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Structural Studies of a Liquid Crystalline Compound, 2-(4-Cyanophenyl)-5-(4-butylphenyl)-1,3,2-dioxaborinane, by Means of Nuclear Magnetic Resonance and X-Ray Analyses

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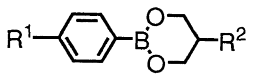
The crystal and molecular structure of the title nematogen (**1**), has been determined by an X-ray analysis. Compound **1** belongs to the triclinic system with space group P-1, a=9.798(2), b=11.579(2), c=9.716(2) Å, α=74.081(13), β=117.766(14), γ=108.179(13) °, and with two molecules in the unit cell. The geometry around the boron atom is planar, and the plane defined by O2BC is parallel to the phenyl ring bonded to the boron atom. The angle between two phenyl rings is 74.3°. The molecules are in their most extended conformation, with nearest neighbors oriented antiparallel to each other. The ^{1}H NMR studies have indicated that the half-chair conformation of the dioxaborinane is kept in a solution even at 125 °C where **1** forms a nematic phase, and the rigidity is essential for the formation of mesophases.

Relation between molecular structure and property of liquid crystalline materials are of current interest. In order to understand molecular arrangements in mesophases on the basis of the molecular structure, direct analyses of nematic or smectic phases by spectroscopic and X-ray methods have been made,[1] but only a little information has been obtained to date. Thus at present in many cases it may be obliged to infer the molecular structure and arrangement in a liquid crystalline state from those in a crystalline one.[2]

Previously we have shown[3] that 2-aryl-1,3,2-dioxaborinane derivatives (I) provide a new series of liquid crystalline materials and form nematic, smectic A and C, and chiral smectic C phases depending on their structures. Since they contain a metalloid atom, boron, in the six-membered ring, it is supposed that they have a unique structural feature. In order to discuss the characteristics of the dioxaborinane compounds, especially in terms of the influence of the boron atom on the molecular structure and liquid crystalline property, we have performed structural analyses of a representative nematogen among them both in a solution and in a crystalline state. Here we report the NMR and X-ray analyses of 2-(4-cyanophenyl)-5-(4-butylphenyl)-1,3,2-dioxaborinane (**1**)[4] which forms a stable nematic phase in the temperature range of 120—128 °C as shown in Fig. 1.



(I)

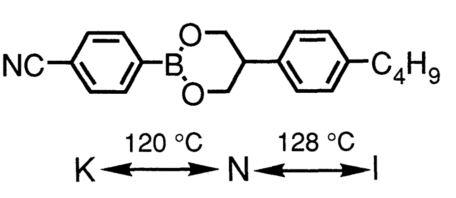


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Fig. 1. Structure and phase sequence of **1**.

Experimental

Materials. 2-(4-Cyanophenyl)-5-(4-butylphenyl)-1,3,2-dioxaborinane (**1**) and 2-(4-butoxyphenyl)-5-octyl-1,3,2-dioxaborinane (**6a**) were prepared by the method[4] reported previously and the single crystals of **1** were obtained by slow evaporation from a solution of **1** in hexane.

2-(4-Butoxyphenyl)-5-octyl-4,4,6,6-tetradeuterio-1,3,2-dioxaborinane (**6b**) was similarly prepared by dehydrocondensation in toluene between 4-butoxyphenylboronic acid and 2-octyl-1,1,3,3-tetradeuterio-1,3-propanediol which was obtained by the reduction of diethyl octylmalonate with lithium alminum deuteride. Recrystallization from hexane gave colorless crystals of **6b** in 40% yield. IR (KBr) 2920 (ν_{CH}), 2220 and 2110 (ν_{CD}), 1340 cm^{-1} (ν_{BO}); MS m/z 350 (M$^+$).

Collection of X-ray Diffraction Data and Structure Determination. Crystal data and experimental conditions are summarized in Table 1. Three dimensional intensity data were collected on a Rigaku AFC-5FOS automated four circle diffractometer at room temperature. Mo K_α (λ=0.71069 Å) radiation with a graphite crystal monochrometor in the incident beam was used. Unit cell constants were determined by a least-squares fit of 25 reflections in the range of $21° < 2\theta < 27°$. Three standard reflections were checked every 55 reflections during the course of the intensity-collection and no intensity-decrease was observed. Intensity data were reduced to structure factors without any absorption corrections.

