Monomeric and Dimeric Acyloxydialkylboranes†

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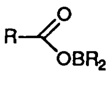
The carboxylic acids RCO_2H [R = Bu^t **a**, Et **b**, 3,4,5-$(MeO)_3C_6H_2$ **c**, 4-$MeOC_6H_4$ **d**, Ph **e**, 2,4,6-$Me_3C_6H_2$ **f**, 2,6-$Cl_2C_6H_3$ **g**, or 3,5-$(CF_3)_2C_6H_3$ **h**] were treated with triethylborane or with bis(9-borabicyclo[3.3.1]nonane) to give the acyloxydiethylboranes **1a–1h** and the 9-acyloxy-9-borabicyclo[3.3.1]nonanes) **2a–2h**, respectively. Compounds **1a–1h** are largely unassociated in non-polar solvents (^{11}B NMR, IR spectroscopy). As pure liquids, or in the solid state, they form equilibrium mixtures of monomeric and associated (dimeric) molecules (IR spectroscopy). Compounds **2a–2f** are completely associated as pure liquids and in the solid state, but only weakly associated in non-polar solvents. Based on the crystal structure of dimeric **2e**, it is proposed that, when associated, derivatives of both **1** and **2** form cyclic dimers.

Several years ago one of us reported the synthesis and reactivity of the addition complexes **II** of the acyloxydiorganoboranes **I** with dimeric dialkylboranes.[1] The complexes **II** were thermally unstable in solution at above room temperature and in the solid state at about 125–130 °C. The thermal decomposition (probably *via* the corresponding aldehyde stage) leads, in a series of redox and elimination steps, reminiscent of the Cannizaro reaction, to an equimolar mixture of the starting compound **I**, the alkoxydialkylborane **III**, and the bis(dialkylboryl) oxide **IV**.

In extension of the above study, we have found renewed interest in the structure of acyloxydiorganoboranes. The surprisingly sparce published data available to date on this class of compounds suggest the presence of the monomeric structure **I** in the gas phase (*e.g.* $Me_2BOCOMe$)[2] and probably a dimeric structure **V** [*e.g.* $(1,5\text{-}C_8H_{14}BOCOMe)_2$][3] in solution and in the solid state. Other derivatives studied appear to consist of temperature-dependent equilibrium mixtures of these two forms, both in solution and in the solid states.[4–6] To explain the observed infrared absorption bands an intramolecularly co-ordinated monomeric species **VI**, an unsymmetrical dimer **VII** and even polymeric structures have been suggested.[4] A study of the structural features responsible for the shift in the monomer–dimer equilibrium concentration and an X-ray analysis of a crystalline derivative have so far not been carried out. Herein we report our results on these.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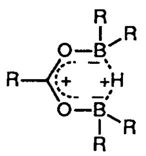
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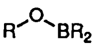
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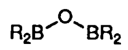
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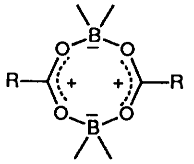
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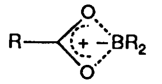
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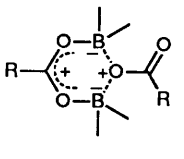
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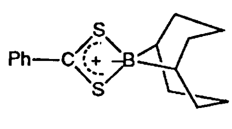
VIII

Results and Discussion

The acyloxydialkylboranes used in this study were prepared by two different methods: diethylboryl derivatives **1a–1h** were obtained from the reaction of the corresponding carboxylic acids with triethylborane[6] and cyclooctane-1,5-diylboryl derivatives **2a–2h** by the reaction of the respective carboxylic acid with stoichiometric amounts of bis(9-borabicyclo[3.3.1]-nonane).[1] In all cases the calculated amounts of gas (EtH or H_2, respectively) was released and the products formed were essentially quantitative and were generally used without further purification. Substituents on the carboxylic acids were selected to exert the maximum amount of electronic or possibly steric effects on the monomer:dimer ratios. We expected the significantly larger Lewis acidity of the boron atom in the 9-borabicyclononane moiety[7] to increase the tendency to form dimers.

