Carbon-13 Nuclear Magnetic Resonance Spectroscopy as a Method to Determine Relative Acidity of Boron Lewis Acids in Pyridine Complexes

Norberto Farfán* and Rosalinda Contreras
Centro de Investigación y de Estudios Avanzados del I.P.N., Departamento de Química, Apartado Postal 14-740, 07000 México, D.F.

Complexes of pyridine and 2-ethylpyridine with a series of boron Lewis acids have been studied using ^{1}H, ^{11}B, and ^{13}C n.m.r. The difference in chemical shifts ($\Delta\delta_{C-4}$) between the boron complex and the free pyridine were correlated with calorimetric data. The ^{13}C data show that $\Delta\delta_{C-4}$ of pyridines provides a measure of the strength of the N ——→ B bond, thus allowing a scale of acidity for boron compounds to be derived.

The co-ordination chemistry of boron Lewis acids and their extensive use as reagents for organic synthesis are of continuing interest.[1] In particular, considerable attention has been devoted to establishing a relative scale of acidity for boron acids which have been studied using mainly calorimetric data[2] and n.m.r. spectroscopy.[3,4] Although the latter method has been recognized as a powerful method to relate the enthalpy of formation of boron complexes to an easily determined parameter, namely the chemical shift, there are, to our knowledge, no comparative studies concerning the ^{13}C, ^{1}H, and ^{11}B n.m.r. analyses of pyridine and 2-ethylpyridine adducts with various Lewis acids. The data afforded by this investigation not only provide information concerning the nature of the N ——→ B bond but also allow a scale of acidity for boron compounds to be derived.

Table 1. Enthalpy, pK_a, and carbon-13 and fluorine-19 chemical shifts for BF_3 complexes of pyridines

Pyridine substituent	pK_a at 25° [b]	δ (p.p.m.) C-2 [a]	$\Delta\delta_{C-2}$ [c]	C-4 [a]	$\Delta\delta_{C-4}$ [c]	^{19}F [a]	ΔH^b/kcal mol^{-1}
4-CH_3	6.02	146.9	2.70	151.9	0.15	11.0	33.4
4-C_2H_5	6.02	150.1	0.40	153.2	0.50	10.9	33.2
3-CH_3	5.68	150.7	0.64	136.9	0.75	11.0	33.2
3-C_2H_5	5.70	149.9	0.50	136.1	1.00	11.0	33.1
None	5.17	150.2	0.00	136.9	1.00	11.1	32.9
2-CH_3	5.97	158.7	0.60	137.2	1.25	14.7	31.2
2-C_2H_5	5.92	163.5	0.10	138.0	1.90	16.4	30.6
2,6-$(CH_3)_2$	6.75	156.3	−1.20	138.5	2.20	25.0	25.4

[a] Data from ref. 4. [b] Data from ref. 2*b*. [c] $\Delta\delta = \delta_{pyBF_3} - \delta_{py}$, δ_{py} data from ref. 5.

Results and Discussion

In a previous study Fratiello[4] showed that ^{19}F n.m.r. chemical shifts can be correlated with enthalpy values and reflect the strength of interaction in the complexes. However, no correlation was observed for the ^{13}C n.m.r. data because the C-2 chemical shifts are sensitive to electronic and also to steric factors.

Re-evaluation of the ^{13}C data for the substituted pyridines summarized in Table 1 shows that, in contrast to previous results, the difference between the chemical shift of C-4 in the pyridine adducts and the free compounds ($\Delta\delta_{C-4}$) may be successfully correlated with the enthalpy values which, as observed, follow the same trend. The Figure shows a plot of the enthalpies of complex formation *versus* $\Delta\delta_{C-4}$. It is evident that C-4 reflects pure electronic effects. Once $\Delta\delta_{C-4}$ was established as an appropriate parameter, the strength of the co-ordination bond in pyridine adducts can be obtained.

The Lewis acids studied were BF_3, BH_3, $B(C_6H_5)_3$, $B(C_2H_5)_3$, $B(OC_6H_5)_3$, $B(OCH_3)_3$, $B(OH)_3$, $C_6H_4O_2BOC_6H_5$, $C_6H_4O_2BOCH_3$, $C_6H_4O_2BC_6H_5$, and $C_6H_5B(OH)_2$. In all cases equimolecular amounts of pyridine or 2-ethylpyridine were reacted with the corresponding Lewis acid in $CDCl_3$ solution and then i.r., ^{11}B, ^{1}H, and ^{13}C n.m.r. spectra were obtained. When an excess of pyridine was added, the free base signals were observed in the spectra, showing that solutions of the complexes do not involve rapid (on an n.m.r. time scale) equilibrium between the complex on the one hand, and the free base and Lewis acid on the other and therefore the chemical shifts can be used for acidity correlations. $B(OH)_3$, $B(OCH_3)_3$, and $C_6H_5B(OH)_2$ were not acidic enough to allow complex formation with pyridine. Also $C_6H_4O_2BOCH_3$ and $B(C_2H_5)_3$ did not form complexes with 2-ethylpyridine.

