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^{13}C NMR Chemical Shifts and Ring Conformations of 2-Hydroxy-1,3,2-dioxaborolane and 2-Hydroxy-1,3,2-dioxaborinane and Their Methyl Derivatives

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The ^{13}C NMR chemical shifts of 2-hydroxy-1,3,2-dioxaborolane (half-chair) and -borinane (chair) and their methyl derivatives are reported. Substituent effects on the chemical shifts have been derived, and their type and magnitude shown to be closely related to the ring size, geometry, and other conformational aspects. ^1H NMR data for some 2-hydroxy-1,3,2-dioxaborinanes have been used to confirm the populations of their interconverting chair forms as deduced from the ^{13}C NMR chemical shift correlations.

Much interest has been shown in the last years in five-[1–5,9] and six-membered[3–12] organoboron heterocycles, in which the boron atom joins two more ring heteroatoms together. For instance, two oxygens,[1–5,7–12] one oxygen and one sulfur[6] or two nitrogen[9] atoms. Furthermore, the boron atom carries a hydrogen atom,[3,10] or an alkyl,[3,5,11,12] alkenyl,[11] alkynyl,[11] aryl,[1,2,9] a hydroxy[4,7,8] or an alkoxy[6,11] substituent. However, little attention has previously been paid to the conformational analysis of methyl substituted 2-hydroxy-1,3,2-dioxaborolanes (*1–7; cf.* Scheme 1) and -borinanes[4,7,8,13] (*8–31; cf.* Scheme 2). Dale[4] supposed that the five-membered 1,3,2-dioxaborolane ring should be essentially planar and the conformation of the corresponding six-membered ring similar to that in cyclohexane. Also the X-ray results of 4,6-dimethyl-2-hydroxy-1,3,2-dioxaborinane ring reported by Kuribayashi[7,8] are best explained in accordance with a chair conformation.

Davis *et al.*[9] have studied ^1H and ^{11}B NMR data of some 2-phenyl substituted 1,3,2-dioxaborinanes. They suggest that their $O-C_4-C_5-C_6-O$ regions adopt rapidly inverting chair type conformations where the lone pairs of oxygens and the vacant p orbital on boron are coplanar and overlap most effectively. Carton *et al.*[11] published ^{13}C NMR data of some 1,3,2-dioxaborinanes and explained them with a flattened chair conformation. Although Barton *et al.*[3] argued that substituent effects cannot be regarded as important in determining the ^1H NMR chemical shifts of 1,3,2-dioxaborinanes and -borolanes, the situation is just opposite in their ^{13}C NMR spectra. In the following, the ^{13}C NMR chemical shifts for parent and all methyl substituted 2-hydroxy-1,3,2-dioxaborolanes (*1–7*, Table 1) and 2-hydroxy-1,3,2-dioxaborinanes (*8–31*, Table 2) will be discussed. From them the substituent effects on the ^{13}C chemical shifts of the ring carbon atoms are estimated to clarify the ring conformations and possible conformational equilibria in detail.[14–18] To get further

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Table 1. ^{13}C Chemical Shifts of 2-Hydroxy-1,3,2-dioxaborolanes.

2-Hydroxy-1,3,2-dioxaborolane	C(4)	C(5)	C(Me)
1 Parent	65.09	65.09	
2 4-Me	72.53	71.59	21.48
3 4,4-Me_2	79.31	76.95	28.14
4 *cis*-4,5-Me_2	75.25	75.25	16.45
5 *trans*-4,5-Me_2	79.75	79.75	20.67
6 4,4,5-Me_3	81.34	80.85	27.98(4), 22.94(4), 16.81(5)
7 4,4,5,5-Me_4	83.09	83.09	24.45

Table 2. ^{13}C Chemical Shifts of 2-Hydroxy-1,3,2-dioxaborinanes.

