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^{17}O and ^{11}B NMR Spectroscopic Study of Substituted Benzo[d]-2,2-difluoro-1,3,2-oxoniaoxaboratins

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ABSTRACT

^{17}O NMR data are reported for 10 benzo[d]-2,2-difluoro-1,3,2-oxoniaoxaboratins derived from various ortho-hydroxyacetophenones and for 2,2-difluoro-1,3,2-oxoniaoxaboratins derived from related hydroxyacetyl naphthalenes and hydroxybenzophenones. The signal for the carbonyl-like oxygen for these compounds is substantially shielded and appears at 288 ± 22 δ. The single bonded oxygen signal for the 1,3,2-oxoniaoxaboratins appears at 122 ± 6 δ, except for the naphthalene analogs, whose signal appears at 146 ± 10 δ. The ^{11}B NMR signal for these compounds is insensitive to structural changes and appears at 0.85 ± 0.25 δ.

INTRODUCTION

There is considerable current interest in developing a clear understanding of the role of Lewis acids in numerous catalysis processes [1]. Boron trifluoride has been used as a Lewis acid catalyst for numerous organic reactions [2]. In addition, boron trifluoride, unlike boron trichloride and boron tribromide, forms relatively stable 1,3,2-oxoniaoxaboratin adducts from β-hydroxycarbonyl compounds and other 1,3-difunctional groups [3,4]. Certain 2,2-difluoro-1,3,2-oxoniaoxaboratins have been found to be useful intermediates for synthesis of heterocyclic compounds [5,6]. Other difluoro 1,3,2-oxoniaoxaboratin compounds have also been studied as models for enols of 1,3-diketones [7]. No study of the ^{17}O NMR spectroscopic characteristics of the 2,2-difluoro-1,3,2-oxoniaoxaboratins has been reported, even though several reports have appeared which describe the ^{17}O NMR chemical shifts of other boron-oxygen compounds [8–14]. This report describes the results of an investigation of the effect of structure on both the ^{17}O and ^{11}B NMR chemical shifts of 2,2-difluoro-1,3,2-oxoniaoxaboratins obtained from various substituted 2′-hydroxyacetophenones and related compounds which should ultimately contribute to understanding the interactions of boron trifluoride and carbonyl groups.

RESULTS AND DISCUSSION

The ^{17}O NMR spectroscopic data obtained in acetonitrile solution at natural abundance for 2,2-difluoro-1,3,2-oxoniaoxaboratins derived for various *ortho*-hydroxyacetophenones are listed in Table 1. In each case, two ^{17}O NMR spectroscopic signals are observed for the 1,3,2-oxoniaoxaboratins. The signal for the carbonyl-like oxygen appears at 288 ± 22 δ, and the single bonded oxygen signal appears at approximately 122 ± 6 δ.

The carbonyl-like oxygen ^{17}O NMR signal is dramatically shielded compared to the values of similarly substituted acetophenones [15]. For example, the carbonyl ^{17}O NMR chemical shift of *para*-hydroxyacetophenone is 531 δ, 234 δ downfield of the value for **1** [15]. The carbonyl ^{17}O NMR chemical shift of the intramolecularly hydrogen bonded *ortho*-hydroxyacetophenone is 491 δ, which is 194 δ downfield of the value of **1** [15]. Bonding of the

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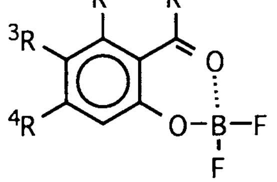
TABLE 1 ^{17}O NMR Data for 2,2-Difluoro-1,3,2-oxoniaoxaboratins in Acetonitrile at 75°C[a,b]



Compound	*R¹*	*R²*	*R³*	*R⁴*	$\delta_{(C=O)}$	$\delta_{(O-B)}$	$\delta_{(other)}$[c]
1	CH_3	H	H	H	297.6 (280)	121.4 (340)	—
2	CH_2CH_3	H	H	H	294.0 (398)	120.1 (414)	—
3	CH_3	H	H	OCH_3	266.2 (469)	128.7 (520)	89.5 (440)
4	CH_3	H	H	OH	263.7 (435)	126.4 (500)	113.6 (550)
5	CH_3	H	H	Br	299.1 (409)	129.5 (535)	—
6	CH_3	H	CH_3	H	293.2 (350)	116.1 (440)	—
7	CH_3	H	OCH_3	H	293.4 (317)	117.0 (479)	46.8 (345)
8	CH_3	OCH_3	H	H	289.4 (428)	121.8 (426)	76.2 (541)
9	CH_3	OH	H	H	289.9 (410)	119.3 (475)	103.9 (351)
10	CH_3	CH_3	H	CH_3	291.4 (285)	124.2 (324)	—

[a] δvalues in ppm.

