2,5-Diaryl-1,3,2-dioxaborinanes: A New Series of Liquid Crystals

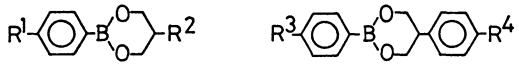
Hiroshi MATSUBARA, Koji SETO,† Tadasu TAHARA,† and Shigetoshi TAKAHASHI*
The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka, Ibaraki, Osaka 567
†Research & Development Division, Nitto Kasei Co., Ltd., 3 Nishiawaji, Higashiyodogawa, Osaka 533
(Received July 31, 1989)

2,5-Diaryl-1,3,2-dioxaborinane derivatives having various terminal groups were synthesized and found to form mesomorphic phases in a wide temperature range. They 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, oxgen, 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 based on the incorporation of metals having special electric and magnetic properties.

In general, organometallic compounds are thermally and chemically unstable, however, 1,3,2-dioxaborinane derivatives are fairly stable and we recently reported a preliminaly result that the compounds having 2,5-disubstituted 1,3,2-dioxaborinane structure **1** form stable nematic and/or smectic mesophases.[2] They are the first examples of thermotropic liquid-crystalline molecules with a boron atom in the principal structure. Boron atoms have vacant p-orbitals and are electron-deficient, hence conjugation between the p-orbital and aromatic π-electron system may be expected for 2-aryl-1,3,2-dioxaborinane derivatives. This conjugation may give a double bond character to the bond between boron atom and aromatic ring, resulting in a rigid core structure favorable to liquid-crystalline materials.

In this paper we report in detail on the synthesis and properities of liquid-crystalline compounds **2** which are constructed by three rings containing the dioxaborinane ring as the principal structure. And we wish to discuss especially the influence of terminal groups on mesomorphic properties, as well as the comparison with other liquid-crystalline materials



1 2

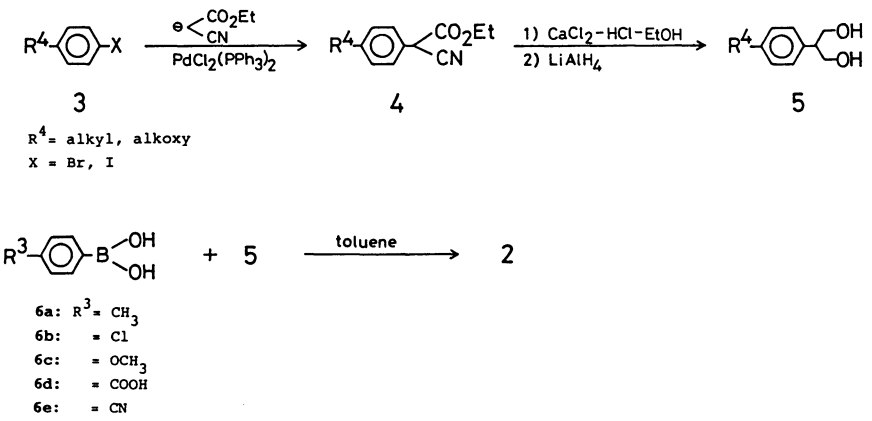
having the analogous structure.

Results and Discussion

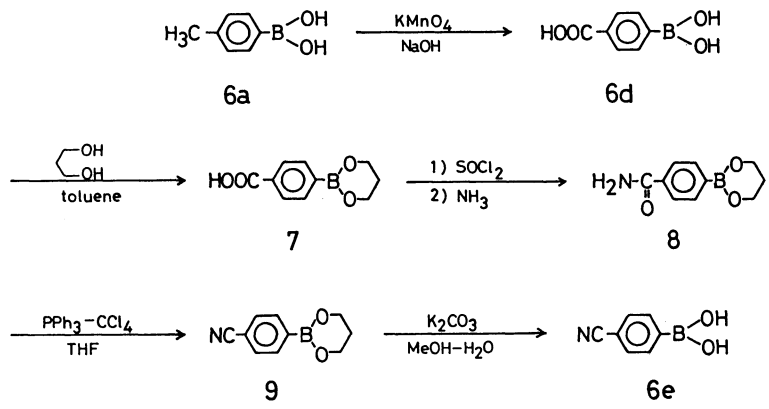
A simple approach to the synthesis of compound **2** has been developed according to Scheme 1. The synthetic intermediate **4** was prepared by the palladium-(0)-catalyzed cross-coupling reaction of ethyl cyanomalonate with aryl halides **3**.[3] The aryl halides were prepared by the halogenation of arenes according to a literature method.[4] Although a small amount of the ortho-substituted isomer was formed as a by-product, a mixture of the isomers was used for the coupling reaction, since the ortho-isomer has a less reactivity and recrystallization gave pure diols **5**.