2-Hydroxy-1,3,2-dioxaborinane	C(4)	C(5)	C(6)	C(Me)
8 Parent	62.98	26.95	62.98	–
9 4-Me (7 % a=93 % e)	68.75	33.85	62.09	22.73[a]
10 5-Me (25 % a=75 % e)	68.87	31.11	68.87	12.10[a]
11 4,4-Me_2	71.63	37.77	60.18	29.08(4av.)
12 5,5-Me_2	73.18	31.76	73.18	21.52(5av.)
13 *trans*-4,6-Me_2	65.79	38.74	65.79	22.42($^4_6$av.)
14 *cis*-4,6-Me_2	68.95	42.23	68.95	23.07($^4_6$e)
15 *trans*-4,5-Me_2	74.56	37.48	68.47	20.87(4e), 12.67(5e)
16 *cis*-4,5-Me_2	71.35	34.07	66.44	17.46(4e), 10.88(5a)
17 4,4,6-Me_3	71.92	45.57	65.87	31.07(4e), 27.74(4a), 22.98(6e)
18 4,4,5-Me_3 (16 % 5a=84 % 5e)	74.88	40.04	66.03	28.91(4e), 22.58(4a), 12.02(5e)[a]
19 *r*-4,*cis*-5,*trans*-6-Me_3 (40 % aae=60 % eea)	70.58	40.36	70.82	21.44(4e), 12.75(5e), 17.22(6a)[a]
20 *r*-4,*trans*-5,*cis*-6-Me_3	74.11	44.51	74.11	19.61($^4_6$e), 13.24(5e)
21 *r*-4,*cis*-5,*cis*-6-Me_3	72.89	38.46	72.89	21.08($^4_6$e), 3.08(5a)
22 4,5,5-Me_3	76.26	34.35	73.42	16.97(4e), 22.33(5e), 17.30(5a)
23 4,4,5,5-Me_4	77.16	37.04	71.47	24.93(4av.), 20.95(5av.)
24 4,4,6,6-Me_4	72.04	48.49	72.04	31.51($^4_6$av.)
25 *cis*-4,5,5,6-Me_4	77.36	37.32	77.36	16.45($^4_6$e), 21.97(5e), 10.44(5a)
26 *trans*-4,5,5,6-Me_4	74.60	36.71	74.60	17.22($^4_6$av.), 20.83(5av.)
27 *trans*-4,4,5,6-Me_4	75.86	47.19	71.15	29.16(4e), 22.90(4a), 12.91(5e), 21.52(6e)
28 *cis*-4,4,5,6-Me_4	75.13	41.75	68.47	29.73(4e), 27.69(4a), 6.66(5a), 19.74(6e)
29 4,4,5,6,6-Me_5	75.61	49.38	75.61	32.08($^4_6$e), 24.20($^4_6$a), 12.83(5e)
30 4,4,5,5,6-Me_5	77.73	39.55	72.69	25.42(4e), 24.53(4a), 21.36(5e), 14.05(5a), 16.81(6e)
31 4,4,5,5,6,6-Me_6	78.98	42.56	78.98	28.55($^4_6$av.), 20.87(5av.)

[a] The more favoured orientation shown in parentheses.

insight into compounds with possible conformational equilibria, the ^1H NMR spectra of *9*, *10*, *17* and *18* were also completely analyzed (Table 6).

EXPERIMENTAL

All compounds in this study were prepared by a modification of the method described by Dale.[4] An appropriate diol in benzene was added by stirring to an equimolar amount of the boric acid in benzene. Then the reaction mixture was heated to 393–403 K and refluxed, using an azeotropic distillation assembly. When about 80 % of the theoretical amount of the water formed in the reaction had been removed, the solvent was distilled off at room temperature and reduced pressure until the pressure was 2.7–3.3 kPa. The products were used as such, since their further purification, *e.g.*, by distillation, produced a viscous oil which contained oligomeric and decomposed material in comparison with the original proper borolane. All products were characterized and identified by the ^{1}H and ^{13}C NMR method. 2-Hydroxy-1,3,2-dioxaborolanes (*1–7*) and 2-hydroxy-1,3,2-dioxaborinanes (*8–31*) were prepared from suitable 1,2- and 1,3-diols and boric acid respectively, by the method described above.

The characterization of the products was performed by ^{1}H and ^{13}C NMR spectra. The noise-decoupled ^{13}C NMR spectra were recorded with a Jeol FX-60 NMR spectrometer at 298 K using 10 % (w/v) $CDCl_3$-solutions and TMS as internal standard. The spectral width was 2.5 kHz and the data memory 8 K. The signals in the spectra were assigned on the basis of empirically established trends in ^{13}C chemical shifts or with the aid of the C–H coupled spectra. The reported ^{13}C chemical shifts are considered to be accurate within 0.1 ppm.

The ^{1}H NMR spectra were recorded with a Jeol PMX-60 spectrometer at 303 K, using 10 % (w/v) CCl_4- or $CDCl_3$-solutions and TMS as internal standard. The spectra of 5-methyl- (*10*) and 4,4,5-trimethyl-2-hydroxy-1,3,2-dioxaborinane (*18*) were recorded both on the Jeol PFT-100 in Helsinki and on a 200 MHz Jeol FX-200 spectrometer at Jeol/Tokyo. The spectra of 4-methyl-(*9*) and 4,4,6-trimethyl-2-hydroxy-1,3,2-dioxaborinane (*17*) were recorded on a WM 360 and/or WM 500 Bruker apparatus at Bruker/Karlsruhe (Table 6). These spectra were recorded using $CDCl_3$ as solvent and TMS as internal standard.

The substituent effects on all ring carbon atoms of 2-hydroxy-1,3,2-dioxaborolanes (Table 3) and 2-hydroxy-1,3,2-dioxaborinanes (Tables 4 and 5) were solved on a DEC-20 computer using a linear regression analysis.

The values of the shift parameters are considered significant if they are 0.2 ppm or larger and/or at least twice their standard deviations. With this criterion in mind, the mole fractions of the conformationally inhomogeneous compounds were obtained iteratively to discover the best fit, for the substituent effect correlations.

Table 3. The shift parameters at C($\frac{4}{5}$) of 2-hydroxy-1,3,2-dioxaborolanes.

