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Fast Thermal Breaking and Formation of a B – N Bond in 2-(Aminomethyl)benzeneboronates [1)]

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The title compounds **1** to **6** (Table 1) are shown by ^1H, ^{11}B, and ^{15}N NMR shifts to form an intramolecular B – N bond which, according to ^1H and ^{13}C NMR, is frequently broken ($\Delta G_c^{\neq}$ = 40 to 54 kJ/mol, Table 2) and re-formed.

Rasche thermische Öffnung und Schließung einer B – N-Bindung in 2-(Aminomethyl)benzolboronaten [1)]

^1H-, ^{11}B- und ^{15}N-NMR-Verschiebungen weisen darauf hin, daß die Titelverbindungen **1 – 6** (Tab. 1) eine intramolekulare B – N-Bindung ausbilden, die laut ^1H- und ^{13}C-NMR mit hoher Frequenz geöffnet ($\Delta G_c^{\neq}$ = 40 bis 54 kJ/mol, Tab. 2) und wieder geschlossen wird.

Boronic acid groups were used as the binding sites at enzyme-analogue built polymers for the specific binding of diols[2,3)]. Binding of the diols to these polymers occurs on formation of cyclic boronic diesters in an equilibrium reaction. Enhancement of the rate of such equilibration should improve the binding properties of the boronic acid. It was also considered desirable to fix the steric arrangement of the boronic acid by hindrance to rotation around the B – C axis. Investigations along these lines were first performed with low molecular weight analogues, where it was shown that the introduction of $N(CH_3)_2$ as a neighbouring group to the boronic ester function enhanced by several orders of magnitude[4)] the rate of establishing the above equilibrium in areneboronates like **1** (Table 1). Therefore, the occurrence of a B – N bond in such compounds in solution and the kinetic stability of this bonds were investigated.

1[5)], (4*S*)-**2**, **3**, (4*R*)-**4**, and **5** (Table 1) were prepared by esterification of 2-(dimethylaminomethyl)benzeneboronic anhydride[7)] with the corresponding 1,2-diols. Similarly, the known 2-tolueneboronic anhydride was converted to **7**, (4*S*)-**8**, **9**, and (4*RS*)-**10**. **6**, an ester of a new areneboronic acid, was synthesized from 2-[2-(bromomethyl)phenyl]-1,3,2-dioxaborolane and isoindoline.

The NCH_2 and NCH_3 proton-NMR signals of **1** to **5** are shifted to lower field by Δδ = +0.3 to +0.6 relative to the corresponding signals of the boron-free amine **11**

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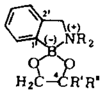
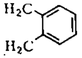
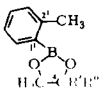
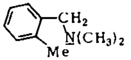
Table 1. ^1H and ^{11}B NMR shifts in $CDCl_3$ or $CHCl_3$. ^1H: 25 – 28 °C; ^{11}B: 30 °C, referred to external F_3B-OEt_2

		R_2	R′	R″	δ(^{1}H) OCH[a]	OCH$_2$	NCH$_2$	NCH$_3$	Others	δ(^{11}B)
	**1**[5]	$(CH_3)_2$	H	H	–	4.03	3.83	2.53	–	14.3
	(4*S*)-**2**	$(CH_3)_2$	H	CH_3	≈4.4	3.4 – 4.3[b]	3.85[d]	2.55	1.32, 4-CH_3	14.5
	3	$(CH_3)_2$	CH_3	CH_3	–	3.72	3.84	2.54	1.39, 4-CH_3	14.8
	(4*R*)-**4**	$(CH_3)_2$	H	C_6H_5	≈5.2	3.7 – 4.5[b]	3.91[c]	2.62	–	15.0
	5	$(CH_3)_2$	C_6H_5	C_6H_5	–	4.60	3.90	2.50	–	15.2
	6		H	H	–	3.70	4.14[e]	–	4.33, NCH_2[f]	16.1
	**7**	–	H	H	–	4.25	–	–	2.50, 2′-CH_3	32.3
	(4*S*)-**8**	–	H	CH_3	≈4.6	3.7 – 4.4[b]	–	–	2.54, 2′-CH_3 1.35, 4-CH_3	32.0
	9	–	CH_3	CH_3	–	4.00	–	–	2.52, 2′-CH_3 1.43, 4-CH_3	31.9
	(4*RS*)-**10**	–	H	C_6H_5	≈5.5	4.0 – 4.7[b]	–	–	2.60, 2′-CH_3	32.7
	**11**[6]	$(CH_3)_2$	–	–	–	–	3.32	2.20	2.32, C – CH_3	–

[a] C parts of ABC spectra. – [b] AB part of an ABC spectrum. – [c] Average shift of diastereotopic protons; $\delta_A = 3.85$, $\delta_B = 3.97$, $^2J_{AB} = 13.6$ Hz. – [d] Singlet (60 MHz) of diastereotopic protons. – [e] NCH_2 group of the ring which contains the $B-N-CH_2$ fragment. – [f] NCH_2 group of the isoindoline ring.

