A New Series of Liquid Crystalline Materials containing Boron Atoms

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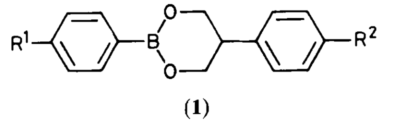
The dioxaborinane derivatives, which were synthesized by a method including a new Pd-catalysed coupling reaction, form mesomorphic phases in a wide temperature range, and provide a new series of liquid crystalline compounds containing a boron atom in the principal structure.

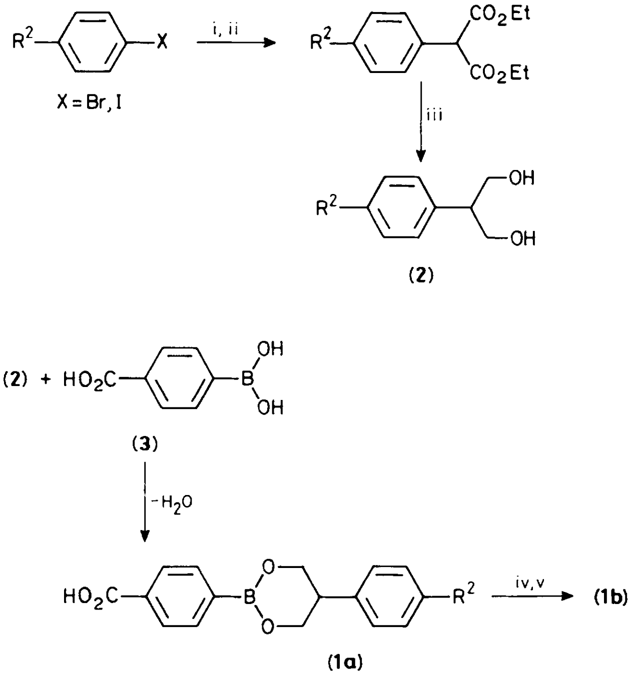
The majority of liquid crystalline molecules consist of carbon, oxygen, nitrogen, and hydrogen atoms. Though a few examples containing heteroatoms are known,[1] liquid crystalline materials containing metal atoms are of special interest since they are expected to have unique properties.[2] Previously, we have reported on lyotropic liquid-crystalline materials containing transition metals.[3] Here we report the synthesis and properties of the 1,3,2-dioxaborinanes (**1**) which may be the first examples of thermotropic liquid-crystalline molecules with a boron atom in the principal structure.

The compound (**1**) was synthesized *via* the reactions shown in Scheme 1. The intermediate compound (**2**) was obtained from the coupling between the ethyl cyanoacetate anion and a 4-substituted phenyl halide, followed by esterification and reduction. The key step in the synthesis of (**2**) may be the coupling reaction which was found to proceed smoothly in the presence of a palladium catalyst in monoglyme at 70 °C.[4] The compound (**3**) was prepared from tolylmagnesium bromide and trimethoxyborane by a two-step synthesis.[5] Condensation



(**1**)

a; R^1 = CO_2H
b; R^1 = CN
c; R^1 = CO_2Me
d; R^1 = OMe



Scheme 1. *Reagents*: i, $^-CH(CN)CO_2Et$, $Pd(PPh_3)_4$; ii, EtOH–HCl–$CaCl_2$; iii, $LiAlH_4$; iv, $SOCl_2$, then NH_3; v, CCl_4–PPh_3/tetrahydrofuran.

Table 1. Transition temperatures[a] of compounds (**1**).

(**1**)	R^1	R^2	T(C–meso)/°C[c]	T(meso–I)/°C[c]
a	CO_2H	n-C_6H_{13}	200(n)	260[b]
		n-C_4H_9O	250 (n)	280[b]
		n-$C_8H_{17}O$	202 (n)	273[b]
b	CN	n-C_6H_{13}	98 (n)	122.4
		n-C_4H_9O	117.0 (n)	166.0
		n-$C_8H_{17}O$	95.0[d]	144.8
c	CO_2Me	n-C_4H_9O	156.2 (n)	158.5
		n-$C_8H_{17}O$	134.0 (s)	164.6
d	OMe	n-C_4H_9O	133.9 (n)	146.6
		n-$C_8H_{17}O$	110.6[e]	132.3

[a] Measured with a Mettler Thermal Microscope FP5 + FP52. [b] With decomposition. [c] C = crystal, I = isotropic, n = nematic, s = smectic. [d] T(C–smectic) 95.0, T(smectic–nematic) 113.6 °C. [e] T(C–smectic) 110.6, T(smectic–nematic) 118.7 °C.

between (**2**) and (**3**) in toluene gave (**1a**), which, on conversion of the hydroxycarbonyl group into the nitrile group yielded (**1b**).[6] The structures of compounds (**1**) are consistent with analytical data including mass, i.r., and n.m.r. spectra. The mesomorphic ranges of (**1**) were measured visually with an optical microscope and are summarized in Table 1.

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