The source of the substituent effects		Parameters/ppm[a]	No. of occurrences
4-Me	α	7.42±0.05(8.66)[b]	10
5-Me	β	6.47±0.06(5.73)	10
4,4-Me_2	G_α	−0.63±0.10(−0.61)	3
5,5-Me_2	G_β	−1.08±0.12(−1.18)	3
4e5e	$\alpha_e\beta_e$	0.76±0.11(0.57)	4
4a5e	$\alpha_a\beta_e$	−7.49±0.21(−5.20)	4
4a5a	$\alpha_a\beta_a$	−1.38±0.30(−)	3

[a] rms 0.063 ppm, av.diff. ±0.02 ppm, range 18.00 ppm. [b] Values in parentheses for 2-oxo-1,3-dioxolanes.

Table 4. The shift parameters at C($\frac{4}{6}$) of 2-hydroxy-1,3,2-dioxaborinanes.

Source of the substituent effects		Parameters/ppm[a]	No. of occurrences
4e	α_e	6.03±0.11(5.76;7.83)[b]	23
4a	α_a	2.67±0.16(0.95;5.37)	12
5e	β_e	6.52±0.11(6.34;5.41)	19
5a	β_a	4.01±0.23(4.93;4.01)	19
6e	γ_e	−0.96±0.11(−0.38;−0.91)	23
6a	γ_a	−1.82±0.14(−4.74;−2.29)	12
5,5-Me_2	G_β	−0.33±0.11(−0.81;−)	9
4e5e	$\alpha_e\beta_e$	−1.01±0.14(−;−)	12
4e5a	$\alpha_e\beta_a$	−1.32±0.24(−2.43;−1.80)	12
5a6e	$\beta_a\gamma_e$	0.86±0.23(2.01;1.59)	12
4e6e	$\alpha_e\gamma_e$	0.70±0.15(0.32;0.39)	12
4e6a	$\alpha_e\gamma_a$	−0.92±0.14(−0.47;−0.79)	8
4a6e	$\alpha_a\gamma_e$	0.52±0.18(0.31;−)	8
4e4a5e	$\alpha_e\alpha_a\beta_e$	−2.37±0.19(−0.59;−1.90)	4
4e4a5a	$\alpha_e\alpha_a\beta_a$	0.83±0.18(−0.75;−)	4
4e5e5a	$\alpha_e\beta_e\beta_a$	−0.91±0.14(−;−0.63)	6
4a5a6e	$\alpha_a\beta_a\gamma_e$	−1.86±0.18(−;−0.72)	6
4a5e6e	$\alpha_a\beta_e\gamma_e$	0.77±0.21(−;0.22)	4
4e5a6e	$\alpha_e\beta_a\gamma_e$	0.66±0.27(−0.70;−)	6
5e5a6a	$\beta_e\beta_a\gamma_a$	0.60±0.19(−;−)	3
5e6e6a	$\beta_e\gamma_e\gamma_a$	−0.45±0.15(0.79;0.21)	4

[a] rms 0.135 ppm, av. diff. ±0.05 ppm, range 17.55 ppm. [b] Values in parentheses for 1,3-dioxane and 2-oxo-1,3-dioxane, respectively.

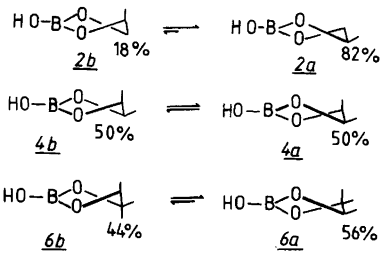
RESULTS

The ^{13}C chemical shift data for compounds *1*–*7* are collected in Table 1 and those for compounds *8*–*31* in Table 2. The chemical shift parameters (Tables 3–5) were derived using equation

$$\delta C(x) = \delta_p C(x) + \Sigma n_x^y \, SE(x) \qquad (1)$$

where $\delta C(x)$ is the chemical shift of a given carbon atom in a substituted derivative, $\delta_p C(x)$ is that of the same carbon atom in the parent compound and n_x^y are the numbers of parameters $SE(x)$ caused by the substitution y at the carbon x.

The chemical shift parameters of the 2-hydroxy-1,3,2-dioxaborolanes (Table 3) were calculated using the shift data for compounds *1*–*7*. The parametrization was based on a half-chair conformation [18] where the methyl substituents should have more or less equatorial



Scheme 1.

Table 5. The shift parameters at C(5) of 2-hydroxy-1,3,2-dioxaborinanes.

Source of the substituent effects		Parameters/ppm[a]	No. of occurrences
4e	β_e	6.75±0.09(7.10;7.34)[b]	26
4a	β_a	5.81±0.28(3.84;5.29)	11
5e	α_e	3.89±0.11(3.59;4.14)	12
5a	α_a	4.56±0.18(3.30;4.30)	12
4,4-Me$_2$	G_β	−1.70±0.21(−0.74;−1.91)	7
5,5-Me$_2$	G_α	−3.67±0.12(−2.60;−2.17)	6
4e5a	$\alpha_a\beta_e$	−4.13±0.11(−3.27;−2.86)	14
4e6e	$\beta_e^4\beta_e^6$	1.76±0.20(0.37;−)	8
4e6a	$\beta_e^4\beta_a^6$	−0.72±0.22(−;−)	7
4e4a5e	$\alpha_e\beta_e^5\beta_a^4$	−1.38±0.20(−;−)	4
4e5e6e	$\alpha_e\beta_e^4\beta_e^6$	−1.51±0.17(−;−)	4
4e5a6a	$\alpha_a\beta_e^4\beta_a^6$	−3.27±0.36(−0.55;−)	4
4a5e6e	$\alpha_e\beta_a^4\beta_e^6$	0.55±0.26(−;−)	4
4e4a5a6e	$\alpha_a\beta_e^5\beta_a^4\beta_e^6$	3.06±0.37(−;−)	2

[a] rms 0.134 ppm, av. diff ±0.06 ppm, range 18.27 ppm. [b] Values in parentheses for 1,3-dioxane and 2-oxo-1,3-dioxane, respectively.