(Table 1). A similar trend is detected for the trimethylamine/trimethylborane complex relative to free trimethylamine ($\Delta\delta = +0.27$ at $-70\,°C$)[8] and for the socalled triethanolamine borate[9] relative to tris(2-hydroxyethyl)amine (triethanolamine) ($\Delta\delta = +0.5$ at $+35\,°C$)[10]. We conclude that our 2-(dimethylaminomethyl)boronates **1**–**6** exist in solution at room temperature as spiro compounds with intramolecular B–N bonds (see formula in Table 1), either exclusively or in fast equilibrium[11] with a small amount of the B – N-opened analogue. Such bonds are known for some other N-containing boranes[9,12,13,14]. *Inter*molecular B – N bonding is apparently not significant, as judged from molecular weight measurements[15] for **4** and from the insensitivity of its ^1H shifts to a concentration change by a factor of 10.

The ^{11}B shifts of **1** to **6** are to higher field by $\Delta\delta = -17$ to -18 relative to the nitrogen-free boronates[16] **7** to **10** (Table 1). This finding for our 2-(aminomethyl)benzeneboronates indicates *tetra*coordinate boron which generally[13] shows a shift to higher field compared with a tricoordinate environment[18].

The ^{15}N shift of **4** ($\delta = -327.2$, [D$_6$]acetone, 32 °C, referred to $^{15}NO_3^{\ominus}$) is to lower field by $\Delta\delta = +25.7$ relative to the boron-free amine **11** ($\delta = -352.9$ neat)[19]. This finding for **4** again indicates a tetracoordinate nitrogen, which generally[20] shows a shift to lower field compared with a tricoordinate one.

The ^1H and ^{13}C NMR spectra of **1** to **6** show reversible broadening and splitting of certain signals at temperatures below $-15\,°C$. For example, geminal CH_2 protons of **5** show unequal shifts (Figure 1). The coupling constants $^2J_{HH} = 8.8$ and 14.4 Hz thus obtained served for the distinction[21] between OCH_2 and NCH_2 absorptions in Figure 1. Such $^2J_{HH}$-values (Table 2) were also used for the assignments of CH_2 groups in Table 1. $\Delta G_c^{\ddagger}$ was determined[22] from the coalescence of corresponding signals (Table 2).

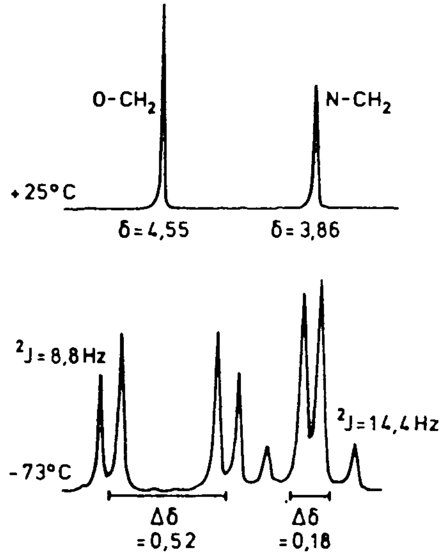
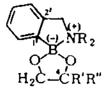
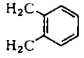


Figure 1. ^1H PFT-NMR (90 MHz) of CH_2 groups of **5** in CD_2Cl_2. See Figure 2 for formulae

Table 2. ^{1}H and ^{13}C NMR data at low temperatures T and $\Delta G_c^{\ddagger}$-values for B – N bond breaking determined[22] from coalescence in CD_2Cl_2. ^{1}H at 90 MHz; ^{13}C at 22.63 MHz. Cf. Figure 2 and text for steric details. $\Delta\delta_T$: Shift difference at temperature T for the nuclei used