Structure was solved by direct methods (MULTAN84), refined by block-diagonal least-squares methods and RASA software was employed for the entire structure analyses. Non-hydrogen atoms were assigned with anisotropic temperature factors. Hydrogen atoms were found by difference Fourier calculations and refined with isotropic thermal parameters. The structure has been refined to R=0.070 (R_w=0.056) for 2121 observed reflections.

Computations were carried out on a FACOM S3500 superminicomputer at Material Analysis Center, ISIR, Osaka University.

NMR Measurement. High resolution ^{1}H NMR spectra of **1**

Table 1. Crystal and Experimental Data

Empirical formula	$C_{20}H_{22}NBO$
Crystal system	Triclinic
Space group	P-1
a/Å	9.798
b/Å	11.579
c/Å	9.716
α/°	74.081
β/°	117.766
γ/°	108.179
V/Å^3	915.700
Z	2
D/g cm^{-3}	1.1581
μ(Mo $K\alpha$)/Å	0.71069
Scan method	θ–2θ
Scan range d(2θ)	1.4+tanθ°
Scan speed in 2θ/° min^{-1}	4
$2\theta_{\max}$/°	50
Background/s^{-1}	2×5.0
Refl. measd	2625
Refl. used ($F>2\sigma(F)$)	2121
Final R (R_w)	0.070 (0.056)

were recorded on a Bruker WM360 spectrometer. Deuteriochloroform and 1,2-dideuterio-1,1,2,2-tetrachloroethane were used as solvents on the measurements at a room temperature and at a higher temperature, respectively.

Results and Discussion

Description of Structure. The crystal and molecular structures of **1** have been determined by a single-crystal X-ray analysis. This is the first X-ray structural analysis of the 1,3,2-dioxaborinane derivatives. The molecular structure of **1** is illustrated in Fig. 2. The final positional and thermal parameters of all the non-hydrogen atoms are listed in Table 2, and Tables 3 and 4 list the bond length and the angles, respectively.

It can be seen from the projection that the geometry around the boron atom is planar and the plane defined by O2BC is coplanar with the phenyl ring bonded to the boron atom. The conformation of the dioxaborinane ring is characterized to be in a half-chair form.

The bond length between boron and carbon is 1.562 Å, shorter than those of borates, compounds **2** (1.590 Å)[5] and **3** (1.628, 1.630 Å).[6] The length is somewhat shorter than that of triphenylborane **4** (1.571, 1.589 Å),[7] because

Table 2. Final Atomic Coordinates and Isotropic Thermal Parameters with esd's in Parentheses for the Non-Hydrogen Atoms of **1**

Atom	x	y	z	B_{eq}[a)]
O(1)	0.7477(3)	0.2660(2)	0.1809(3)	6.6
O(2)	0.7905(3)	0.3672(3)	0.3850(3)	7.4
N(1)	−0.0649(4)	0.4237(3)	−0.1698(5)	7.9
B(1)	0.6987(5)	0.3259(4)	0.2463(5)	5.4
C(1)	1.1363(5)	0.2199(4)	0.5256(5)	6.1
C(2)	0.5266(4)	0.3475(3)	0.1544(4)	4.9
C(3)	0.2693(5)	0.3140(4)	−0.0633(5)	6.4
C(4)	0.0614(5)	0.4068(4)	−0.0987(5)	5.9
C(5)	0.9069(5)	0.2468(4)	0.2596(5)	6.5
C(6)	0.3212(5)	0.4395(4)	0.1222(5)	6.2
C(7)	0.4721(5)	0.4190(4)	0.2036(4)	6.0
C(8)	0.9480(5)	0.3443(4)	0.4763(5)	7.6
C(9)	0.4208(5)	0.2955(4)	0.0193(4)	5.9
C(10)	0.2189(4)	0.3859(3)	−0.0112(4)	5.1
C(11)	1.3138(5)	0.0931(4)	0.7187(5)	6.2
C(12)	1.2635(5)	0.3069(4)	0.5073(5)	6.9
C(13)	0.9655(5)	0.2384(4)	0.4336(5)	7.1
C(14)	1.1631(5)	0.1142(4)	0.6324(5)	6.2
C(15)	1.4432(5)	0.1792(4)	0.7030(5)	6.5
C(16)	1.4173(5)	0.2863(4)	0.5960(5)	7.2
C(17)	1.6084(5)	0.1541(5)	0.7973(6)	8.7
C(18)	1.6346(6)	0.0630(5)	0.7265(6)	9.9
C(19)	1.8051(8)	−0.0644(6)	0.7475(8)	11.6
C(20)	1.7925(7)	0.0295(6)	0.8182(8)	11.1