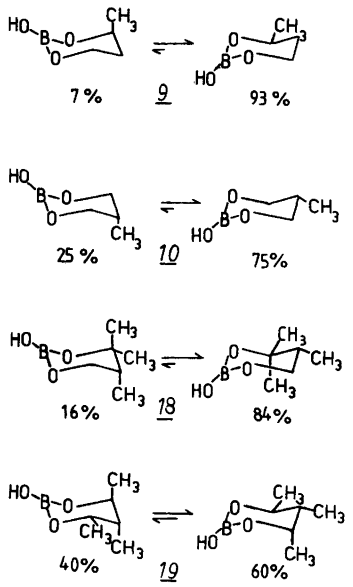
and/or axial character. The best fit, however, was obtained when SE(4e)=SE(4a)=SE(4), SE(5e)=SE(5a)=SE(5) but SE(4a5e)≠SE(4e5a)=O and SE(4e5e)≠SE (4a5a). *cis*-4,5-Dimethyl-2-hydroxy-1,3,2-dioxaborolane (*4*) included equal amounts of the 4e5a and 4a5e conformations (Scheme 1). Only the ^{13}C chemical shifts of the 4,4,5-trimethyl derivative (*6*) show that this compound and hence also the 4-methyl derivative (*2*) are not conformationally homogeneous. By iteration, the best fit was found when *6* was taken to be 56 % in the 4e4a5e and *2* 82 % in the 4e form.

In the case of 2-hydroxy-1,3,2-dioxaborinanes (Table 2) the values of substituent effects (Tables 4 and 5) were solved first using the shift data for *8, 11–17, 20–23, 25–28* and *30* with anancomeric (=one predominant) or two equivalent chair conformations as reported before for 1,3-dioxanes[17] and their 2-oxo derivatives[15,18] and 2-oxo-1,3,2-dioxathianes.[19]

The values of shift parameters so obtained were then used to estimate the mole fractions of the two unequal chair conformations for compounds *9, 10, 18* and *19* (Scheme 2). The numerical values of the shift parameters remained practically the same, before and after including the shift data of compounds *9, 10, 18* and *19* weighed by the pertinent mole fractions (Scheme 2), giving the best fit for the total correlation. 4-Methyl-2-hydroxy-1,3,2-deioxaborinane (*9*) seems to exist slightly more in the axial conformer (Scheme 2) than 4-methyl-1,3-dioxane[17] or its 2-oxo derivative.[15] It could be concluded that *9* consists of at least 93 % of the equatorial conformer. Also 5-methyl (*10*), 4,4,5-trimethyl-(*18*) and *r*-4,*cis*-5,*trans*-6-trimethyl-2-hydroxy-1,3,2-dioxaborinanes(*19*) prefer clearly the 5-equatorial conformer like the corresponding 1,3-dioxanes[17] and 2-oxo-1,3-dioxanes.[15]

Additional evidence for the conformational equilibria was obtained from the ^{1}H NMR parameters (Table 6).

The data for 4,4,6,6-tetramethyl- (*24*), 4,4,5,6,6-pentamethyl- (*29*) and 4,4,5,5,6,6-hexamethyl-2-hydroxy-1,3,2-diaxaborinane (*31*) were not used for deriving the shift parameters (Tables 4 and 5) since they are the only compounds with independent 4a6a, 4a5e6a and 4a5a6a substitution patterns, respectively. The values of these effects have been calculated manually and are shown in Table 7.



Scheme 2.

Table 6. ^{1}H NMR parameters of 4-methyl-(*9*), 5-methyl-(*10*), 4,4,6-trimethyl-(*17*) and 4,4,5-trimethyl-2-hydroxy-1,3,2-dioxaborinanes (*18*).

Compound	Proton	δ/ppm	J/Hz			
9[a,d]	4a	4.18	4a,CH_3	6.3	4a5a	9.45
	5e	1.86	4a5e	3.15	5e6e	3.45
	5a	1.66	5a6a	10.72	5e5a	−14.24
	6e	4.05	5a6e	4.77	6e6a	−11.06
	6a	3.97	5e6a	3.31		
	4e-CH_3	1.26				
10[b,d]	$^4_6$e	4.01	4e4a	−10.86	4e6e	~0.8
	$^4_6$a	3.62	4e5a	4.46	4a5a	9.83
	5a	2.11	5a,CH_3	6.7		
	5e-CH_3	0.87				
17[a,d]	5e,5a	1.76;1.52	5e5a	−14.10	5e6a	2.83
	6	4.28	5a6a	11.58	6a,CH_3	6.2
	4e-CH_3,4a-CH_3	1.32;1.31	5a,4a-CH_3	0.73		
	6e-CH_3	1.27				
18[c,d]	5a	1.79	5a,CH_3	6.95	5a6e	4.74
	6e	3.77	6e6a	−11.27		
	6a	3.61	5a6a	10.76		
	4e-CH_3,4a-CH_3	1.18;1.06				
	5e-CH_3	0.75				

[a] Bruker WM-500. [b] Jeol PFT-100. [c] Jeol FX-200. [d] Only the main orientations of the protons are shown.