[b] Values in parentheses are half-height peak widths in Hz.

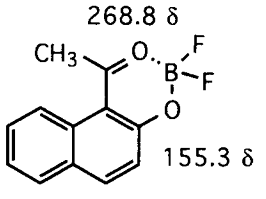
[c] Chemical shifts and half-height peak widths for other oxygen containing functional groups.

carbonyl oxygen to the complexed difluoro boron unit causes an approximately 200 δ shielding shift of the carbonyl oxygen ^{17}O NMR signal; this carbonyl shielding shift is approximately four times larger than that noted for the formation of an intramolecular hydrogen bond [15,16].

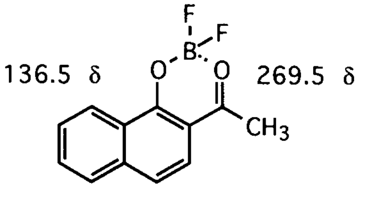
Recently, Dahn has shown that rho values obtained from correlation of substituent effects on the ^{17}O NMR chemical shift with Hammett sigma plus values are valuable indicators for quantitatively assessing the electron attracting ability of a wide variety of carbonyl containing functional groups [17–21]. Dahn observed rho values ranging from 6 for weak electron attracting carbonyl groups such as amides and esters to values near 30 for the very strong electron attracting trifluoromethylcarbonyl groups [17–21]. Albeit based upon a limited number of 7-substituted compounds (**1**, **3**–**5**), it is clear that the boron complexed carbonyl group in the 1,3,2-oxoniaoxaboratins will exhibit a large rho value (tentatively 35) and suggests an extremely electron deficient carbonyl group. This result is consistent with the properties noted for boron trifluoride-benzaldehyde complexes [22].

It has been noted that the effect of 6-substituents on the phenol oxygen chemical shifts is substantially smaller than those of carbonyl groups [23]. The chemical shift difference between the phenolic oxygen signal of **1** and **8** is only 4 δ shielding, whereas that difference for the corresponding 4-substituted phenols is 9 δ shielding [23]. Although the current study does not include a wide range of substituents, it appears that the effect of bonding to boron further reduces the effect of substituents on the phenolic oxygen chemical shift.

Typically, the effect of steric interactions on the ^{17}O NMR chemical shifts of carbonyl groups, which are free to rotate around single bonds to reduce van der Waals interactions, is deshielding [23]. Comparison of the data for **3** and **8**, which are electronically equivalent but sterically different, shows the normal deshielding trend. The ^{17}O NMR signal for the carbonyl-like oxygen of the hindered compound **8** is 23 δ downfield of that of **3**, consistent with rotation of the carbonyl-like group from the plane of the aromatic ring. The 1- and 2-acetylnaphthalene systems have been used to evaluate torsion angle effects on carbonyl ^{17}O NMR chemical shifts [24,25]. The ^{17}O NMR chemical shifts of 1-acetyl and 2-acetylnaphthalene are 585 δ and 553 δ, respectively, and the downfield shift of the 1-acetyl compound was attributed to torsion angle rotation [26]. In the case of 1-hydroxy-2-acetyl and 2-hydroxy-1-acetylnaphthalene, the carbonyl ^{17}O NMR signal of the latter was downfield of that of the former by 46 δ [14]. The ^{17}O NMR data for the 2,2-difluoro-1,3,2-oxoniaoxaboratin analogs **11** and **12** derived from the acetylnaphthols are given with the following structures.