Boronic acids **6a—c** were obtained by the reaction of Grignard reagents with trimethoxyborane in tetrahydrofuran at temperatures below −60 °C. Boronic acid **6a** was converted to **6d** by oxidation with potassium permanganate in an alkaline solution.[5] *p*-Cyanophenyl derivative **6e** was prepared according to Scheme 2. The intermediate **8** was transformed into **9** by a literature method.[6]

Finally, condensation between **5** and **6** was carried out in a toluene solution and we obtained dioxaborinane derivatives **2** in nearly quantitative yields. Pur-



Scheme 1.



Scheme 2.

ification of **2** was achieved by column chromatography and recrystallization. The structures of compound **2** are consistent with analytical data including mass, IR, and NMR spectra. The present method for the preparation of **2** has a great advantage because their various derivatives are prepared easily by the simple condensation of selected pairs of **5** and **6**. A number of 2,5-disubstituted 1,3,2-dioxaborinanes thus synthesized are listed in Table 1. The table shows that the dioxaborinane derivatives form mesophases with a variety of terminal groups, indicating that the dioxaborinane ring provides a suitable core structure for the formation of liquid crystals.

The terminal groups can promote the formation of mesophases in the following order, -CN>-OMe, -Cl>-Me>-COOMe. The order is almost same as the tendency for organic liquid-crystalline materials shown by Gray et al.[7] Especially, the cyano gruop is a good terminal group for the formation of mesophases. It is known that cyano groups lead molecules to a dimer structure favorable to the formation of liquid crystals.

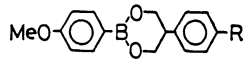
In order to investigate the influence of alkyl chain length on the formation of mesophases, compounds **2**, (R^3=CN or CH_3O) bearing a variety of alkyl groups (R^4) were synthesized, and the results are summarized in Tables 2 and 3. The compounds having a cyano group at the terminal form a stable nematic phase for various alkyl chains, while those having a methoxyl group exhibit only a monotropic nematic phase. The transition temperatures for the compounds having a cyano group are plotted against the alkyl chain length in Fig. 1. An odd-even effect was observed for the nematic-to-isotropic (N-I) transition temperatures,

Table 1. Transition Temperatures for 2,5-Disubstituted 1,3,2-Dioxaborinanes (**2**)

	R^3	R^4	Transition temperatures (°C)[a]		
			Cryst.	N	Iso
2a	CH_3	OC_4H_9	· 126.4	· (124.0)[b]	·
2b	Cl	OC_4H_9	· 145.0	· (132.8)[b]	·
2c	OCH_3	OC_4H_9	· 133.9	· 146.6	·
2d	CN	OC_4H_9	· 117.0	· 166.0	·
2e	CO_2CH_3	OC_4H_9	· 156.2	· 158.5	·
2f	CH_3	C_6H_{13}	· 100.0	· (83.0)[b]	·
2g	Cl	C_6H_{13}	· 124.8		·
2h	OCH_3	C_6H_{13}	· 103.0	· (91.4)[b]	·
2i	CN	C_6H_{13}	· 98.0	· 122.4	·
2j	CO_2CH_3	C_6H_{13}	· 140.5	· 130.3	·

a) N: nematic; Iso: isotropic liquid. b) Monotropic transition.

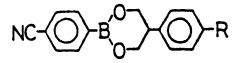
Table 2. Transition Temperatures for 2-(4-Methoxyphenyl)-5-(4-alkylphenyl)-1,3,2-dioxaborinanes



R	Transition temperatures (°C)[a]		
	Cryst.	N	Iso
CH_3	· 147.8	· (91.3)[b]	·
CH_3CH_2	· 144.0		·
$CH_3(CH_2)_2$	· 139.6	· (91.0)[b]	·
$CH_3(CH_2)_3$	· 109.9	· (88.3)[b]	·
$CH_3(CH_2)_4$	· 114.1	· (99.7)[b]	·
$CH_3(CH_2)_5$	· 103.0	· (91.4)[b]	·
$CH_3(CH_2)_6$	· 108.3	· (97.3)[b]	·
$CH_3(CH_2)_7$	· 94.8	· (93.3)[b]	·

a) N: nematic; Iso: isotropic liquid. b) Monotropic transition.