Table 7. The values of the substituent effects derived manually from compounds *24, 29* and *31* together with those of 1,3-dioxanes[17b] and its 2-oxo derivatives.[15]

Substituent effect/ppm	Ring carbon atom	
	C($^4_6$)	C(5)
4a6a	+2.84(+3.44,+2.88)	−0.50(−1.02, +0.05)
4a5e6a	+0.11(+0.79,[a] +0.29	+0.17(+0.30,[a] +0.57)
4a5a6a	+0.83(+3.18,[b] +0.95)	+0.97(+3.82,[b] +1.15)

[a] Estimated from *trans*-2,4,4,5,6,6-hexamethyl-1,3-dioxane.[17]. [b] Estimated from *cis*-2,4,4,5,6,6-hexamethyl-1,3-dioxane.[17]

DISCUSSION

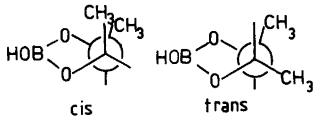
Shift Parameters and Ring Conformation of 2-Hydroxy-1,3,2-dioxaborolanes

The substituent effects on C($^4_5$) of 2-hydroxy-1,3,2-dioxaborolanes (Table 3) are very similar to those of 2-oxo-1,3-dioxolanes (Table 3). Thus it can be concluded that the 1,3,2-dioxaborolane ring favours a half-chair conformation, a conclusion which led to a very good fit between the observed and calculated chemical shifts. One might think that perhaps the 2-hydroxy-1,3,2-dioxaborolane ring like 1,3-dioxolane would be more flexible[16] than that of 2-oxo-1,3-dioxolane.[14] Taking the bond lengths of 2-hydroxy-1,3,2-dioxaborolanes as approximately equal to those of the corresponding six-membered ring,[8] the ring size of the former is rather larger than that of 2-oxo-1,3-dioxolane.[14] Therefore, ring size may be one of the factors reflected in the magnitude of the α substituent effect which is smaller for 2-hydroxy-1,3,2-dioxaborolanes than for 2-oxo-1,3-dioxolanes (Table 3). The β effect in turn is greater in the former ring system. At least theoretically, it is possible that one of the lone pair orbitals on each of the three oxygen atoms overlaps with the vacant orbital on the boron.[9] Thus the boron atom and all three oxygen atoms would be nearly coplanar, which increases the rigidity of the 2-hydroxy-1,3,2-dioxaborolane ring. This view is supported by the observation that both geminal and *trans* (SE(4e5e)) vicinal substituent effects are very similar for 2-hydroxy-1,3,2-dioxaborolanes and 2-oxo-1,3-dioxolanes[14] (Table 3). However, the *cis*-vicinal substituent effect (SE(4a5e)) is more shielding for 2-hydroxy-1,3,2-dioxaborolanes than it is for 2-oxo-1,3-dioxolanes.[14]

Davis *et al.*[9] have concluded that the π bonding is weaker in the five than in the six-membered 1,3,2-dioxaboracycloalkanes, but in all of the compounds they studied, the boron has a phenyl substituent, the π electron system of which would decrease the double bond character between the boron and oxygen atoms. Obviously the oxygen atom of the hydroxyl substituent in our compounds increases the π-bonding character between the boron and the three oxygen atoms, and hence also the rigidity of the molecule.

The similarity of the 2-hydroxy-1,3,2-dioxaborolane (Table 3) and 2-oxo-1,3-dioxolane[14] ring is also seen in the fact that the methyl carbons of their *cis*-4,5-dimethyl derivatives are 4–4.5 ppm more shielded than those of the *trans*-forms. This shielding difference for the corresponding isomers of cyclopentanes,[22] 1,3-dithiolanes[23] and 1,3-dioxolanes[24] (3.6, 3.0 and 2.2 ppm, respectively) is always smaller. The upfield shift of the methyl carbons when going from the *trans*- to *cis*-isomers has been explained[24] as due to the decrease in the dihedral angle between the vicinal methyl groups in the *cis* forms. Thus, if the dihedral

angles of *cis*- and *trans*-4,5-dimethyl isomers of 2-hydroxy-1,3,2-dioxaborolanes are nearly equal to those of 2-oxo-1,3-dioxolanes, then the ring conformations of these compounds must also be very similar:



(2)

This result is in close agreement with the conformational equilibrium (Scheme 1) from which we estimate that the conformational energy ($-\Delta G°=4.2$ kJ mol^{-1}) of the axial methyl group in 1,3,2-dioxaborolanes is slightly less than that in 2-oxo-1,3-dioxolanes (4.6 kJ mol^{-4}).[14] Accordingly, the 4-methyl-2-hydroxy-1,3,2-dioxaborolane would be an 82:18 mixture of the equatorial (2a) and axial (2b) forms.