	R_2	R′	R″	Nuclei used	T [°C]	$\Delta\delta_T$ [–]	$^2J_{HH}$ [Hz]	T_c [°C]	$\Delta G_c^{\ddagger}$ [kJ/mol]
1	$(CH_3)_2$	H	H	$\mathrm{N-C}\mathit{H}_2$	– 71	< 0.03	?	–	–
				$\mathrm{N-C}\mathit{H}_3$	– 71	< 0.03	–	–	–
				$\mathrm{N-}\mathit{C}\mathrm{H}_3$	– 30	< 0.1	–	–	–
				$\mathrm{O-C}\mathit{H}_2$	– 71	< 0.02	?	?	?
3	$(CH_3)_2$	CH_3	CH_3	$\mathrm{N-C}\mathit{H}_2$	– 88	0.26	14.1	?	?
				$\mathrm{N-C}\mathit{H}_3$	– 91	0.17	–	– 73	41.7 ± 0.8
				$\mathrm{N-}\mathit{C}\mathrm{H}_3$	– 89	1.59	–	– 73	40.0 ± 1.0
				$\mathrm{O-C}\mathit{H}_2$	– 88	0.08	8.5	?	?
				$\mathrm{C-}\mathit{C}\mathrm{H}_3$	– 89	1.46	–	– 75	40.1 ± 1.0
				$\mathrm{C-C}\mathit{H}_3$	– 91	< 0.03	–	?	?
4	$(CH_3)_2$	H	C_6H_5	$\mathrm{N-C}\mathit{H}_3$	– 50	0.05[c]	–	– 30	53.5 ± 0.8
				$\mathrm{N-}\mathit{C}\mathrm{H}_3$	– 30	0.85[c]	–	≈ – 15	54.0 ± 1.6
5	$(CH_3)_2$	C_6H_5	C_6H_5	$\mathrm{N-C}\mathit{H}_2$	– 73	0.18	14.4	≈ – 38	49.1 ± 1.6
				$\mathrm{N-C}\mathit{H}_3$	– 73	∼0.04	–	?	?
				$\mathrm{N-}\mathit{C}\mathrm{H}_3$	– 40	1.83	–	≈ – 27	49.4 ± 1.6
				$\mathrm{O-C}\mathit{H}_2$	– 73	0.52	8.8	– 31	48.4 ± 0.8
				ipso-C in C_6H_5	– 40	0.87	–	≈ – 32	49.9 ± 1.6
6		H	H	$\mathrm{N-C}\mathit{H}_2$[a]	– 92	0.63	14	– 52	43.4 ± 0.8
				$\mathrm{O-C}\mathit{H}_2$	– 92	∼0.3[b]	?	?	?

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[a] NCH_2 groups in R_2 (isoindoline ring). – [b] Two broad absorptions (widths ≈ 18 Hz) at – 90 °C, the coalescence of which results in a singlet (linewidth 0.7 Hz) at + 25 °C. – [c] Intensities ≈ 1 : 1; cf. text.

As far as the underlying process or processes are concerned, motions of nonplanar intact five-membered rings would have much lower[23] $\Delta G_c^{\ddagger}$-values than observed here. Therefore, opening of the B – N or B – O bond in our dioxoborolanes must occur. We assume B – N opening since B – N has a much lower bond energy[24] and is opened much faster in a somewhat similar oxazaborolidine[14]. The B – N opened 2-(aminomethyl)benzeneboronates like **12** (Figure 2) have not been detected in the ^1H NMR spectra at low temperatures and should therefore correspond to higher free enthalphy than the spiro ground states. The processes responsible for the spectral changes in Table 2 are symbolized in Figure 2 for **5** as an example. Interconversions **5** $\rightleftharpoons$ **5'** are brought about by B – N bond breaking, nitrogen inversion, $CH_2 - N$ rotation, and B – N bond formation; the environments of $(CH_3)^1/(CH_3)^2$ are thereby exchanged. Interconversions $(R) \rightleftharpoons (S)$ are brought about by B – N bond breaking, boron inversion, C – B rotation, and B – N bond formation; the environments of $(CH_3)^1/(CH_3)^2$, H^1/H^2, H^3/H^4, and C^1/C^2 are thereby exchanged. Since the barriers to the above inversions and rotations must be considered as low with regard to the observed barriers (Table 2), B – N bond breaking is apparently rate-determining*). From these facts we derived $k_e = k/2$, where k is the rate constant for the B – N bond breaking (Figure 2) and k_e the experimental rate constant. This factor of 2 has been applied for the calculations of $\Delta G_c^{\ddagger}$ in Table 2.