a) $B_{eq}=(4/3)\sum_{ij}\beta_{ij}(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

Table 3. Bond Length (l/Å) of **1**

Atoms	l/Å	Atoms	l/Å
C(1)–C(12)	1.387(7)	B(1)–C(2)	1.562(7)
C(2)–C(9)	1.392(6)	C(1)–C(14)	1.375(6)
C(3)–C(10)	1.383(6)	C(3)–C(9)	1.373(6)
C(6)–C(10)	1.383(6)	C(4)–C(10)	1.436(6)
O(1)–B(1)	1.360(6)	C(5)–C(13)	1.496(7)
O(2)–B(1)	1.345(6)	C(11)–C(15)	1.390(7)
O(2)–C(8)	1.446(6)	C(12)–C(16)	1.405(8)
C(1)–C(13)	1.540(7)	C(15)–C(16)	1.388(7)
C(2)–C(7)	1.389(6)	C(11)–C(14)	1.380(7)
C(6)–C(7)	1.377(6)	C(15)–C(17)	1.520(7)
C(8)–C(13)	1.477(7)	C(17)–C(18)	1.544(9)
O(1)–C(5)	1.442(5)	C(18)–C(20)	1.496(10)
N(1)–C(4)	1.152(6)	C(19)–C(20)	1.497(11)

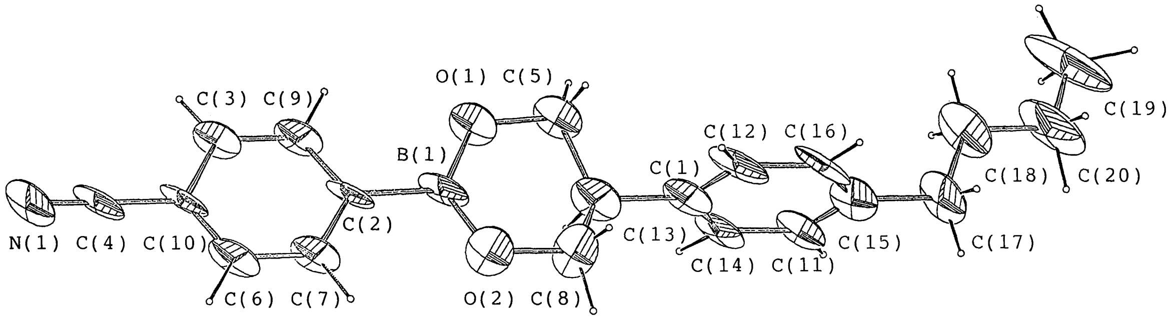


Fig. 2. ORTEP view of **1** with 50% probability thermal ellipsolids.