Shift Parameters of 2-Hydroxy-1,3,2-dioxaborinanes

α-effects. The value of the equatorial α-effect at C($\frac{4}{6}$) for *8–31* (Table 4) resembles more that in 1,3-dioxanes[17] than that in 2-oxo-1,3-dioxanes.[15] The differences between the equatorial α-effects of these sets of compounds indicate that structurally 1,3,2-dioxaborinanes are half-way between 1,3-dioxanes and their 2-oxo derivatives. The same trend is also seen in the axial α-effects (2.67, 0.95 and 5.37 ppm, respectively). Thus it may be supposed that 2-hydroxy-1,3,2-dioxaborinanes attain a chair-conformation[7,9,11,25] where the BO_3 moiety should be essentially planar.[7,8,25]

At C(5) both axial and equatorial α-effects (Table 5) are again very close to each other, although α_e is more like that of 1,3-dioxanes[17] and α_a equals that of 2-oxo-1,3-dioxanes.[15]

The geminal α-effect (G_α) at C($\frac{4}{6}$) for 1,3,2-dioxaborinanes is negligible, as is that of 2-oxo-1,3-dioxanes (additional evidence for the importance of the lack of synaxial hydrogen at C(2)). At C(5) G_α is about 1 ppm more shielding than in 1,3-dioxanes[17] and their 2-oxo derivatives.[15]

β-effects. $\beta_e-\beta_a$ at C($\frac{4}{6}$) (2.5 ppm) is greater than that in 1,3-dioxanes[17b] and its 2-oxo derivatives[15] (1.6 ppm and 1.4 ppm, respectively) although the equatorial β-effect is practically equal to that in the former, and the axial one is similar to that in the latter (Table 4). At C(5) both β-effects are close to those in 2-oxo-1,3-dioxanes[15] (Table 5). Thus the shift parameters support the view that structurally and electronically C($\frac{4}{6}$) of 2-hydroxy-1,3,2-dioxaborinanes is rather close to that of 1,3-dioxanes, whereas the spatial and electronic environment of C(5) in the former, resembles more that of 2-oxo-1,3-dioxanes. The ^{13}C chemical shifts of C($\frac{4}{5}$) for the studied 1,3,2-dioxaborolanes, 1,3-dioxolanes[16] and its 2-oxo derivatives[14] are almost equal, whereas those of C($\frac{4}{6}$) for the corresponding six-membered rings differ more from each other (Table 8). This is perhaps affected by the greater structural

Table 8. ^{13}C chemical shifts (δ/ppm) of C($\frac{4}{6}$) for 2-hydroxy-1,3,2-dioxaborinane, 1,3-dioxane, 2-oxo-1,3,2-dioxathiane and 2-oxo-1,3-dioxane.

2-Hydroxy-1,3,2-dioxaborinane	62.98
1,3-Dioxane	66.92
2-Oxo-1,3,2-dioxathiane	67.1[a]
2-Oxo-1,3-dioxane	68.09

[a] Calculated for the conformation with an equatorial S(=O) group: 57.3+9.8=67.1.

differences in the six-membered rings in comparison with the five-membered ones which can be caused at least partly by differences in the double bond character of the CO_3 and BO_3 moieties.[9] However, it can be concluded[11,12] that although the hydroxy (or methoxy) substitution at the boron atom possibly increases the π bond character[12] in the BO_3 grouping, it has quite a small influence on the electron density at C($\frac{4}{6}$), and hence it is the boron atom itself, rather than resonance, which is shielding C($\frac{4}{6}$) in comparison with the situation in 1,3-dioxane,[17] and also in its 2-oxo derivative.[15] The C(5) of 2-hydroxy-1,3,2-dioxaborinanes is about 2 ppm more shielded than that of its 2-ethyl derivatives.[11,12] This is the case also between a pair 2-oxo-1,3,2-dioxathianes[19] and 2-methoxy-1,3,2-dioxaphosphorinanes[25] with an axial and equatorial substituent at position 2, respectively.[18] Consequently, it can be thought that in 2-hydroxy-1,3,2-dioxaborinanes, the hydroxy group at position 2 is equatorial (or coplanar with the $\begin{matrix}-O\\-O\end{matrix}\!\!>$B moiety) whereas an ethyl group is not.

γ-effects. Both equatorial and axial γ-effects at C($\frac{4}{6}$) are close to those in 2-oxo-1,3-dioxanes of which especially the γ_a effects support the functional similarity of the BO_3 and carbonate moieties. In other words, both sets of compounds are essentially planar in these parts of the molecules and lack the C(2) axial hydrogen atom, contrary to the situation in 1,3-dioxanes.

Vicinal, buttressing, synaxial and polysubstitution effects. In our recent reports on 1,3-dioxanes[17] and its 2-oxo derivatives[15] we pointed out that in addition to vicinal effects $\alpha_e\beta_e$, $\alpha_e\beta_a$, $\alpha_a\beta_e$, $\beta_e\gamma_a$nd $\beta_a\gamma_e$[26] one should take into account their combined influences since, for instance, the real effect of $\alpha_e\beta_a\gamma_e$ substitution can differ from the value of $\alpha_e\beta_a+\beta_a\gamma_e$. This is also the case in 2-hydroxy-1,3,2-dioxaborinanes, which supports further the postulation that vicinal polysubstitution ($n \geq 3$) has a further perturbation effect on the basic ring geometry. The vicinal $\alpha\beta$-effects at C($\frac{4}{6}$) of 2-hydroxy-1,3,2-dioxaborinanes are smaller than those of 2-oxo-1,3-dioxanes[15] (Table 4) whereas at C(5) the $\alpha_a\beta_e$ effect is about 1 ppm more shielded than those of 1,3-dioxanes[17] or its 2-oxo derivatives[15] (Table 5).