(*a*) ^{11}B *NMR Study.*—Table 1 shows the results of our ^{11}B NMR studies. The acyloxydialkylboranes are arranged in order of the expected net increase in electron-withdrawing power of the substituent(s) on the carboxyl group, *i.e.* on the pK_a values of the parent carboxylic acid.[8] It is seen that the ^{11}B NMR chemical shifts of the diethylboryl derivatives **1a–1h** are generally insensitive to the carboxylic acid structure and the

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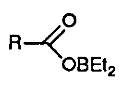
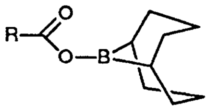
† *Supplementary material available:* Further details of the crystal structure investigation are available on request from the Fachinformation Zentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany on quoting the depository number CSD-320530, the names of the authors, and the journal citation.



1

	R
a	Bu^t
b	Et
c	3,4,5-$(MeO)_3C_6H_2$
d	4-$MeOC_6H_4$



2

	R
e	Ph
f	2,4,6-$Me_3C_6H_2$
g	2,6-$Cl_2C_6H_3$
h	3,5-$(CF_3)_2C_6H_3$

Table 1 ^{11}B NMR chemical shifts (δ) for compounds **1a–1h** and **2a–2h**

R	Solvent	1	2
a	$CHCl_3$	58	31
	$CHCl_3$	41 (−30 °C)	14 (−30 °C)
b	$CHCl_3$	58	32
c	$CHCl_3$	57	28
	thf	n.m.	14
d	$CHCl_3$	56	30
	thf	n.m.	14
e	$CHCl_3$	57	
	$CHCl_3$	37 (−30 °C)	n.m.
	thf	n.m.	15
f	$CHCl_3$	56	48
g	$CHCl_3$	61	64
h	$CHCl_3$	61	56

n.m. = Not measured.

Table 2 Infrared carbonyl bands (cm^{-1}) for compounds **1a–1h** and **2a–2h**

	1		2	
R	30 °C	80 °C	30 °C	80 °C
a	1600s* 1750m*	1595m* 1750s*	1590s	1575s 1750m
b	1600s* 1745m*	n.m.	1575s 1610(sh)	1575m 1610s 1760m
c	1560s	1580s 1725m	1550s	1550s
d	1555m 1595s	1555m 1595s 1730m	1540m 1590s	1540s 1590s
e	1555s 1600s 1722s	1555m 1600m 1722s	1555s 1592s	1555s 1592s
f	1575w 1600m	1580m 1600m 1730s	1550m 1585s	1550m 1585m
g	1585s	1580w 1750s	1640s 1755w	1580w 1600m 1750s
h	1610m 1735s	1612w 1740s	1590s 1630s 1740w	1600w 1630m 1740s

n.m. = Not measured. * Measured as liquid film.

compounds are certainly monomeric [δ(^{11}B) ≈ 60][9] and unassociated in non-polar solvents ($CDCl_3$, at room temperature). Those corresponding to the 9-borabicyclononane derivatives **2a–2h** have ^{11}B chemical shift, ranging from δ ≈ 28 for the carboxylic acids with strong electron-donating groups to δ 64.0 for one with a strong electron-withdrawing group. The chemical shifts of all derivatives **2** are concentration dependent. The values given in Table 1 are from *ca.* 6 × 10^{-1} mol dm^{-3} solutions. At such concentrations most derivatives **2a–2e** in non-polar solvents are only loosely associated, despite the fact that the 9-borabicyclononane moiety in these molecules acts as a stronger Lewis acid than the diethylboryl group in **1**. The presence of very strong electron-donor substituents has little effect. With increasing electron-withdrawing power of the substituents and therefore decreasing donating power of the carbonyl oxygen atom, *e.g.* in **2h** and **2f**, the presence of only the non-associated monomeric species is indicated. The unusually large low-field shift of the ^{11}B NMR signal of the 2,4,6-trimethylbenzoic acid derivative **2f** points to the presence of a largely monomeric species. On purely electronic considerations it is to be expected that **2f** would give a more stable dimer and therefore have a smaller chemical shift (to higher field) than observed for the benzoic acid derivative **2e**. Similarly, it is reasonable to expect that the 2,6-dichlorobenzoic acid derivative **2g** should also have a stronger tendency for dimer formation and have a signal at higher field in its ^{11}B NMR spectrum than that of the 3,5-bis(trifluoromethyl)benzoic acid derivative **2h**. The discrepancies observed can be attributed to steric interactions of the *ortho* substituents in **2f** and **2h** which prevent the efficient π-orbital overlap of the corresponding aryl ring with the carbonyl group and therefore decrease its Lewis basicity [see also section (*c*)].