Table 4. Bond Angles ($\phi/°$) of **1**

Atoms	$\phi/°$	Atoms	$\phi/°$
B(1)-O(1)-C(5)	119.73(35)	B(1)-O(2)-C(8)	120.21(37)
O(1)-B(1)-C(2)	117.81(41)	O(2)-B(1)-C(2)	118.77(41)
C(12)-C(1)-C(14)	119.25(44)	C(13)-C(1)-C(14)	118.35(40)
B(1)-C(2)-C(9)	121.31(39)	C(7)-C(2)-C(9)	116.95(39)
O(1)-C(5)-C(13)	110.09(36)	C(3)-C(10)-C(6)	120.05(40)
C(7)-C(6)-C(10)	119.39(42)	C(1)-C(13)-C(8)	110.79(39)
C(2)-C(7)-C(6)	122.05(42)	C(11)-C(15)-C(17)	120.48(43)
O(2)-C(8)-C(13)	111.59(39)	O(1)-B(1)-O(2)	123.42(43)
C(2)-C(9)-C(3)	122.04(41)	C(12)-C(1)-C(13)	122.38(42)
C(3)-C(10)-C(4)	119.56(40)	B(1)-C(2)-C(7)	121.73(39)
C(14)-C(11)-C(15)	120.98(43)	C(9)-C(3)-C(10)	119.51(42)
C(1)-C(12)-C(16)	120.11(48)	N(1)-C(4)-C(10)	179.52(49)
C(1)-C(13)-C(5)	113.03(39)	C(4)-C(10)-C(6)	120.37(40)
C(5)-C(13)-C(8)	112.37(40)	C(16)-C(15)-C(17)	120.93(44)
C(1)-C(14)-C(11)	120.85(43)	C(17)-C(18)-C(20)	113.99(54)
C(11)-C(15)-C(16)	118.55(44)	C(18)-C(20)-C(19)	110.70(61)
C(12)-C(16)-C(15)	120.25(48)		
C(15)-C(17)-C(18)	111.16(46)		

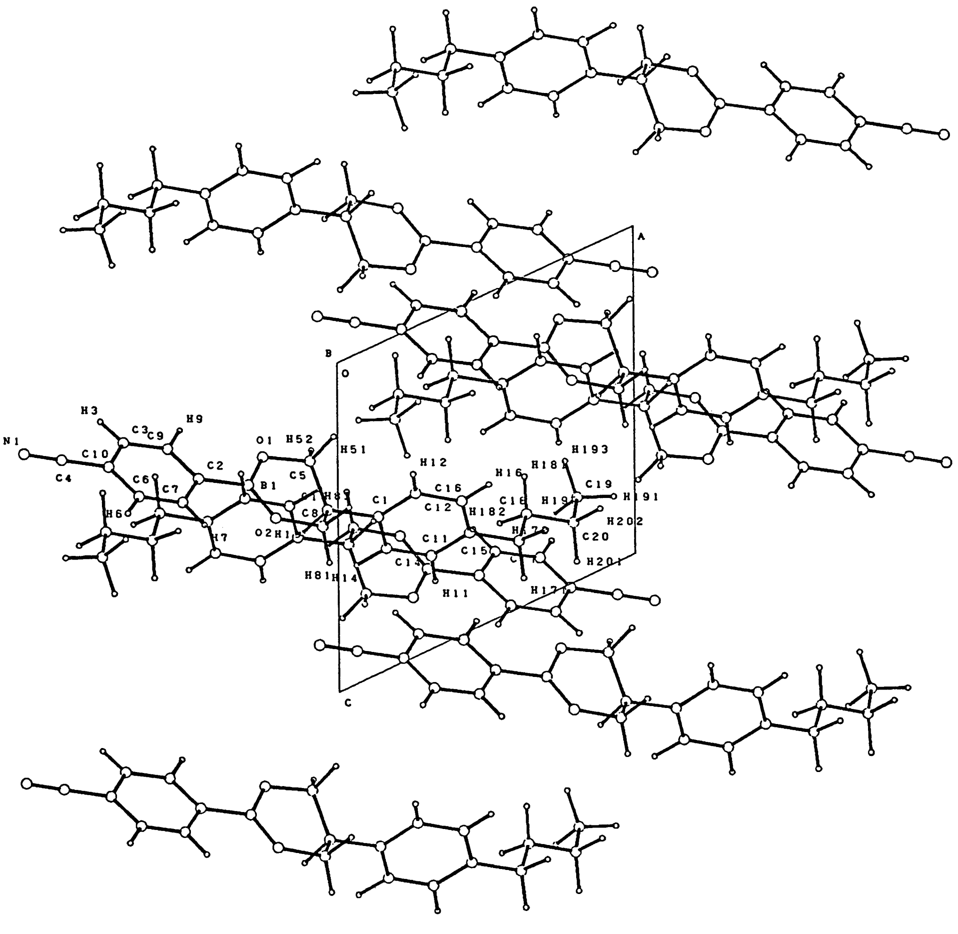
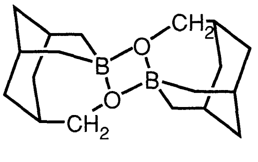


Fig. 3. Crystal structure of **1** viewed along *b* axis.

the boron atom in **4** is not in conjugation with the phenyl rings. The bond length between boron and oxygen are also shorter than those of compounds **2** and **3**. The amine adduct of boronic acid trimer **5** has rather longer B–O (1.400 Å) and B–C (1.574 Å) bonds,[8] which may be due to a borate character.