There are three buttressing effects at C($\frac{4}{6}$), namely $\alpha_a\gamma_e$, $\alpha_e\gamma_a$ and $\alpha_e\gamma_e$ which have numerical values very close to those of 1,3-dioxanes and its 2-oxo derivatives (Table 4).

At C(5) the $\beta_e^4\beta_e^6$ effect (1.76 ppm) is still greater than that of 2-oxo-1,3-dioxanes and about five times that of 1,3-dioxanes. However, $\beta_a^4\beta_a^6$ at C(5) has a numerical value between those of 1,3-dioxane and its 2-oxo derivative (Table 5).

Such polysubstitution effects as $\alpha_e\alpha_a\beta_e$ and $\alpha_a\beta_a\gamma_e$ (−2.37 and −1.86 ppm) at C($\frac{4}{6}$) are clearly more shielding than those in 2-oxo-1,3-dioxanes (−1.90 and −0.72 ppm) and 1,3-dioxanes (−0.59 and 0 ppm, respectively). At C(5) $\alpha_a\beta_e^4\beta_a^6$, $\alpha_e\beta_e^4\beta_e^6$, and $\alpha_e\beta_e^4\beta_a^4$ effects (−3.27, −1.51 and −1.38 ppm, respectively) are again more shielding than those in 2-oxo-1,3-dioxanes or 1,3-dioxanes, for which these effects are negligible. The differences and similarities of the substituent effects described above can, in general, be understood either by means of deviations in the molecular geometries or differences in the electronic effects.

Chair-chair Equilibria and ^{1}H NMR Spectra of 2-Hydroxy-1,3,2-dioxaborinanes

4-Methyl-2-hydroxy-1,3,2-dioxaborinane (*9*) is not conformationally homogeneous (Scheme 2) as shown in solving the ^{13}C NMR substituent effects. By using the values of the coupling

constants listed in Table 6, the position of the chair-chair equilibria of *9*, *10* and *18* can be estimated and compared with the results obtained from the ^{13}C shift data (Scheme 2).

For 4-methyl-1,3,2-dioxaborinane (*9*) the model value J_{5a6a}=11.58 Hz can be taken from the ^{1}H spectrum of *17* to solve J_{5e6e} and X_{4e}:

$$3.45=X_{4e}\times J_{ee}+(1-X_{4e})\times 11.58$$
$$10.72=X_{4e}\times 11.58+(1-X_{4e})\times J_{ee}$$

from which J_{ee}=2.6 Hz and X_{4e}=0.90. By assuming that J_{4a5a}=10.3 Hz ($J_{5a6a}-J_{4a5a}$=1.3 Hz taken equal to that of 4-methyl-2-oxo-1,3-dioxane)[15,18] and $J_{4e5e}=J_{5e6e}$ we obtain

$$9.45=10.3\times X_{4e}+(1-X_{4e})\times 2.6$$

from which X_{4e}=0.89. These results are in agreement with the result 0.93, given by the ^{13}C chemical shift correlation, taking into account that the error limits in these calculations are ca. 0.03.

From the ^{13}C chemical shift correlation, one concludes below that the *cis*-4,5-dimethyl derivative (*16*) attains the 4e5a chair form exclusively. Consequently, the interactions due to the axial 5-methyl (5a+4e5a) are somewhat less severe than in the case of 1,3-dioxanes[17] and 2-oxo-1,3-dioxanes.[15]

Thus we can predict that the 4,4,5-trimethyl derivative (*18*) should also include more of the 5-axial chair form than the corresponding 2-oxo-1,3-dioxane. This is indeed the case since from the ^{13}C chemical shift correlations we found that *18* is an 84:16 mixture of 5e and 5a chair conformations.

If we accept this result and the value 2.6 Hz for the J_{5e6e} coupling, we obtain:

$$10.76=J_{5a6a}\times X_{5e}+(1-X_{5e})\times 2.6$$
$$=J_{5a6a}\times 0.84+0.16\times 2.6$$

from which J_{5a6a}=12.3 Hz (cf. the corresponding case of 2-oxo-1,3-dioxanes where J_{5a6a}=12.1 Hz). This result and J=2.6 Hz should now serve as good model values for 5-methyl-1,3,2-dioxaborinane (*10*):

$$9.83=12.3\times X_{5e}+(1-X_{5e})\times 2.6$$

From which X_{5e}=0.74 in excellent agreement with the result X_{5e}=0.75 given by the ^{13}C chemical shift correlations (Scheme 2).

