborinane, revealed a three-co-ordinate planar geometry around the boron atom, indicating that no geometrical isomers exist. However heterocyclic derivatives of 1,3-dioxane and 1,3-dithiane, both common structures in liquid crystalline materials, have *cis* and *trans* isomers at the C-2 position.[4]

Compound (**5**) was treated with (*R*)-1-methylheptyl 4-hydroxybenzoate ([α] −30.7°) to give (**1a**) {$R^1 = C_6H_{13}$

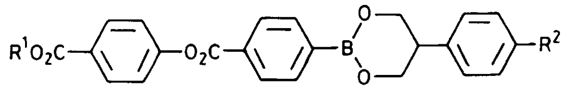
Table 1. Phase transition temperatures (T/°C)[a,b] of compounds (**1**) and (**2**).

	R^1	R^2	$T(C—S_1)$	$T[C—S(C^*)]$	$T[S_1—S(C^*)]$	$T[S(C^*)—S_A]$	$T(S_A—I)$
(**1a**)	(R)-$C_6H_{13}CH(Me)$	n-$C_{12}H_{25}$		55		65	76
(**1b**)	(S)-$C_2H_5CH(Me)CH_2$	n-C_8H_{17}		56		59	116
(**1c**)	(S)-$C_2H_5CH(Me)CH_2$	n-$C_{12}H_{25}$		69		85	114
(**2a**)	(R)-$C_6H_{13}CH(Me)$	n-$C_8H_{17}O$	97		140	164	193
(**2b**)	(R)-$C_6H_{13}CH(Me)$	n-$C_{12}H_{25}O$	85		114	163	174
(**2c**)	(S)-$C_2H_5CH(Me)(CH_2)_4$	n-$C_{12}H_{25}O$	55		116	180	199

[a] Measured with a Metler Thermal Microscope FP5 + FP52. [b] C = crystal, S(C*) = chiral smectic C, S_A = smectic A, I = isotropic; the phase S_1 not been identified yet.



(**1**)

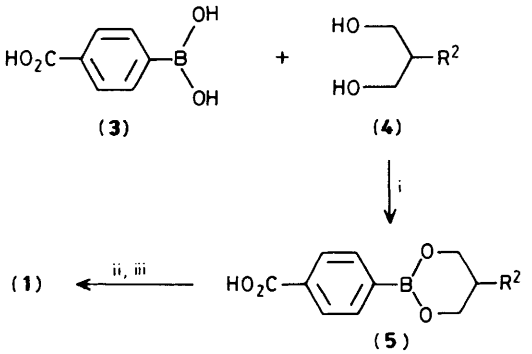


(**2**)

(Me)CH; R^2 = n-$C_{12}H_{25}$, [α] −19.1°} in 70% yield based on (**3**). Similarly, (**2**) was synthesized using aryl-substituted propane-1,3-diols instead of (**3**).

Various derivatives of (**1**) and (**2**), having different tail groups, were synthesized by similar methods. They were obtained as colourless crystals in good yields and characterized by spectral methods including m.s., i.r., and n.m.r. The thermal properties of (**1**) and (**2**) were examined visually with an optical microscope and the results are summarized in Table 1.

The results show that the four-ring systems, (**2a**—**c**), formed more stable smectic C phases than the three-ring (**1**) and in the same series the longer tail groups stabilized the phase as is usual for liquid crystals. It should be noted that (**1**) and (**2**) exhibited ferroelectric properties, and in particular (**1a**) and (**2b**) showed very large spontaneous polarizations of 48 and 100 nC cm^{-2} respectively. In recent years some liquid crystalline materials incorporating metal atoms have been prepared,[5] in expectation of novel properties, and compounds (**1**) and (**2**) provide the first examples of ferroelectric liquid crystalline materials incorporating boron atoms.



Scheme 1. *Reagents and conditions*: i, toluene reflux; ii, $SOCl_2$; iii, $R^1O_2CC_6H_4OH$-4, pyridine/tetrahydrofuran.

Received, 17th September 1987; Com. 1357

References

1 *E.g.*, D. M. Walba, S. C. Slater, W. N. Thurmes, N. A. Clark, M. A. Handschy, and F. Supon, *J. Am. Chem. Soc.*, 1986, **108**, 5210.
2 K. Seto, S. Takahashi, and T. Tahara, *J. Chem. Soc., Chem. Commun.*, 1985, 122.
3 M. Sawada and T. Tanaka, personal communication.
4 Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 477.
5 S. Takahashi, Y. Takai, H. Morimoto, and K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, 1984, 3; D. W. Bruce, L. Lalinde, P. Styring, D. A. Dunmur, and P. M. Maitlis, *ibid.*, 1986, 581, and references cited therein.