When measured in tetrahydrofuran (thf) the ^{11}B NMR signals are, as a result of complexation with the polar solvent, shifted to δ 13–15, nearer to the values expected for tetravalent boron atoms.[9]

The contribution of the proposed intramolecularly co-ordinated four-membered ring species **VI** is probably insignificant. The ^{11}B NMR experiments show a continuous low-field shift upon dilution. Species **VI** should remain largely unaffected by concentration variations. It is interesting that the 9-borabicyclononane derivatives of dithiocarboxylic acids are monomeric even in the solid state. An X-ray structure determination of the corresponding derivative of dithiobenzoic acid **VIII** shows that, in analogy to **VI**, it is intramolecularly complexed.[10] In the few cases studied, the observed large temperature dependence of the ^{11}B chemical shifts of the derivatives of **1** and **2** also points to the formation of intermolecular complexes. In case of **1a** only a weak complex is present at −30 °C, while the corresponding 9-borabicyclononane derivative **2a** appears to have a four-co-ordinated boron atom at the same temperature. Similarly, the alternative dimer **VII**, if at all viable, could not be detected. The ^1H and ^{13}C NMR spectra of, *e.g.*, **2c** show only one set of signals for the respective atoms of the carboxylic acid moiety, in agreement with a symmetrical dimeric structure, or a loosely associated species.

(*b*) *Infrared Study*.—Infrared spectra were generally measured as liquid films, solution-suspensions in paraffin, and in some cases as solutions in CCl_4 or $CHCl_3$. [Generally (with the exception of **1g**) the infrared spectra of the acyloxydialkylboranes showed varying extents of hydrolysis products (the corresponding free carboxylic acid) when the measurements were made on sample probes in KBr.] Table 2 lists the bands observed for the associated (1550–1610 cm^{-1}) and free (1700–1760 cm^{-1}) carbonyl groups, at room temperature and at +80 °C. As expected, with the exception of **2c–2f**, a free C=O band develops, or the existing weak band shows enhanced intensity at +80 °C. This increase in intensity at >1700 cm^{-1} and thus the associate–monomer conversion is however not complete at 80 °C and in some cases heating to above 80 °C is necessary to affect complete monomerization. Thus for example **2e** shows a free carbonyl band at 1755 cm^{-1} at about 90 °C and, as can be seen from the spectra in Fig. 1, heating to 130 °C is necessary to complete the process. Compound **2c** develops a weak band at 1770 cm^{-1} only above 140 °C. It should be noted that recooling of the samples generally restores the original spectra. Within the accuracy of the temperature measurements at the sample site, irrespective of the direction of approach (heating or cooling), an identical spectrum is obtained at any given temperature. As in the case of **2e**, there is no carbonyl absorption at > 1700 cm^{-1} in the room-temperature spectra of the acyloxydialkylboranes **1c**, **1d**, **1f** and **2a–2f**. However, the derivatives **1a**, **1b**, **1e**, **1g**, **1h** and **2g**, **2h**