Chair-chair Equilibria and the ^{13}C Chemical Shifts

To check anancomerism of 4-methyl-1,3,2-dioxaborinane (*9*), the values of the substituent effects on the ^{13}C chemical shifts were calculated using different axial-equatorial conformer ratios. The best fit was found when 93 % was assumed to exist in the equatorial chair form. The clear predominance of the equatorial conformer is also supported by the observation that the positions of the chair-chair equilibria of *10*, *18* and *19* (Scheme 2) do not deviate significantly from those of the corresponding 1,3-dioxanes[17] and their 2-oxo derivatives.[15] The conformational energy (2.7 kJ mol^{-1}) of an axial 5-methyl group is almost the same as

that for 2-oxo-1,3-dioxane and hence it could be expected that the *cis*-4,5-dimethyl derivative would also contain little of the 4a5e chair form.

To test, the values of the susbtituent effects were again calculated using different conformer ratios for *cis*-4,5-dimethyl-2-hydroxy-1,3,2-dioxaborinane (*16*). However, the best fit was always obtained when this compound was taken to exist exclusively in the 4e5a chair form in a rather good agreement with the situation in 1,3-dioxanes (97:3)[17a] and not too far from that of 2-oxo-1,3-dioxanes (95:5). This result again supports the view that 2-hydroxy-1,3,2-dioxaborinanes, 1,3-dioxanes[17] and 2-oxo-1,3-dioxanes[15] are stereochemically very similar.

Finally, compounds *24, 29* and *31* include 4a6a, 4a5e6a and 4a5a6a type increments respectively. The values of these effects have been calculated manually and are shown in Table 7, together with the comparable data for 1,3-dioxanes[17] and 2-oxo-1,3-dioxanes.[15] The values of the 4a6a and 4a5e6a effects are practically equal for the three sets of compounds (Table 7). The value of the 4a5a6a increment at $C(\frac{4}{6})$ for *cis*-2,4,4,5,6,6-hexamethyl-1,3-dioxane differs, however, clearly from that for 2-oxo-1,3-dioxanes and 2-hydroxy-1,3,2-dioxaborinanes. The former compound has been stated to attain a heavily deformed chair form or at least to some extent the 1,4-twist form.[17] Hence the above observations still speak for the situation that 2-hydroxy-1,3,2-dioxaborinanes favour a chair conformation with a planar

O–B–O grouping as the O=C–O group in 2-oxo-1,3-dioxanes.[15]
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The Importance of the ^{13}C Shift Method in the Conformational and Configurational Analysis

Saturated five-membered rings have often quite small demands of their own, but exist as a dynamic mixture of different envelope or half-chair forms.[16,25,27,28] The substituents at the five-membered rings are not purely equatorial or axial like those of the six-membered rings which normally attain the chair form. This is certainly one reason for the difference in behaviour of these compounds in the parametrization of the ^{13}C chemical shift effects. The values of the substituent effects derived, for instance, for 1,3-dioxolanes[16,25] with a few substituents, are additive and comparable with similar parameters for the six-membered rings.[17] Increasing substitution, however, also increases the steric demands in the former ring system, and the ring becomes less flexible than before, and may cause difficulties in explaining the conformational properties of heavily methyl-substituted derivatives. The change in the average ring conformation proceeds slowly but continuously. The limiting conformation does not differ very clearly from the average ring conformation of the parent compound, although the conformational libration becomes more restricted with the more substituents one has. This is why the basic shift parameters can be different for the parent compound and its less substituted derivatives, from those with heavy methyl substitution (like chair *vs.* twist in 1,3-dioxanes[17b]).

The ^{13}C NMR chemical shift method can at any rate indicate the conformational likeness or unlikeness of two sets of five-membered compounds. For instance, the dissimilarity of 2-oxo-1,3-dioxolanes and 4-oxo-1,3-dioxolanes[29] (half-chair vs. envelope form, respective-

ly). The pseudolibration of five-membered heterocyclanes including groups like CO_3 and BO_3 (with two or three of the heteroatoms in the ring) is very much restricted, but on the other hand the number of available methyl derivatives for a precise clarification of the conformational details in these compounds is also limited. That is to say, that these compounds have practically only two ring carbon atoms, the ^{13}C chemical shifts of which can be used to estimate the populations of conformational isomers, and hence the result is less accurate than in the case of six-membered rings. In the latter, *e.g.*, 2-oxo-1,3-dioxanes,[15] 2-hydroxy-1,3,2-dioxaborinanes and 2-oxo-1,3,2-dioxathianes[19] there are (i) three useful ring carbon atoms, and hence two to three equations for solving each conformational equilibrium, (ii) a greater number of methyl-substituted derivatives than in the case of five-membered rings, and (iii) practically all of them exist in a well-defined chair form. Accordingly, the conformer ratio can be estimated fairly accurately (in most cases within ±3 %). If we have very many conformational equilibria as in 2-oxo-1,3,2-dioxathianes,[19] the overall fit becomes a little less accurate and the rms larger than in the cases where we have only few conformational equilibria (like 1,3-dioxanes,[17] 2-oxo-1,3-dioxanes[15] and 2-hydroxy-1,3,2-dioxaborinanes), but the relative errors as to the conformer populations remain, however, practically the same. Thus the ^{13}C NMR chemical shift method can be regarded as an accurate and successful application to structure elucidation, and to both configurational and conformational analysis.

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