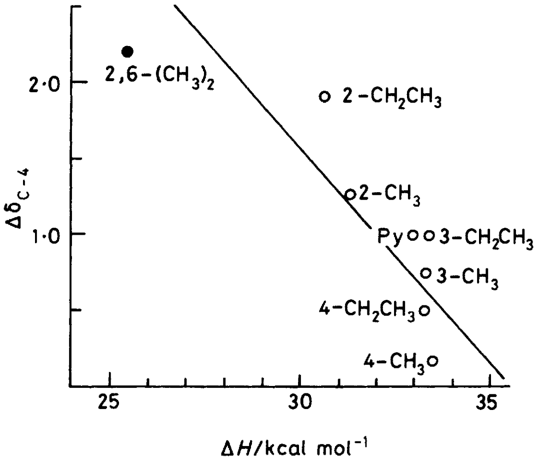

Figure 1. Plot of $\Delta\delta_{C-4}$ *versus* enthalpy of formation for several boron trifluoride–pyridine complexes

The pyridine complexes obtained are shown in Table 2. Based on the $\Delta\delta_{C-4}$ parameter the following approximate order of acid strength is proposed: BF_3 > $C_6H_4O_2BOC_6H_5$ > $C_6H_4O_2BOCH_3$ > $C_6H_4O_2BC_6H_5$ > $(C_6H_5O)_3B$ > $(C_6H_5)_3B$ > $(C_2H_5)_3B$.

Careful examination of the data in Table 2 shows that the C-2 chemical shift in the $B(OC_6H_5)_3$–pyridine complex is considerably shifted to lower field compared with the remaining complexes where it exhibits chemical shifts between δ 143 and 148 p.p.m. This deshielding may be attributed to steric and electronic effects operating on C-2. This effect is less evident in the ^{1}H chemical shifts of H-2 which are summarized in Table 3.

In contrast to the carbon-13 n.m.r., the i.r.[7] and ^{11}B data do not show a correlation between N $\longrightarrow$ B frequency or chemical shifts and bond strength. A similar analysis using 2-ethylpyridine and Lewis acids afforded the data in Table 4. As expected, steric hindrance plays an important role in 2-ethylpyridines where the following approximate order of acid strength is proposed: $BF_3 > C_6H_4O_2BOC_6H_5 > BH_3 > B(OC_6H_5)_3 > B(C_6H_5)_3 > C_6H_4O_2BC_6H_5$.

As in the case of pyridine complexes, the i.r. and ^{1}H n.m.r. spectra of 2-ethylpyridines (Table 5) do not seem to provide information concerning bond strength.

It is interesting to notice that the complexes formed by reaction of pyridine and 2-ethylpyridine with BH_3 and BF_3 showed very similar $\Delta\delta_{C-4}$ values (BH_3 $\Delta\delta_{C-4}$ 3.79 and 3.88, BF_3 $\Delta\delta_{C-4}$ 7.72 and 7.44). This may be attributed to the absence of steric effects on the Lewis acid during complexation.

Table 2. Boron-11 and carbon-13 chemical shifts for several boron Lewis acid complexes of pyridine

	δ (p.p.m.)					
	^{13}C				^{11}B	
Lewis acid	C-2	C-3	C-4	$\Delta\delta_{C-4}$[a]	^{11}B	$\Delta\delta^{11}$B[b]
BF_3	143.19[c]	126.19	143.42	7.72	0.05	9.35
$C_6H_4O_2BOC_6H_5$	144.13	125.62	141.80	6.10	9.53	14.14
$C_6H_4O_2BOCH_3$	144.14	125.42	141.50	5.80	9.63	14.12
$C_6H_4O_2BC_6H_5$	144.32	125.16	140.59	4.89	12.89	19.22
$B(OC_6H_5)_3$	155.70	125.09	140.15	4.45	3.67	14.33
$B(C_6H_5)_3$	148.27	125.30	139.55	3.85	1.50	71.50
BH_3	147.30	125.68	139.49	3.79	−11.20	81.00[d]
$B(C_2H_5)_3$	145.66	124.76	138.47	2.77	1.94	84.56

[a] $\Delta\delta_{C-4} = \delta_{pyBR_3} - \delta_{py}$. [b] $\Delta\delta^{11}B = \delta_{BR_3} - \delta_{pyBR_3}$. [c] q, $^3J_{CF}$ 2.4 Hz. [d] Ref. 6.