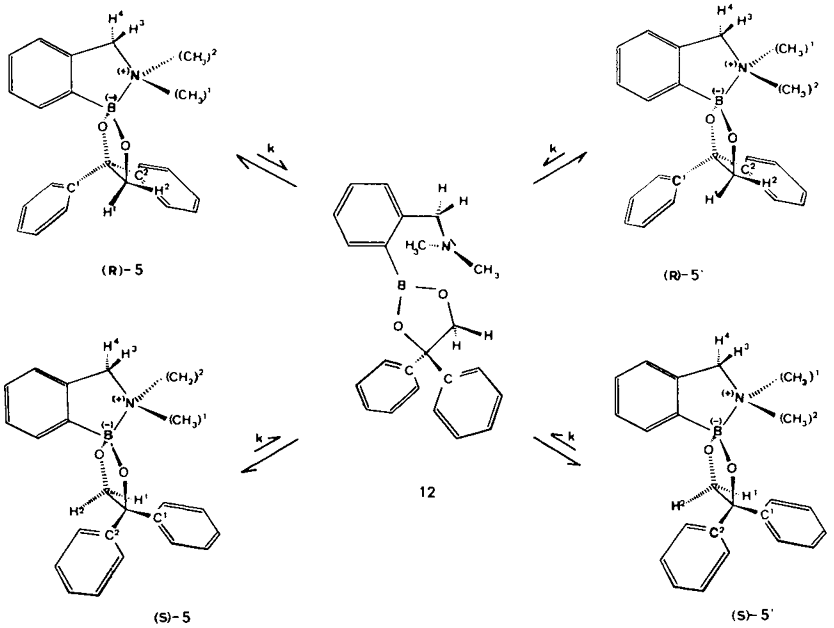

Figure 2. Intramolecular processes in **5**. Indices 1 and 2 as well as 3 and 4 mark individual *groups* (not environments). Cf. text for description of processes

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*) *Note added in proof (15. 7. 81):* Similar intramolecular Sn – N bond breaking and formation have been described by *G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, G. J. Verhoeckx, A. L. Spek,* and *J. Kroon,* J. Chem. Soc. Dalton Trans. **1980**, 1352, and earlier papers.

The two methyl signals (intensities 1:1) in the ^{1}H and ^{13}C spectra of **4** at low temperatures are assigned to diastereotopic groups in only one of the two possible diastereomers, because their shift differences (Table 2) are similar to the ones of **5** which cannot form diastereomers. From their line-shapes, we suggest that the absorption of the less abundant diastereomer is hidden. The ^{13}C spectrum of **2** at −60°C indicates both diastereomers in a ≈ 2:1 ratio.

Inter-comparisons of our $\Delta G_c^{\neq}$-values, e.g. for **3** and **5**, must be postponed until further measurements, including the ones of $\Delta S^{\neq}$, have been carried out.

The only known barriers to B−N bond breaking seem to be the ones in the trimethylamine/trimethylborane complex[8] ($\Delta G^{\neq}$ = 54 kJ/mol, −24°C) and in an oxazaborolidine[14] ($\Delta G^{\neq}$ = 51 kJ/mol[25], −17°C). Their height is similar to the results in Table 2. The ease and reversibility of these reactions suggest that NMR at room temperature averages between free and complexed amines and boronates. Since the latter are obtained optically active more easily than boranes, our above results may be extended to the study of the intermolecular interaction between chiral amines and boronates by NMR splittings due to diastereomeric complexes[26].

This research was supported by *Deutsche Forschungsgemeinschaft*, the *Minister für Wissenschaft und Forschung von Nordrhein-Westfalen*, and *Fonds der Chemischen Industrie*. We are grateful to Mr. *H.-H. Henschel* for running some of the spectra and to Dipl.-Phys. *R. Küspert* for helpful discussions.

Experimental Part

Melting points: Kofler-Weygand hot bank (Leitz). − Microanalyses: Microanalytical laboratory Dr. F. Pascher, Bonn, or microanalytical laboratories of the Universities of Bonn and Düsseldorf. − ^{1}H NMR: Some spectra were taken on Varian EM 360 or EM 390 at 32°C. Most measurements were performed on a Bruker WH-90 (normal temperature +25°C) with 8 K data points for the interferogram and sweep widths between 500 and 900 Hz; temperatures were measured according to *Van Geet*[27] by calibration of the Bruker methanol tube *vs.* a Varian methanol tube on a Varian XL-100 spectrometer. − ^{11}B NMR: Bruker WH-90 at 30°C. − ^{13}C NMR: Bruker WH-90 (normal temperature +32°C) with 8 K data points for the interferogram and sweep widths between 3000 and 4200 Hz; temperatures were measured by a "Thermocoax" thermocouple (Chromel-Alumel) from Philips GmbH, Kassel. − Optical rotations: Perkin-Elmer 241 polarimeter. − Mol. weight determinations: Vapour-phase osmometer (Knauer).