Table 3 Selected bond lengths and angles for compound **2e**

B–O(1)	1.555(3)	O(1)–C(1)–O(2′)	124.4(2)
B–O(2)	1.555(2)	B–O(1)–C(1)	126.9(1)
B–C(8)	1.592(2)	B–O(2)–C(1′)	127.5(1)
B–C(12)	1.592(3)	O(1)–B–O(2)	108.7(1)
O(1)–C(1)	1.269(2)	C(8)–B–C(12)	108.9(1)
O(2)–C(1′)	1.273(2)	C(8)–B–O(1)	107.6(1)
C(1)–C(2)	1.471(3)	C(12)–B–O(1)	111.9(1)

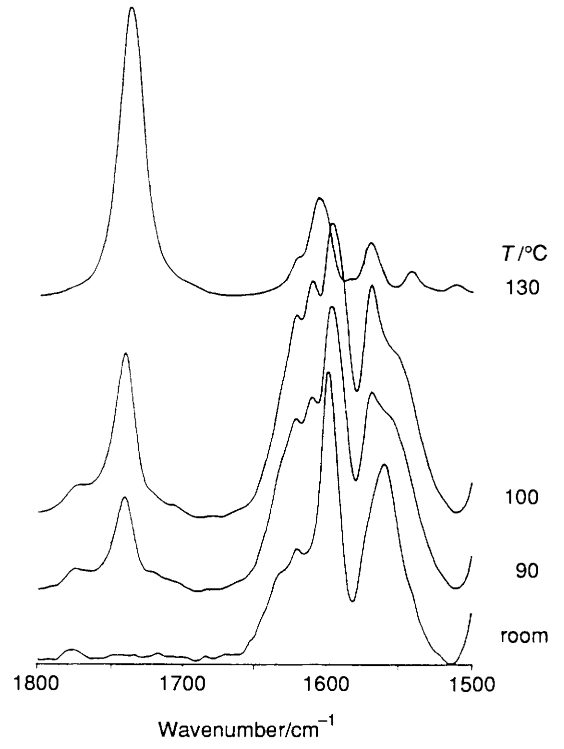


Fig. 1 Temperature dependence of the infrared spectra of compound **2e**

all possess free C=O bands of varying intensity at 1720–1755 cm^{-1}.

(*c*) *X-Ray Study of Dimeric* **2e**.—The structure of the crystalline dimer was obtained by X-ray analysis. Fig. 2 shows the molecular structure and selected bond lengths and angles are given in Table 3. It can be seen that the central eight-membered ring has a chair conformation with an interplanar angle between the planes defined by the atoms O(1)BO(2) and O(1)C(1)O(2′)O(1′)C(1′)O(2) of 116.0°. Each of the substituent phenyl rings is coplanar with the atoms O(1)C(1)O(2′) reflecting π-orbital overlap of the arene with the trigonal C(1) carbon atom. This electronic interaction results in shortening of the C(1)–C(2) bond to 1.471 Å, showing a considerable double-bond character. Similar and significant double-bond character is also present between C(1) and atoms O(1) and O(2), respectively. The bond angles about C(1) reflect the trigonal nature of this atom and those about B its tetravalency. The angles O(1)–C(1)–O(2′) and B–O(1)–C(1) are with 124.4 and 126.9°, somewhat widened, indicating the existence of strain in the ring. For comparison the bond angles O(1)–C(1)–O(2) and C(1)O(1)B in **II** (R = 1,5-C_8H_{14}) are 120.9 and 125.7°, respectively.[11] Fig. 2 shows that while in **2e** the intramolecular non-bonded distance of 2.39 Å between H(3) or H(3′) and C(9)C(13) of the neighbouring 9-borabicyclononane moiety indicates no significant crowding, *ortho* substitution by large groups such as methyl or chlorine, as in **2f** or **2g**, should bring them to within the van der Waals radii of H(3) and H(7) unless the phenyl rings rotate out of the O(1)C(1)O(2) plane and thereby loosen the favourable π orbital overlap. The existence of these interactions are considered to favour the existence of a monomeric structure in **1g**, **1h**, **2g** and **2h** in solution.