Table 3. Transition Temperatures for 2-(4-Cyanophenyl)-5-(4-alkylphenyl)-1,3,2-dioxaborinanes



R	Transition temperatures (°C)[a]			
	Cryst.	S_A	N	Iso
CH_3	· 151.9		· 157.2	·
CH_3CH_2	· 121.6		· 136.0	·
$CH_3(CH_2)_2$	· 117.1		· (115.2)[b]	·
$CH_3(CH_2)_3$	· 120.4		· 128.0	·
$CH_3(CH_2)_4$	· 103.0		· 132.7	·
$CH_3(CH_2)_5$	· 98.0		· 122.4	·
$CH_3(CH_2)_6$	· 95.0		· 127.0	·
$CH_3(CH_2)_7$	· 87.3	· 102.0	· 120.6	·

a) S_A smectic A; N: nematic; Iso: isotropic liquid. b) Monotropic transition.

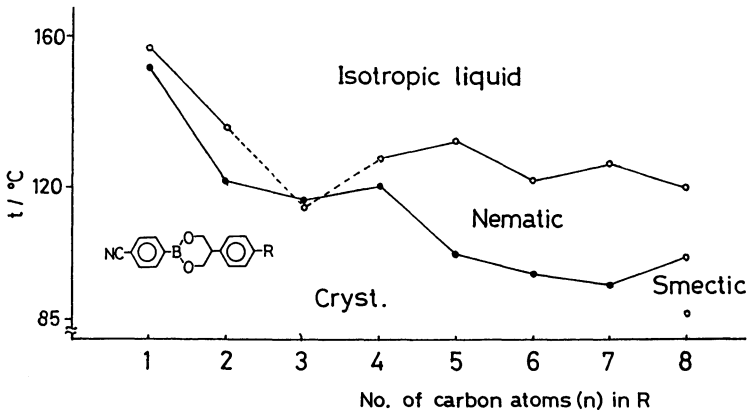


Fig. 1. Plot of transition temperatures against the number of carbon atoms (n) in alkyl chain (R) of the 2-(4-cyanophenyl)-5-(4-alkylphenyl)-1,3,2-dioxaborinanes.

Table 4. Comparison of Liquid-Crystalline Behavior for Tricyclic Compounds

	Transition temperatures (°C)[a]		
	Cryst.	N	Iso
NC-Ph-Ph-Ph-C_5H_{11}	· 130	· 239	·
NC-Ph-H-Ph-C_5H_{11}	· 84	· 154	·
NC-Ph-O,O-Ph-C_5H_{11}	· 110	· 164	·
NC-Ph-B(O,O)-Ph-C_5H_{11}	· 103.0	· 132.7	·

a) N: nematic; Iso: isotropic liquid.

and the longer alkyl groups showed the wider temperature range of mesophases. These facts also agree with the tendency of liquid-crystalline materials reported by Gray et al.[7,8] As described later, the dioxaborinane derivatives show lower N-I transition temperatures than other liquid-crystalline materials having analogous three-ring structures.

The dioxaborinane derivatives have a unique structure containing a metalloid atom, boron, in the principal structure, however, they are fairly stable in air and moisture, and showed similar thermal properties of organic liquid-crystalline materials.

It is known that the structures of rigid core in liquid-crystalline materials give strong influence to their clearing points, that is mesophases-to-isotropic transition temperatures. For examples, displacement of the central benzene ring in a terphenyl system by other six-membered rings such as cyclohexane and dioxane results in lowering the clearing points.[9] The dioxaborinane ring exhibited the same influence and compound **9** showed the lowest clearing point among the compounds summarized in Table 4.

Experimental

Measurements of transition temperatures and observations of mesophases were made using Olympus BH-2 polarising microscope in conjunction with Metler FP52 heating stage and FP5 control unit. ^{1}H NMR spectra were measured for solutions in $CDCl_3$ with tetramethylsilane as internal standard using a Bruker WM-360 spectrometer. IR spectra were recorded with a Hitachi 295 infrared spectrophotometer, and mass spectra were taken on a JEOL JMS06 instrument.