The preparations of **1**[5], **11**[6], isoindoline[28], 2-tolueneboronic anhydride[29], and 2-(dimethylaminomethyl)benzeneboronic anhydride[7] have been described before. The desired diols (*S*)-1,2-propanediol[30], 2-methyl-1,2-propanediol[31], (*R*)-1-phenyl-1,2-ethanediol[32], and 1,1-diphenyl-1,2-ethanediol[33] were prepared as described.

General procedure for the preparation of boronic esters (Table 3): Equimolar amounts of substituted boronic anhydrides (triphenylboroxins) and diols were stirred mechanically in boiling toluene, the water being collected in a Dean and Stark apparatus. After evaporation under vacuum the residue was destilled or crystallized. ^{1}H and ^{11}B NMR spectra see Table 1, ^{13}C NMR see Table 4.

Table 3. Synthesized boronic esters

	Name	Yield (%)	b.p. [°C]/ p[Torr] (m.p.) [°C]	Optical rotation	Mol. formula (Mol. weight)	Calc. Found	C C	H H	B B	N N
(4*S*)-**2**	(*N* – *B*)-2-[2-(Dimethylaminomethyl)phenyl]-(4*S*)-4-methyl-1,3,2-dioxaborolane	72	124 – 125/0.1	$[\alpha]_{436}^{20}$ = +34.2 (c = 2.1, CH_3CN)	$C_{12}H_{18}BNO_2$ (219.1)		65.79 64.78	8.28 8.12	4.93 4.86	6.39 6.26
3	(*N* – *B*)-2-[2-(Dimethylaminomethyl)phenyl]-4,4-dimethyl-1,3,2-dioxaborolane	63	92/0.05	–	$C_{13}H_{20}BNO_2$ (233.1)		66.98 66.69	8.65 8.68	4.64 4.74	6.01 5.98
(4*R*)-**4**	(*N* – *B*)-2-[2-(Dimethylaminomethyl)phenyl]-(4*R*)-4-phenyl-1,3,2-dioxaborolane	71	(86 – 88)	$[\alpha]_{589}^{20}$ = –39.1 (c = 2.9, $CHCl_3$)	$C_{17}H_{20}BNO_2$ (281.2)		72.62 72.84	7.17 6.94	3.85 3.78	4.98 5.07
5	(*N* – *B*)-2-[2-(Dimethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane	74	(129 – 132)	–	$C_{23}H_{24}BNO_2$ (357.3)		77.33 77.30	6.77 6.87	3.03 2.95	3.92 3.80
7	2-(2-Tolyl)-1,3,2-dioxaborolane	90	68/0.3	–	$C_9H_{11}BO_2$ (162.0)		66.73 66.74	6.84 6.85	– –	– –
(*S*)-**8**	(*S*)-4-Methyl-2-(2-tolyl)-1,3,2-dioxaborolane	78	63 – 65/0.4	$[\alpha]_{436}^{20}$ = +37.6 (c = 0.7, $CHCl_3$)	$C_{10}H_{13}BO_2$ (176.0)		68.24 68.03	7.44 7.41	– –	– –
9	4,4-Dimethyl-2-(2-tolyl)-1,3,2-dioxaborolane	77	46/0.05	–	$C_{11}H_{15}BO_2$ (190.1)		69.52 69.28	7.96 8.08	5.69 5.83	– –
(*RS*)-**10**	(*RS*)-4-Phenyl-2-(2-tolyl)-1,3,2-dioxaborolane	60	144/0.1	–	$C_{15}H_{15}BO_2$ (238.1)		75.67 75.71	6.35 6.41	– –	– –