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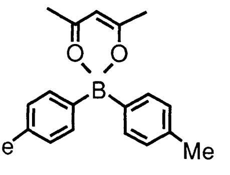

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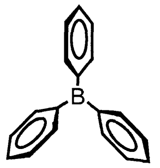

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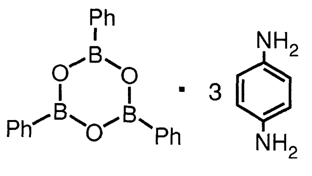


5

The two phenyl rings in compound **1** lie nearly perpendicular, i.e. the torsion angle between them is 74.3°, which compares well with the angles of 81.5° in the molecule of 4-(4-propylcyclohexyl)benzonitrile[9] and 64.5° of 4-(4-octylcyclohexyl)benzonitrile[10] which are well-known to form mesophases. The butyl chain is extended in a trans conformation and the molecule adopts a widely stretched and nearly linear form.

Molecular Packing. In Fig. 3 a projection along the *b*-axis is depicted, which shows the molecules of **1** are arranged in a head-to-tail manner parallel to each other. Such antiparallel arrangement is usually observed in the cases of cyano-substituted mesomorphic molecules (e.g. cyanobiphenyl and cyclohexylbenzonitrile[10,11]) and it is believed that the antiparallel imbricated molecular arrangement in the crystalline state would be kept in the nematic phase. As reported previously for dioxaborinane derivatives[4] the cyano terminal is actually effective for the formation of a nematic phase. The antiparallel dimer structure due to the cyano group effectively contributes to the thermal stability of nematic phases formed by the cyano derivatives of dioxaborinane compounds.

The distance between the cyano groups of neighboring molecules is 3.65 Å, which is within the distance (3.5—4.3 Å) reported on the nematogens having a cyano group by Haase et al.[10–12] The nearest atoms of the neighboring molecules are H3–H81: 2.447 Å, H14–H52:

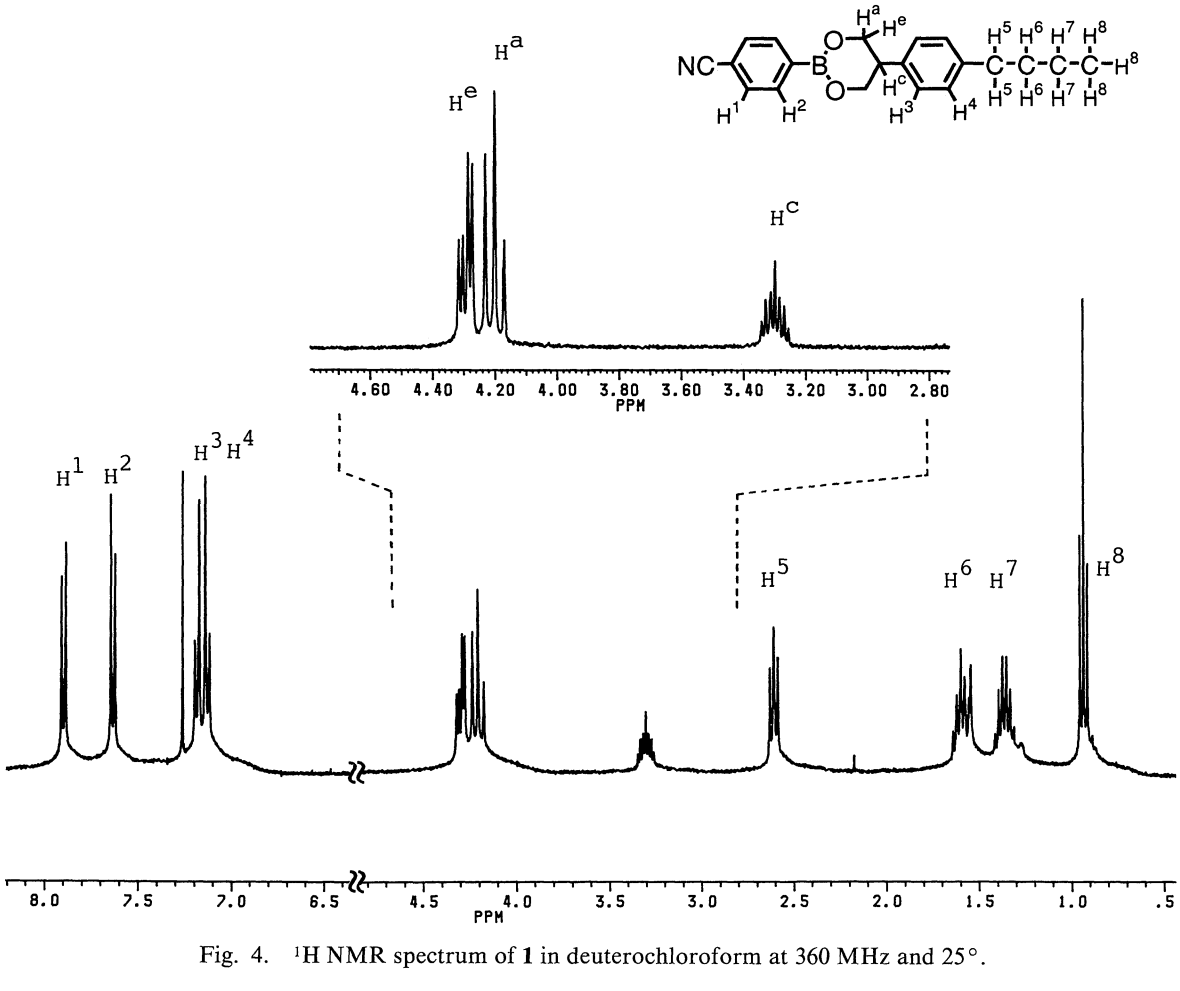
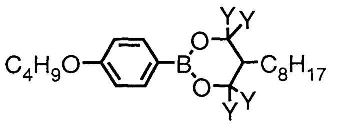


Fig. 4. ^1H NMR spectrum of **1** in deuterochloroform at 360 MHz and 25°.

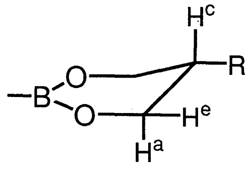
2.448 Å, the dioxaborinane ring is relatively close to a benzene ring, suggesting an interaction between these two rings.

Structure in a Solution. In order to obtain information on the molecular structure, in particular on the dioxaborinane ring of compound **1** in a solution, we have performed detailed investigations by an NMR method. In the $^{11}B\{^1H\}$ NMR spectrum of **1** in acetone-d_6 at ambient temperature showed a relatively broad singlet at 8.3 ppm down field from triethoxyborane as an internal standard. The chemical shift is comparable with that (10.4 ppm) of diethyl phenylboronate.13) The ^1H NMR spectrum at room temperature is shown in Fig. 4 along with the expanded spectrum in the region of δ=5—3 ppm. Assignment of the signals observed at 4.20 and 4.29 ppm have been made by comparison between ^1H NMR spectra of 2-(4-butoxyphenyl)-5-octyl-1,3,2-dioxaborinane (**6a**) and its 4,4,6,6-tetradeuterio derivative (**6b**). The spetrum of **6a** exhibited three signals at 3.73, 3.97, and 4.14 ppm in the region of δ=3—5 ppm, whereas in the spectrum of deuterio derivative **6b** two of them completely disappeared and only the signal at 3.97 ppm remained, clearly indicating that the signals at 3.73 and 4.14 ppm can be assigned to the methylene protons attached to 4- and 6-carbons of the dioxaborinane ring and the signal at 3.97 ppm to the methylene protons (-O-CH_2-) of the butoxyl group. Thus we can assign the signals observed for compound **1** at 4.20 and 4.29 ppm to the methylene protons of the dioxaborinane ring which were shifted, as compared with **6a**, to a down field due to the phenyl substituent. The signals at 4.29 ppm appeared as a double doublet and at 4.20 ppm apparently as a triplet. The latter is expected to appear as a triplet by accidental superposition of a double doublet.