Diethyl 4-Butylphenylmalonate.[3] To a suspension of potassium *t*-butoxide (6.73 g, 60 mmol) in 1,2-dimethoxyethane (50 ml), ethyl cyanoacetate (3.97 g, 35 mmol) was added at room temperature with stirring. After 10 min 4-butylphenyl iodide (**3**, R=C_4H_9, X=I, 7.80 g, 30 mmol) and a catalytic amount of dichlorobis(triphenylphosphine)-palladium (600 mg, 0.85 mmol) were added, and then the mixture was heated at 70 °C for 8 h under nitrogen. After cooling the reaction mixture, 1 M hydrochloric acid was added and the product was extracted with ether. The extract was washed with water and dried over sodium sulfate. After evaporation of ether the residue was purified by chromatography on silica gel using hexane/dichloromethane as eluent. The viscous, oily product was distilled using a Kugelrohr bulb-to-bulb distillation apparatus to give ethyl 4-butylphenylcyanoacetate (as a colorless oil; yield 4.13 g (56%); IR (neat) 2240 (CN), and 1760 cm^{-1} (C=O). The product obtained here was contaminated by a small amount of impurity, but the next procedure for saponification of the cyano group was carried out without further purification of the product. A mixture of the crude cyanoacetate (4.00 g), ethanol (15 ml), concd hydrochloric acid (18.6 ml), calcium chloride (20.1 g), and benzene (6 ml) was stirring at room temperature for 3 h, then heated at 55 °C for 2 h, and finally under reflux for 5 h. After cooling to room temperature, water was added and the product was extracted with benzene. The extract was dried over sodium sulfate, and after concentration the crude product was purified by chromatography on silica gel using dichloromethane as an eluent. The resultant oily product was distilled using a Kugelrohr bulb-to-bulb distillation apparatus, affording diethly 4-butylphenylmalonate as a colorless oil; yield 3.32 g (70%); IR (neat) 1765 and 1750 cm^{-1} (C=O); ^{1}H NMR δ=0.90—2.10 (13H, m, alkyl), 2.50 (2H, t, J=8 Hz, $CH_2C_6H_4$), 4.20 (4H, q, J=7 Hz, CH_2O), 4.57 (1H, s, CH), and 7.27 (m, 4H, Ar).

2-(4-Butylphenyl)-1,3-propanediol (5, R=C_4H_9). To a suspension of lithium aluminum hydride (0.76 g, 20 mmol) in diethyl ether (60 ml), diethyl 4-butylphenylmalonate (2.92 g, 10 mmol) in diethyl ether (10 ml) was added dropwise with stirring at 0 °C. And then the reaction mixture was heated to reflux temperature. After 6 h the mixture was cooled to 0 °C again, and ethyl acetate (5 ml), and 5% sodium hydroxide solution (10 ml) were added successively. After the reaction at room temperature for 10 h, the inorganic salt precipitated was separated by filtration, then the organic layer was separated and the aqueous layer was extracted with ether. The combined ether solution was dried over sodium sulfate. After evaporation of ether, the resultant product was purified by recrystallization from hexane, affording 2-(4-butylphenyl)-1,3-propanediol as white needles; yield 3.32 g (70%); mp 74.5—76.0 °C; IR (Nujol) 3250 cm^{-1} (OH); ^1H NMR δ=0.87—1.59 (7H, m, alkyl), 2.57 (2H, t, J=8 Hz, $C\underline{H}_2C_6H_4$), 3.02 (1H, m, CH), 3.86—3.96 (4H, m, OCH_2), and 7.11 (4H, s, Ar).

***p*-Tolylboronic Acid (6a).** To a solution of trimethoxyborane (20.4 g, 194 mmol) in dry tetrahydrofuran (100 ml), *p*-tolylmagnesium bromide, prepared from *p*-bromotoluene (22.4 g, 131 mmol) and magnesium (3.41g, 140 mmol), was added dropwise at −70 °C. After the Grignard reagent had been added, the reaction mixture was stirred below −60 °C for one hour, and then hydrolyzed with 10% sulfuric acid (70 ml). The inorganic salt formed was filtered off and the tetrahydrofuran layer was separated and then the aqueous layer was extracted with ether. The combined organic layer was washed with water and dried over sodium sulfate. Consentration of the solution gave white crystals, which was washed with hexane and water, affording pure *p*-tolylboronic acid; yield 15.0 g (86%); mp 245—247 °C; IR (Nujol) 3480, 3400 (OH), and 1365 cm^{-1} (BO).

Similarly, *p*-chloro- (**6b**) and *p*-methoxyphenylboronic acid (**6c**) were prepared by starting from *p*-chloro and *p*-methoxyphenyl bromide, respectively.

4-Carboxyphenylboronic Acid (6d).[5] *p*-Tolylboronic acid (6.8 g, 50 mmol) was dissolved in 40 ml of water containing sodium hydroxide (4 g), and then 290 ml of water was added to the solution. Into the agitated mixture a solution of potassium permanganate (16.6 g, 105 mmol) in water (500 ml) was added in the following way. The permanganate solution was devided into eight volumes, and each volume was added in turn every one hour. After all portions of the permanganate solution had been added, the mixture was stirred overnight. Excess of permanganate was destroyed by addition of ethanol (20 ml) at 50 °C, and the manganese dioxide was filtered off. The filtrate was concentrated to about 200 ml below 40 °C, and then acidified carefully with hydrochloric acid. The crystal separated was collected, washed with water, and recrystallized from water; yield 4.82 g (58%); mp 232—234 °C; IR (Nujol) 3500—2500 (OH), 1700 (C=O), and 1355 cm^{-1} (BO).