Table 4. Shifts δ(^{13}C) in CD_2Cl_2 at +32°C. See Table 1 for formulae

	C-1′	C-2′	Carbons in C_6H_5 C-1	C-2	C-3	C-4	C-3′	C-4′ (not assigned)	C-5′	C-6′	OCH_2	NCH_2	NCH_3	Further carbons
1	[a]	140.76		–			131.10	127.86	127.51	123.21	65.16	64.77	45.30	–
3	≈144[b]	140.46		–			130.94	127.59	127.36	123.01	76.16	64.52	45.17	28.50, 4-CH 76.84, C-4
4	[a]	140.48	144.43	125.90	128.48	[c]	131.06	[c]	[c]	123.09	72.59	64.85	45.30	77.67, C-4
5	≈143[b]	140.46	148.63	126.16	128.27	126.71	131.47	127.80	127.45	122.96	75.41	65.05	45.56	84.98, C-4
11	137.5[d]	137.63[d]		–			130.40	130.05	127.19	125.67	–	62.54	45.46	19.08, *C* – CH

[a] Not observed. – [b] Broad signal. – [c] The signals at δ = 127.23, 127.54, and 127.86 could not be assigned. – [d] Assignment may be reversed.

2-[2-(Bromomethyl)phenyl]-1,3,2-dioxaborolane: 18.6 g (0.115 mol) 2-(2-tolyl)-1,3,2-dioxaborolane (**7**), 20.6 g (0.116 mol) *N*-bromosuccinimide and 0.3 g benzoyl peroxide were refluxed in 650 ml carbon tetrachloride for 2 h under illumination with a 500 W photolamp. The mixture was filtered, evaporated in vacuo and destilled. Yield: 15.8 g (59%), b. p. 108°C/0.6 Torr.

$C_9H_{10}BBrO_2$ (240.9) Calc. C 44.86 H 4.19 Found C 45.00 H 4.19

(N – B)-2-[2-(2-Isoindolinylmethyl)phenyl]-1,3,2-dioxaborolane (**6**): To 2.5 g (10.4 mmol) of 2-[2-(bromomethyl)phenyl]-1,3,2-dioxaborolane in 100 ml of toluene 2.5 g (21.0 mmol) of isoindoline in 50 ml of toluene were added. The mixture was kept at room temperature for one day, then filtered. The filtrate was evaporated to dryness. 1.4 g (48%) of colourless crystals: m. p. 173 – 175°C (benzene). – ^{1}H and ^{11}B NMR: Table 1.

$C_{17}H_{18}BNO_2$ (279.1) Calc. C 73.15 H 6.50 B 3.87 N 5.02
Found C 73.39 H 6.49 B 3.71 N 4.91

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14) *H. Kessler, G. Zimmermann, H. Fietze,* and *H. Möhrle,* Chem. Ber. **111,** 2605 (1978).

15) The molecular weight of **4** was determined by vapour-phase osmometry in chloroform at varying concentrations. For concentrations 7.6 – 140 mmol/l molecular weights ranging from 27 to 265 were obtained (calc. 281). The same measurements were made for **10.** For concentrations 14.4 – 111.8 mmol/l molecular weights from 227 to 237 were found (calc. 238). In botl cases only a slight influence of concentration on the molecular weight was observed, therefor no intermolecular association is assumed.

16) The δ(^{11}B)-values for **7** to **10** (Table 1) are in agreement with the shifts of similar boronates 17)

17) *R. H. Cragg* and *J. C. Lockhart,* J. Inorg. Nucl. Chem. **31,** 2282 (1969).

18) The ^{13}C NMR shifts of amines do not change appreciably by the formation of quarternar compounds (cf. Table 4).

19) *G. J. Martin,* Nantes, France, unpublished result. We are grateful to Professor *Martin* fo these measurements and for helpful discussions.

20) *M. Witanowski, L. Stefaniak,* and *G. A. Webb* in *G. A. Webb* (ed.), Annual Reports on NM Spectroscopy, Vol. 7, p. 117, Academic Press, London 1977.

21) $^{2}J_{HH}$ = 8.1 and 8.7 Hz in the OCH_2 groups of **8** and **10,** respectively (see Table 1 fo formulae). $^{2}J_{HH}$ = 12.5 to 12.8 Hz in the NCH_2 groups of *N,N*-dibenzylanilinium ions: *A Mannschreck* and *H. Münsch,* Tetrahedron Lett. **1968,** 3227, and unpublished results. $^{2}J_{HH}$ = 14.6 Hz in the NCH_2 groups of *N*-(2,6-dimethylphenyl)isoindolinium ion: *A. Mannschrec* and *E. Keck,* unpublished result.

22) The chemical shifts extrapolated to T_c, the linewidths in the absence of exchange, and th coupling constants $^{2}J_{HH}$ were taken into account using a diagram (*H. Friebolin, H. G Schmid, S. Kabuß,* and *W. Faißt,* Org. Magn. Reson. **1,** 147 (1969)).

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