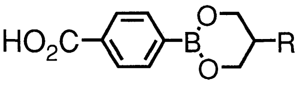


6a: Y=H
6b: Y=D

Table 5. NMR Data for the Methylene (H^e and H^a) and the Methine (H^c) Protons of the 1,3,2-Dioxaborinane Ring



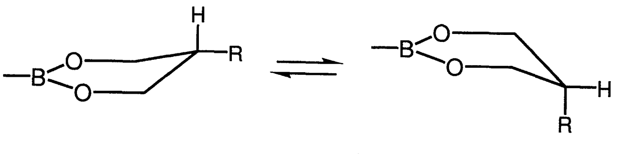
Compounds	H^e	H^a	H^c
1	δ=4.29 2H, dd $J_{H^e-H^a}=11$ Hz $J_{H^e-H^c}=5$ Hz	4.20 2H, dd $J_{H^a-H^a}=11$ Hz $J_{H^a-H^c}=11$ Hz	3.30 1H, m
6a	δ=4.14 2H, dd $J_{H^e-H^a}=11$ Hz $J_{H^e-H^c}=5$ Hz	3.73 2H, dd $J_{H^a-H^a}=11$ Hz $J_{H^a-H^c}=11$ Hz	2.06 1H, m
7	δ=4.18 4H, d J=4 Hz		3.74 1H, t J=4 Hz
8	δ=4.17 2H, dd $J_{H^e-H^a}=11$ Hz $J_{H^e-H^c}=5$ Hz	3.78 2H, dd $J_{H^a-H^a}=11$ Hz $J_{H^a-H^c}=11$ Hz	2.09 1H, m



7: R=$OC_{12}H_{25}$ $\quad K \xrightleftharpoons{130\ ^\circ C} I$

8: R=$C_{12}H_{25}$ $\quad K \xrightleftharpoons{151\ ^\circ C} S_C \xrightleftharpoons{163\ ^\circ C} N \xrightleftharpoons{185\ ^\circ C} I$

Fig. 5. Structure and phase sequence of **7** and **8**.



Scheme 1.

On the basis of the chemical shifts and the coupling constants observed for them the signal at 4.29 ppm is assigned to the equatorial hydrogens (H^e, $J_{H^e-H^a}$=11, $J_{H^e-H^c}$=5 Hz), and at 4.20 ppm to the axial ones (H^a, $J_{H^a-H^e}$=11, $J_{H^a-H^c}$=11 Hz) attached to the C4 and C6 of the dioxaborinane ring as shown in Fig. 4 and Table 5. Consequently observation of such the fine structure in the NMR spectra indicates that the half-chair conformation of the dioxaborinane ring is tightly fixed even in a solution. Moreover the spectra measured in 1,1,2,2-tetrachloroethane-d_2 at 125 °C showed the essentially same fine structure in which the geminal-geminal and geminal-axial proton couplings were observed, that is the rigidity of the ring is still kept at the temperature where compound **1** forms a nematic phase.

On the other hand, compound **7**, which bears an alkoxyl group on 5-carbon of the dioxaborinane ring, showed a signal attributable to the methylene protons at 4.18 ppm as a doublet (J=4 Hz) and a siganal due to the methyne at 3.74 ppm as a triplet (J=4 Hz) in the NMR spectrum recorded at room temperature, and no geminal-geminal proton couplings were observed, indicating a rapid interconversion between two conformers within the NMR time scale for **7** in solution (Scheme 1). The similar phenomenon has recently been observed for a dioxane derivative.14) When the alkoxyl group is replaced by an alkyl group, the dioxaborinane derivative **8** clearly showed a geminal-geminal coupling (11 Hz). Though compound **8** exhibited smectic and nematic phases, **7** did no mesophases, strongly suggesting that the rigidity of the dioxaborinane ring is essential for the formation of mesophases.

In conclusion the rigid half-chair form of the dioxaborinane ring in crystalline state is kept in solution, thus suggesting a similar conformation in liquid crystalline state as well. Loss of the rididity does not lead to the formation of mesophases. The rigid dioxaborinane ring may constitute, in connection with phenyl nuclei, a suitable principal structure required for liquid crystalline compounds.

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