Furthermore, since the infrared experiments had shown, *e.g.* for compound **2g**, the presence and the hysteresis-free temperature-dependent interconversion of both free and associated carbonyl absorption bands at 1755 and 1640 cm^{-1}, respectively, it can be assumed that in these thermal solid-state reactions the dimer molecules are converted into monomers and *vice versa* without significant changes in the crystal-lattice structure.[12]

Conclusion

All acyloxydialkylboranes are monomeric, or only very loosely

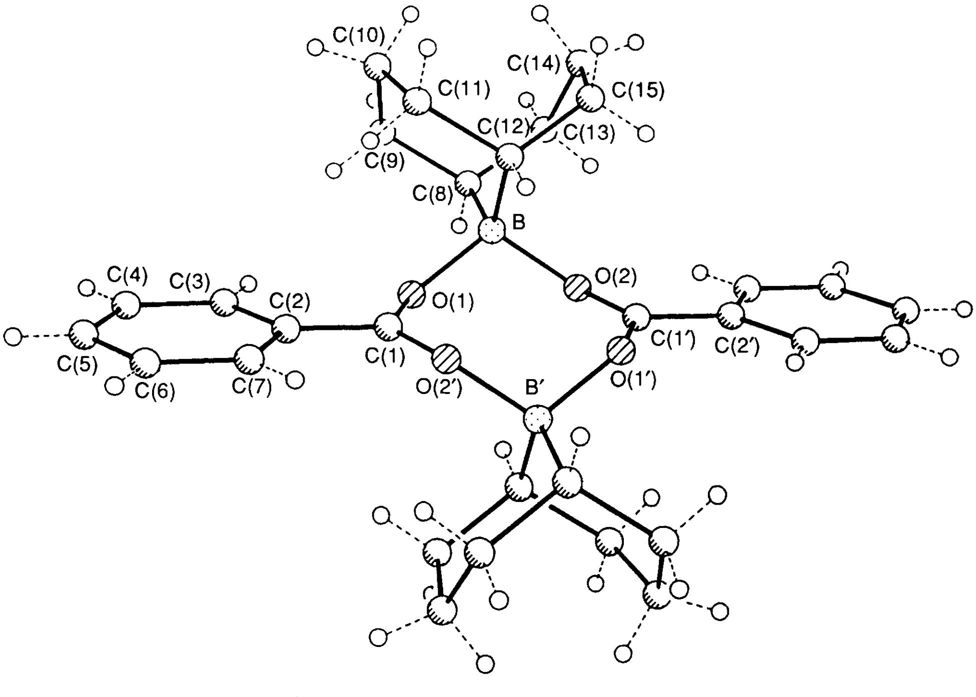


Fig. 2 Molecular structure of compound **2e**

Table 4 Atomic coordinates (× 10^4) for compound **2e**

Atom	*X/a*	*Y/b*	*Z/c*
B	2 941(3)	−1 400(2)	9 072(2)
O(1)	3 230(2)	79(1)	8 753(1)
O(2)	3 306(2)	−889(1)	10 510(1)
C(1)	4 944(3)	696(2)	8 702(2)
C(2)	4 919(2)	1 223(2)	7 663(1)
C(3)	3 007(2)	1 161(2)	6 836(1)
C(4)	2 967	1 672	5 855
C(5)	4 840	2 246	5 701
C(6)	6 752	2 308	6 528
C(7)	6 792	1 796	7 509
C(8)	553(3)	−2 132(2)	8 465(2)
C(9)	130(3)	−2 566(2)	7 047(2)
C(10)	1 715(3)	−3 565(3)	6 410(2)
C(11)	4 034(3)	−3 096(2)	7 109(2)
C(12)	4 468(3)	−2 678(2)	8 531(2)
C(13)	188(3)	−3 533(2)	8 832(2)
C(14)	1 786(3)	−4 752(2)	8 577(2)
C(15)	4 096(3)	−4 081(2)	8 889(2)