2-(4-Carboxyphenyl)-1,3,2-dioxaborinane (7). 4-Carboxyphenylboronic acid (4.82 g, 29 mmol) was reacted with 1,3-propanediol (2.23 g, 29 mmol) in toluene (100 ml) under reflux for 2 h. During the reaction the water formed was removed azeotropically using a Dean-Stark apparatus. When the reaction was completed, the mixture was cooled to room temperature and the crystals separated were collected by filtration; yield 5.78 g (92%); mp 211—213 °C; IR (Nujol) 3400—2500 (OH), 1695 (C=O), and 1315 cm^{-1} (BO).

2-(4-Carbamoylphenyl)-1,3,2-dioxaborinane (8). 2-(4-Carboxyphenyl)-1,3,2-dioxaborinane (5.56 g, 24.9 mmol) was reacted with thionyl chloride (12 ml) in the presence of *N,N*-dimethylformamide under reflux for 2 h. Removal of excess thionyl chloride under a reduced pressure afforded the acid chloride, which was used for the next reaction, ammonolysis, without further purification. To a 28% of aqueous ammonia (65 ml), a solution of the acid chloride in tetrahydrofuran (130 ml) was added dropwise at 0 °C, and then stirred at room temperature for 30 min. The solvent and aqueous ammonia were removed by evaporation, and toluene (100 ml) was added to the residue in order to remove water azeotropically. After completion of dehydration, toluene was distilled away, and the resultant residue was extracted with acetone. Concentration of acetone solution gave 2-(4-carbamoylphenyl)-1,3,2-dioxaborinane as pale yellow crystals; yield 2.87 g (52%); mp 204—206 °C; IR (Nujol) 3550, 3100 (NH), 1685 (C=O), 1625, and 1615 cm^{-1} (NH).

4-Cyanophenylboronic Acid (6e).[6] To a solution of triphenylphosphine (7.32 g, 27.9 mmol) in carbon tetrachloride (30 ml), 2-(4-carbamoylphenyl)-1,3,2-dioxaborinane (**8**, 2.87 g, 13.9 mmol) dissolved in tetrahydrofuran (30 ml) was added, and then the mixture was warmed to 50 °C for 20 h. Insoluble solids precipitated were separated, and the filtrate was concentrated. The residue was extracted with warm hexane, and removal of hexane give crude nitrile (**9**), 2.05 g (78%); IR (Nujol) 2220 (CN), and 1310 cm^{-1} (BO).

Finally, the protective group of boronic acid was taken off as follows. A mixture of (**9**) (2.05 g, 10.9 mmol) and potassium carbonate (3.75 g) in water and methanol (10 ml) was stirred at room temperature for 10 h. Insoluble solids were filtered off, and methanol was removed in vacuo. The aqueous alkali solution was cooled and acidified carefully with hydrochloric acid. The crystal separated was collected by filtration and washed with water; yield 1.26 g (78%); mp>300 °C; IR (Nujol) 3550, 3440 (OH), 2220 (CN), and 1345 cm^{-1} (BO).

2,5-Diaryl-1,3,2-dioxaborinanes (2). General Procedure. A mixture of 4-substituted phenylboronic acid (**6**, 0.5 mmol), 2-(4-substituted phenyl)-1,3-propanediol (**5**, 0.5 mmol), and toluene (25 ml) was stirred under reflux for 2 h. During the reaction the water formed removed azeotropically using a Dean-Stark apparatus. When the reaction was completed, toluene was distilled away, and the resultant residue was purified by chromatography on silica gel using dichloromethane as an eluent. Recrystallization from hexane gave the corresponding products (**2**).

2-(4-Methylphenyl)-5-(4-butoxyphenyl)-1,3,2-dioxaborinane (2a). Found: C, 74.08; H, 7.80%. Calcd for $C_{20}H_{26}BO_3$: C, 73.86; H, 8.06%; IR (Nujol) 1315 cm^{-1} (BO); ^1H NMR δ=0.97 (3H, t, J=8 Hz, $CH_2C\underline{H}_3$), 1.45—1.52 (2H, m, $C\underline{H}_2CH_3$), 1.75 (2H, m, $OCH_2C\underline{H}_2$), 2.36 (3H, s, $C\underline{H}_3C_6H_4$), 3.25 (1H, m, CH), 3.95 (2H, t, J=6 Hz, $OC\underline{H}_2CH_2$), 4.14 (2H, dd, J=11 and 11 Hz, $OC\underline{H}_2CH$, ax), 4.24 (2H, dd, J=5 and 11 Hz, $OC\underline{H}_2CH$, eq), 6.88 (2H, d, J=9 Hz, Ar), 7.12 (2H, d, J=9 Hz, Ar), 7.17 (2H, d, J=8 Hz, Ar), and 7.70 (2H, d, J=8 Hz, Ar).