11



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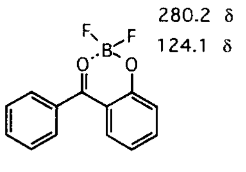
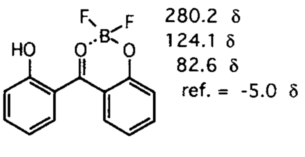
The ^{17}O NMR chemical shifts of the carbonyl-like carbonyl of **11** and **12** are the same within experimental error, which is presumably another example of the consequences of the large shielding effect on the ^{17}O NMR chemical shift of the intramolecularly boron-complexed carbonyl oxygen.

Recently, it was demonstrated by ^{17}O NMR studies [15] that both hydroxyl groups of 2,2′-dihydroxybenzophenone can simultaneously form hydrogen bonds to the benzophenone carbonyl group, depending upon the solvent. Consequently, it was of interest to determine if 2,2′-dihydroxybenzophenone would form a bis-adduct with boron trifluoride. Compounds **13** and **14** were isolated as crystalline solids from the reaction of the hydroxyketones with boron trifluoride. The chemical shift values for the two different oxygens bound to boron in both **13** and **14** are essentially the same, suggesting that only one boron atom is present in **14**. The presence of a free OH group in **14** is indicated by the chemical shift of 82.6 δ for the third signal of **14** and by the 5 δ upfield shift of the signal for the internal reference, 2-butanone. Mass spectral data (*m/e* = 262) from the crystalline solid isolated from the reaction of boron trifluoride and 2,2′-dihydroxybenzophenone are in agreement with the solution phase NMR data. In contrast to intramolecular hydrogen bonding [15,16], and the simultaneous formation of a related bis-adduct with aluminum Lewis acids [27], the coordination of only one boron atom to the carbonyl oxygen of 2,2′-dihydroxybenzophenone is observed.



13



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^{11}B NMR data obtained in acetonitrile at 75°C for representative examples of the 1,3,2-dioxaborins are reported in the Experimental section. The ^{11}B chemical shifts for the 1,3,2-oxoniaoxaboratins are essentially insensitive to substitution on the aryl ring; the values of chemical shift are in the range 0.85 ± 0.25 δ. The relative insensitivity of the ^{11}B chemical shift in this system is consistent with previous results for other oxyboron systems [8–14].

The ^{17}O NMR chemical shift of the carbonyl-like oxygen of the 1,3,2-oxoniaoxaboratins studied is extraordinarily shielded, appearing at 260–300 δ. The observed ^{17}O NMR chemical shift values suggest considerable single bond character for this functional group; however, the chemical shift changes observed with variation of substituent (both steric and electronic changes) are consistent with those noted for typical carbonyl groups. The ^{17}O NMR shielding shifts resulting from the carbonyl-boron intramolecular complex are approximately four times that noted for comparable intramolecular hydrogen bond formation.

EXPERIMENTAL

Three of the compounds **1** [6], **11** [5], and **12** [5] used in this study were previously reported; they were obtained by literature methods and gave physical properties (^{1}H, ^{13}C NMR, mp) consistent with their structure and literature values; their ^{11}B δ values are 0.9, 0.6, and 1.1, respectively. The oxoniaoxaboratins **2**, **3**, and **4** were prepared earlier and directly used [6]; we include physical data for these compounds as well as the new compounds included in this study. The general preparation procedure used to make the 2,2-difluoro-1,3,2-oxoniaoxaboratins follows.

General Procedure for Preparation of 2,2-Difluoro-1,3,2-Oxoniaoxaboratins

To a stirred solution of *ortho*-hydroxyacetophenone (0.01 mole) in 35 mL dry ether/$CHCl_3$ or benzene was added, under nitrogen, 0.01 mole of boron trifluoride etherate; the solution was allowed to stir at room temperature for 2 hours to 2 days. In some cases, a precipitate of the 1,3,2-oxoniaoxaboratins separated, whereas in other cases, it was necessary to remove the solvent under vacuum, and trituration of the residue with dry benzene or acetonitrile was performed in order to obtain crystals. The solid thus obtained was filtered off and recrystallized from ether, benzene, or acetonitrile.