The pivotal atoms of the rigid groups have standard deviations for the first atom only.

self associated in dilute solutions and generally dimeric in the solid state. In some cases, depending on the temperature, even in the solid state (IR) both monomeric and dimeric species are simultaneously present. Apparently three factors, (*a*) the Lewis acidity of the boryl group, (*b*) electronic effects of the substituents on the carboxylic acid group, and (*c*) *ortho* steric effects of these substituents, have some influence on intermolecular complex formation. When either the Lewis acidity of the boryl group or the basicity of the carbonyl oxygen atom is low a monomeric species is present.

Experimental

Instruments used: IR, Perkin Elmer 297, Nicolet 7199 FT-IR system; Raman, CODERG LRT 800; mass spectrum, MAT CH_5; ^1H,^{11}B,^{13}C NMR, Bruker AC 200 with $SiMe_4$ as internal and Et_2O-BF_3 as external standards. All operations were carried out under oxygen-free dry argon. Solvents were freshly dried and distilled.

Acyloxydiethylboranes, **1a**–**1h** (*General Procedure*).[6]—The liquid carboxylic acid (4–6 g) was placed in a cooled vessel (−80 °C) and a slight molar excess of BEt_3 added [the solid carboxylic acids were first dissolved in toluene (10–20 cm^3)]. The mixture was slowly warmed to 50–80 °C and the gas evolved collected in a gasometer. On completion of the reaction the volatiles were removed at reduced pressure. In case of liquid products purification was achieved by vacuum distillation and when solid by crystallisation from a non-polar solvent.

9-*Acyloxy*-9-*borabicyclo*[3.3.1]*nonanes* **2a**–**2h** (*General Procedure*[1]).—To the carboxylic acid (4–6 g) in heptane or toluene (10–20 cm^3) was added 0.5 molar equivalent of bis(9-borabicyclo[3.3.1]nonane). The mixture was heated to 60–80 °C until 1 equivalent of gas was evolved. In case of the solid products the solution was cooled to −60 °C and crystalline **2** was filtered off. The liquid derivatives were obtained as residues after removal of the solvent in vacuum and distillation of the residue. In all cases the yields were almost quantitative, and after recrystallization *ca.* 90%.

X-Ray Single-crystal Structure determination of Compound **2e**.—Data collection at 293 K and calculations were carried out on a Nicolet R 3 m/v four-circle diffractometer using Mo-Kα radiation and MicroVax II and SHELXTL-PLUS[13] programs. The structure solution was performed by direct methods, both phenyl groups and all hydrogen atoms being included as rigid groups (C–H 0.96 Å, C–C–H and H–C–H 109.5 and 120°, respectively). The isotropic displacement parameters of all the atoms were refined without constraints.

Crystal data. $C_{30}H_{38}B_2O_4$, crystal size 0.39 × 0.43 × 0.51 mm, triclinic, space group $P\bar{1}$, $a = 6.505(2)$, $b = 9.196(3)$, $c = 11.823(5)$ Å, $\alpha = 111.02(3)$, $\beta = 102.33(3)$, $\gamma = 90.60(3)°$, $U = 642.2$ Å^3, $Z = 1$, $D_c = 1.25$ g cm^{-3}, $\mu = 0.07$ mm^{-1}, $\theta_{max} = 45°$, λ(Mo-Kα) = 0.710 69 Å, $F(000) = 260$; total number of unique reflections = 1515, 1435 observed [$F_o \geqslant 4\sigma(F)$], $R = 0.043$, $R' = 0.066$, $w^{-1} = [\sigma^2(F_o) + gF_o^2]$ with $g = 2.16 \times 10^{-3}$, residual electron density = 0.2 e Å^{-3}.

Final atomic coordinates are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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