2-(4-Chlorophenyl)-5-(4-butoxyphenyl)-1,3,2-dioxaborinane (2b). Found: C, 66.09; H, 6.53; Cl, 10.10%. Calcd for $C_{19}H_{23}BClO_3$: C, 66.02; H, 6.71; Cl, 10.26%; IR (Nujol) 1315 cm^{-1} (BO); ^1H NMR δ=0.97 (3H, t, J=7 Hz, CH_3), 1.46—1.52 (2H, m, $C\underline{H}_2CH_3$), 1.76 (2H, m, $OCH_2C\underline{H}_2$), 3.25 (1H, m, CH), 3.95 (2H, d, J=6 Hz, $OC\underline{H}_2CH_2$), 4.14 (2H, dd, J=11

and 11 Hz, OCH_2CH, ax), 4.25 (2H, dd, J=5 and 11 Hz, OCH_2CH, eq), 6.89 (2H, d, J=9 Hz, Ar), 7.12 (2H, d, J=9 Hz, Ar), 7.33 (2H, d, J=8 Hz, Ar), and 7.73 (2H, d, J=8 Hz).

2-(4-Methoxyphenyl)-5-(4-butoxyphenyl)-1,3,2-dioxaborinane (2c). Found: C, 70.52; H, 7.42%. Calcd for $C_{20}H_{25}BO_4$: C, 70.61; H, 7.41%; IR (Nujol) 1315 cm^{-1} (BO); ^1H NMR δ=0.93 (3H, t, J=7 Hz, CH_2CH_3), 1.37—1.46 (2H, m, CH_2CH_3), 1.78 (2H, m, OCH_2CH_2), 3.25 (1H, m, CH), 3.83 (3H, s, OCH_3), 3.98 (2H, d, J=6 Hz, OCH_2CH_2), 4.14 (2H, dd, J=11 and 11 Hz, OCH_2CH, ax), 4.24 (2H, dd, J=5 and 11 Hz, OCH_2CH, eq), 6.87 (2H, d, J=9 Hz, Ar), 6.89 (2H, d, J=9 Hz, Ar), 7.12 (2H, d, J=9 Hz, Ar), and 7.75 (2H, d, J=9 Hz); MS, m/z 340 (M^+).

2-(4-Cyanophenyl)-5-(4-butoxyphenyl)-1,3,2-dioxaborinane (2d). Found: C, 71.92; H, 6.62; N, 3.96%. Calcd for $C_{20}H_{22}BNO_3$: C, 71.66; H, 6.62; N, 4.18%; IR (Nujol) 2220 cm^{-1} (CN); ^1H NMR δ=0.93 (3H, t, J=7 Hz, CH_3), 1.17—1.45 (2H, m, CH_2CH_3), 1.74—1.80 (2H, m, OCH_2CH_2), 3.27 (1H, m, CH), 3.94 (2H, d, J=6 Hz, OCH_2CH_2), 4.17 (2H, dd, J=11 and 11 Hz, OCH_2CH, ax), 4.28 (2H, dd, J=5 and 11 Hz, OCH_2CH, eq), 6.89 (2H, d, J=9 Hz, Ar), 7.12 (2H, d, J=9 Hz, Ar), 7.63 (2H, d, J=8 Hz, Ar), and 7.89 (2H, d, J=8 Hz, Ar).

2-(4-Methylphenyl)-5-(4-hexylphenyl)-1,3,2-dioxaborinane (2f). Found: C, 78.39; H, 8.67%. Calcd for $C_{22}H_{29}BO_2$: C, 78.58; H, 8.69%; IR (Nujol) 1310 cm^{-1} (BO); ^1H NMR δ=0.88 (3H, t, J=7 Hz, CH_2CH_3), 1.28—1.36 (6H, m, alkyl), 1.58—1.62 (2H, m, $CH_2CH_2C_6H_4$), 2.37 (3H, s, $CH_3C_6H_4$), 2.59 (2H, t, J=7 Hz, $CH_2C_6H_4$), 3.28 (1H, m, CH), 4.18 (2H, dd, J=10 and 10 Hz, OCH_2CH, ax), 4.27 (2H, dd, J=4 and 10 Hz, OCH_2CH, eq), 7.13 (2H, d, J=9Hz, Ar), 7.17 (2H, d, J=9 Hz, Ar), 7.18 (2H, d, J=8Hz, Ar), and 7.70 (2H, d, J=8 Hz, Ar).