4-Ethyl-2,2-difluoro-1,3,2-oxoniaoxaboratin (**2**)

A 65% yield of white solid, mp 116–117°C, was obtained. ^{1}H NMR (CD_3CN) 7.93–7.78 (m, 2H), 7.09–7.03 (m, 3H), 3.32 (q, 2H, *J* = 7.3) 1.36 (t, 3H, *J* =

7.3). ^{13}C NMR (CD$_3$CN) 208.2, 163.6, 143.9, 141.2, 131.4, 121.4, 121.0, 29.8, 9.0. MS (*m/e*) 198 (M$^+$).

7-Methoxy-4-methyl-2,2-difluoro-1,3,2-oxoniaoxaboratin (**3**)

A 65% yield of pale yellow solid, mp 169–170°C, was obtained. ^{1}H NMR (CD$_3$CN) 7.76 (d, 1H, *J* = 9.3), 6.62 (d, 1H, *J* = 9.3), 6.47 (s, 1H), 3.94 (s, 3H) 2.74 (S, 3H). ^{11}B 0.9. ^{13}C NMR (CD$_3$CN) 198.1, 172.7, 166.9, 133.5, 112.5, 110.9, 56.4, 22.2. MS (*m/e*) 214 (M$^+$).

7-Hydroxy-4-methyl-2,2-difluoro-1,3,2-oxoniaoxaboratin (**4**)

A 72% yield of pale yellow solid, mp 143–144°C, was obtained. ^{1}H NMR (CD$_3$CN) 7.82 (d, 1H, *J* = 9.1), 6.57 (dd, 1H, *J* = 2.4, *J* = 9.1) 6.37 (d, 1H, *J* = 2.44), 2.7 (s, 3H), ^{13}C NMR (CD$_3$CN) 199.8, 172.6, 167.3, 142.3, 136.3, 113.3, 104.3, 23.2. MS (*m/e*) 214 (M$^+$).

7-Bromo-4-methyl-2,2-difluoro-1,3,2-oxoniaoxaboratin (**5**)

A 75% yield of pale yellow solid, mp 165–166°C, was obtained. ^{1}H NMR (CD$_3$CN) 7.85 (d, 1H, *J* = 8.8), 7.34 (s, 1H), 7.25 (d, 1H, *J* = 7.8), 2.85 (s, 3H). ^{11}B 0.8. ^{13}C NMR (CD$_3$CN) 207.8, 164.3, 140.7, 135.1, 126.3, 124.8, 25.2. MS (*m/e*) 263 (M$^+$).

4,6-Dimethyl-2,2-difluoro-1,3,2-oxoniaoxaboratin (**6**)

A 68% yield of pale yellow solid, mp 148–149°C, was obtained. ^{1}H NMR (CDCl$_3$) 7.61 (d, 1H, *J* = 8.8) 7.56 (s, 1H), 6.98 (d, 1H, *J* = 8.3), 2.84 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (CDCl$_3$) 203.2, 162.3, 145.7, 130.6, 129.8, 120.7, 116.3, 23.2, 20.3. MS (*m/e*) 207 (M$^+$).

6-Methoxy-4-methyl-2,2-difluoro-1,3,2-oxoniaoxaboratin (**7**)

A 76% yield of yellow-orange solid, mp 146–147°C, was obtained. ^{1}H NMR (CDCl$_3$) 7.44 (dd, 1H, *J* = 2.9, *J* = 8.2), 7.02 (d, 1H, *J* = 8.3), 7.0 (d, 1H, *J* = 2.9), 3.83 (s, 3H), 2.83 (s, 3H). ^{11}B 1.0. ^{13}C NMR (CDCl$_3$) 202.3, 160.2, 153.1, 135.4, 122.4, 116.0, 108.7, 56.0, 23.5. MS (*m/e*) 214 (M$^+$).

5-Methoxy-4-methyl-2,2-difluoro-1,3,2-oxoniaoxaboratin (**8**)

A 68% yield of yellow solid, mp 134–135°C, was obtained. ^{1}H NMR (CD$_3$CN) 7.77 (m, 1H), 6.6 (m, 2H), 3.97 (s, 3H), 2.87 (s, 3H). ^{11}B 0.6. ^{13}C NMR (CD$_3$CN) 204.4, 164.9, 145.8, 117.4, 112.3, 111.1, 103.8, 57.5, 29.9. MS (*m/e*) 214 (M$^+$).