2-(4-Chlorophenyl)-5-(4-hexylphenyl)-1,3,2-dioxaborinane (2g). Found: C, 70.91; H, 7.06; Cl, 9.99%. Calcd for $C_{21}H_{26}BClO_2$: C, 70.71; H, 7.35; Cl, 9.94%; IR (Nujol) 1320 cm^{-1} (BO); ^1H NMR δ=0.88 (3H, t, J=7 Hz, CH_3), 1.30—1.36 (6H, m, alkyl), 1.56—1.62 (2H, m, $CH_2CH_2C_6H_4$), 2.59 (2H, t, J=8 Hz, $CH_2C_6H_4$), 3.28 (1H, m, CH), 4.18 (2H, dd, J=11 and 11 Hz, OCH_2CH, ax), 4.27 (2H, dd, J=5 and 11 Hz, OCH_2CH, eq), 7.12 (2H, d, J=9 Hz, Ar), 7.17 (2H, d, J=9 Hz, Ar), 7.33 (2H, d, J=8 Hz, Ar), and 7.73 (2H, d, J=8 Hz, Ar).

2-(4-Methoxyphenyl)-5-(4-hexylphenyl)-1,3,2-dioxaborinane (2h). Found: C, 75.25; H, 8.16%. Calcd for $C_{22}H_{29}BO_3$: C, 75.00; H, 8.29%; IR (Nujol) 1320 (BO) and 1240 cm^{-1} (Ar-O); ^1H NMR δ=0.88 (3H, t, J=7 Hz, CH_2CH_3), 1.31—1.36 (6H, m, alkyl), 1.56 (2H, m, $CH_2CH_2C_6H_4$), 2.58 (2H, t, J=8 Hz, $CH_2C_6H_4$), 3.27 (1H, m, CH), 3.82 (3H, s, OCH_3), 4.16 (2H, dd, J=11 and 11 Hz, OCH_2CH, ax), 4.26 (2H, dd, J=5 and 11 Hz OCH_2CH, eq), 6.89 (2H, d, J=8 Hz, Ar), 7.12 (2H, d, J=8 Hz, Ar), 7.16 (2H, d, J=8 Hz, Ar), and 7.76 (2H, d, J=8 Hz, Ar); MS, m/z 352 (M^+). Elemental analysis for the derivatives of **2h** are listed in Table 5.

2-(4-Cyanophenyl)-5-(4-hexylphenyl)-1,3,2-dioxaborinane (2i). Found: C, 76.21; H, 7.59; N, 3.92%. Calcd for $C_{22}H_{26}BNO_2$: C, 76.09; H, 7.54; N, 4.03%; IR (Nujol) 2220 (CN) and 1310 cm^{-1} (BO); ^1H NMR δ=0.88 (3H, t, J=7 Hz, CH_3), 1.31 (6H, m, alkyl), 1.60 (2H, m, $CH_2CH_2C_6H_4$), 2.59 (2H, t, J=8 Hz, $CH_2C_6H_4$), 3.29 (1H, m, CH), 4.19 (2H, dd, J=11 and 11 Hz, OCH_2CH, ax), 4.29 (2H, dd, J=5 and 11 Hz, OCH_2CH, eq), 7.12 (2H, d, J=8 Hz, Ar), 7.18 (2H, d, J=8 Hz, Ar), 7.62 (2H, d, J=8 Hz, Ar), and 7.88 (2H, d, J=8 Hz, Ar). Elemental analysis for the derivatives of **2i** are listed in Table 6.

2-[4-(Methoxycarbonyl)phenyl]-5-(4-butoxyphenyl)-1,3,2-dioxaborinane (2e). 2-(4-Carboxyphenyl)-5-(4-butoxyphenyl)-1,3,2-dioxaborinane (177 mg, 0.50 mmol), prepared from 4-carboxyphenylboronic acid (**6d**) and 2-(4-butoxyphenyl)-1,3-propanediol (**5**, R=C_4H_9O), was reacted with methanol (15 ml) in the presence of sulfuric acid (0.3 ml) under reflux for 6 h. After cooling the reaction mixture, excess methanol was removed off, and the residue was purified by chromatography on silica gel using dichloromethane as an eluent. Recrystallization from hexane gave pure product (**2e**); yield 124 mg (67%); Found: C, 68.76; H, 6.71%. Calcd for $C_{21}H_{25}BO_5$: C, 68.49; H, 6.84%; IR (Nujol) 1735 (C=O), 1320 (BO), and 1280 cm^{-1} (COC); ^1H NMR δ=0.97 (3H, t, J=8 Hz, CH_2CH_3), 1.46—1.52 (2H, m, CH_2CH_3), 1.72—1.80 (2H, m, OCH_2CH_2), 3.27 (1H, m, CH), 3.92 (3H, s, CH_3OCO), 3.95 (2H, t, J=7 Hz, $CH_2OC_6H_4$), 4.17 (2H, dd, J=11 and 11 Hz, OCH_2CH, ax), 4.27 (2H, dd, J=5 and 11 Hz, OCH_2CH, eq), 6.89 (2H, d, J=9 Hz, Ar), 7.13 (2H, d, J=9 Hz, Ar), 7.87 (2H, d, J=8 Hz, Ar), and 8.01 (2H,

Table 5. Elemental Analyses for 2-(4-Methoxyphenyl)-5-(4-alkylphenyl)-1,3,2-dioxaborinanes

R	Found (%)		Molecular formula	Calcd (%)	
	C	H		C	H
CH_3	72.46	6.69	$C_{17}H_{19}BO_3$	72.37	6.79
CH_3CH_2	72.93	6.91	$C_{18}H_{21}BO_3$	73.00	7.14
$CH_3(CH_2)_2$	73.61	7.28	$C_{19}H_{23}BO_3$	73.57	7.47
$CH_3(CH_2)_3$	74.37	7.49	$C_{20}H_{25}BO_3$	74.09	7.77
$CH_3(CH_2)_4$	74.87	8.21	$C_{21}H_{27}BO_3$	74.56	8.04
$CH_3(CH_2)_5$	75.26	8.16	$C_{22}H_{29}BO_3$	75.00	8.29
$CH_3(CH_2)_6$	75.58	8.47	$C_{23}H_{31}BO_3$	75.79	8.75
$CH_3(CH_2)_7$	75.55	8.74	$C_{24}H_{33}BO_3$	75.89	8.74

Table 6. Elemental Analyses for 2-(4-Cyanophenyl)-5-(4-alkylphenyl)-1,3,2-dioxaborinanes

R	Found (%)			Molecular formula	Calcd (%)		
	C	H	N		C	H	N
CH_3	73.97	5.59	4.78	$C_{17}H_{16}BNO_2$	73.68	5.82	5.05
CH_3CH_2	74.36	5.95	4.82	$C_{18}H_{18}BNO_2$	74.25	6.23	4.81
$CH_3(CH_2)_2$	74.68	6.36	4.33	$C_{19}H_{20}BNO_2$	74.78	6.61	4.59
$CH_3(CH_2)_3$	75.23	7.05	4.09	$C_{20}H_{22}BNO_2$	75.25	6.95	4.39
$CH_3(CH_2)_4$	76.00	6.93	4.31	$C_{21}H_{24}BNO_2$	75.69	7.25	4.20
$CH_3(CH_2)_5$	76.21	7.59	3.92	$C_{22}H_{26}BNO_2$	76.09	7.54	4.03
$CH_3(CH_2)_6$	76.40	7.51	3.84	$C_{23}H_{28}BNO_2$	76.46	7.81	3.88
$CH_3(CH_2)_7$	76.58	8.17	3.71	$C_{24}H_{30}BNO_2$	76.81	8.06	3.73

d, J=8 Hz, Ar); MS, m/z 368 (M^+).

2-[4-(Methoxycarbonyl)phenyl]-5-(4-hexylphenyl)-1,3,2-dioxaborinane (2j). Found: C, 73.21; H, 7.71%. Calcd for $C_{24}H_{29}BO_4$: C, 73.48; H, 7.45%; IR (Nujol) 1735 (C=O), 1320 (BO), and 1275 cm^{-1} (COC); ^1H NMR δ=0.88 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 1.30—1.34 (6H, m, alkyl), 1.58—1.62 (2H, m, $C\underline{H}_2CH_2C_6H_4$), 2.59 (2H, t, J=8 Hz, $C\underline{H}_2C_6H_4$), 3.30 (1H, m, CH), 3.92 (3H, s, CH_3OCO), 4.20 (2H, dd, J=11 and 11 Hz, $OC\underline{H}_2CH$, ax), 4.30 (2H, dd, J=5 and 11 Hz, $OC\underline{H}_2CH$, eq), 7.13 (2H, d, J=9 Hz, Ar), 7.18 (2H, d, J=9 Hz, Ar), 7.88 (2H, d, J=8 Hz, Ar), and 8.02 (2H, d, J=8 Hz, Ar).

We thank the Material Analysis Center, I.S.I.R, Osaka University for spectral measurements and micro-analyses.

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