5-Hydroxy-4-methyl-2,2-difluoro-1,3,2-oxoniaoxaboratin (**9**)

A 69% yield of yellow solid, mp 202–203°C, was obtained. ^{1}H NMR (CD$_3$CN) 10.5 (br, 1H), 7.25 (m, 1H), 6.31 (m, 2H), 2.8 (s, 3H). ^{13}C NMR (CD$_3$CN) 204.7, 164.1, 163.6, 145.5, 111.1, 110.7, 108.0, 29.7. MS (*m/e*) 200 (M$^+$).

4,5,7-Trimethyl-2,2-difluoro-1,3,2-oxoniaoxaboratin (**10**)

A 71% yield of yellow solid, mp 145–146°C, was obtained. ^{1}H NMR (CD$_3$CN) 6.77 (br, 2H), 2.88 (s, 3H), 2.61 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (CD$_3$CN) 203.5, 165.7, 156.6, 144.2, 127.3, 119.0, 118.1, 30.3, 25.2. MS (*m/e*) 212 (M$^+$).

4-Phenyl-2,2-difluoro-1,3,2-oxoniaoxaboratin (**13**)

A 72% yield of yellow solid, mp 117–118°C, was obtained. ^{1}H NMR (CDCl$_3$/CD$_3$CN) 7.94–7.63 (m, 7H), 7.23–7.07 (m, 2H). ^{13}C NMR (CDCl$_3$/CD$_3$CN) 198.1, 167.2, 145.0, 137.3, 135.8, 133.9, 133.5, 130.9, 130.7, 122.6, 117.9. MS (*m/e*) 246 (M$^+$).

4-[2-hydroxyphenyl]-2,2-difluoro-1,3,2-oxoniaoxaboratin (**14**)

A 66% yield of yellow solid, mp 139–140°C, was obtained. In this case, an excess of 2 equivalents of boron-trifluoride etherate was employed in an attempt to form a bis-adduct. ^{1}H NMR (CDCl$_3$) 7.9–7.8 (m, 1H), 7.68–7.44 (m, 3H), 7.2–6.9 (m, 4H). ^{13}C NMR (CDCl$_3$) 199.6, 165.9, 160.6, 157.9, 145.1, 137.4, 136.3, 136.2, 133.6, 121.9, 121.4, 121.1, 120.4, 118.6. MS (*m/e*) 262 (M$^+$).

Conditions of NMR Data Collection

The ^{17}O NMR spectra were recorded on a Varian VXR-400 spectrometer equipped with a 10 mm broad-band probe. All spectra were acquired at natural abundance, at 75°C in acetonitrile or toluene (Aldrich, anhydrous gold label under nitrogen) containing 1% 2-butanone as an internal standard. The concentration of the compounds employed in these experiments was 0.50 M. The signals were referenced to external deionized water at 75°C. The 2-butanone resonance (571 δ in toluene and 558 δ in acetonitrile) was used as an internal control for the chemical shift measurements for these compounds. The instrumental settings were 35 kHz spectra width, 2K data points, 90° pulse angle (40 μs pulse width), 100 μs acquisition delay, and 29 ms acquisition time. Typically, 30,000–60,000 scans were required. The spectra were recorded with sample spinning and without lock. The signal-to-noise ratio was improved by applying a

25 Hz exponential broadening factor to the FID prior to Fourier transformation. The data point resolution was improved to ±1.0 ppm.

Broad-band proton decoupled ^{11}B spectra in CD_3CN were obtained at 75°C on a JEOL GX-270 NMR spectrometer equipped with a 10 mm probe operating at 86.6 MHz. The instrumental settings were 5453 Hz spectral width, 16K datapoints, 45° pulse angle (10.5 μs pulse width), 15 s acquisition time, and approximately 100 scans. The FIDs were multiplied by an exponential window with a line broadening factor of 1 Hz before Fourier transformation. The data point resolution is estimated to be 0.01 ppm (0.7 Hz). The chemical shifts reported are referenced to external $BF_3 \cdot Et_2O$ (0 δ) in CD_3CN at 75°C.

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