Table 3. Hydrogen-1 chemical shifts and i.r. data for several boron Lewis acid complexes of pyridine

	^{1}H δ[a]			
Lewis acid	H-2	H-3	H-4	δ/cm^{-1} N $\longrightarrow$ B[a]
BF_3	8.20	7.90	8.40	1 068
$C_6H_4O_2BOC_6H_5$	8.90	7.70	8.10	1 081
$C_6H_4O_2BOCH_3$	8.70	7.50	7.90	1 097
$C_6H_4O_2BC_6H_5$	8.60	7.10	7.30	1 077
$B(OC_6H_5)_3$	8.95	7.60	8.00	1 087
$B(C_6H_5)_3$	8.70	7.65	8.00	1 076
BH_3	8.70	7.65	8.15	1 088
$B(C_2H_5)_3$	8.60	7.50	7.90	1 061

[a] Cl_3CD as solvent.

Experimental

^{1}H, ^{11}B, and ^{13}C spectra were determined with a JEOL FX90Q instrument in deuteriochloroform solution, with tetramethylsilane as internal standard for ^{1}H and ^{13}C, and $BF_3 \cdot Et_2O$ as external standard for ^{11}B. The i.r. spectra were obtained with a Nicolet MX-1 spectrophotometer. The adducts were prepared using a 1:1 molar ratio of pyridine and the corresponding Lewis acid. ^{11}B N.m.r. was used as proof for complex formation. Pyridine and 2-ethylpyridine were dried prior to use by refluxing with KOH followed by distillation. Boron trifluoride was dried with calcium hydride followed by distillation. The Lewis boron acids were commercially available reagents.

Triphenoxyborane $(C_6H_5O)_3B$.—To a stirred ice-cold solution of phenol (3 g, 30 mmol) in tetrahydrofuran (5 ml) was added a 2M solution of $BH_3 \cdot THF$ (5 ml, 10 mmol). After 1 h the solvent was removed to give crystals, δ_H (90 MHz; $CDCl_3$) 6.70—7.40 (m); δ_B (28.6 MHz; THF) +16.4 p.p.m. (s).

Trimethoxyborane $(CH_3O)_3B$.—This was prepared using the procedure described for triphenoxyborane, δ_B (28.6 MHz; THF) +17.8 p.p.m. (s).

2-*Phenyl*-1,3,2-*benzodioxaborole* $C_6H_4O_2BC_6H_5$.—This was prepared by azeotropic dehydration of catechol (1.1 g, 10 mmol) and phenylboric acid (1.2 g, 10 mmol) using a Dean–Stark device with refluxing for 3 h. Evaporation of the solvent yielded crystals, δ_H (90 MHz; $CDCl_3$) 8.00—8.30 (2 H, m), 7.35—7.60 (3 H, m) and 7.00—7.35 (4 H, m); δ_B (28.6 MHz; THF) +32.11 p.p.m. (s).

2-*Phenoxy*-1,3,2-*benzodioxaborole* $C_6H_4O_2BOC_6H_5$.—To a stirred ice-cold solution of 1,3,2-benzodioxaborole (1.2 g, 10 mmol) in THF (10 ml) was added phenol (0.94 g, 10 mmol) in THF (10 ml). After 3 h the solvent was removed to give crystals, δ_H (90 MHz; $CDCl_3$) 6.80—7.40 (m); δ_B (28.6 MHz; THF) +23.70 p.p.m. (s).

2-*Methoxy*-1,3,2-*benzodioxaborole* $C_6H_4O_2BOCH_3$.—This was prepared using the procedure described for 2-phenoxy-1,3,2-benzodioxaborole, δ_H (90 MHz; $CDCl_3$) 6.80—7.13 (4 H, m) and 3.55 (3 H, s); δ_B (28.6 MHz; THF) +23.70 p.p.m. (s).

Table 4. Boron-11 and carbon-13 chemical shifts for several boron Lewis acid complexes of 2-ethylpyridine

	δ(p.p.m.)									
	^{13}C								^{11}B	
Lewis acid[a]	C-2	C-3	C-4	C-5	C-6	CH_2	CH_3	$\Delta\delta_{C-4}$	^{11}B	$\Delta\delta^{11}$B
BF_3	162.41	127.35	143.54[b]	123.80	143.80	27.55[c]	13.92	7.44	0.48	8.92
$C_6H_4O_2BOC_6H_5$	161.33	125.43	140.70	191.00	143.52	27.16	13.29	4.60	9.88	13.92
BH_3	162.41	124.87	139.98	122.38	148.87	27.73	12.18	3.88	−13.53	83.53
$B(OC_6H_5)_3$	162.55	123.01	138.51	121.74	147.14	30.83	13.70	2.41	13.10	4.23
$B(C_6H_5)_3$	163.77	125.01	138.12	121.30	147.68	30.22	13.35	2.02	5.19	67.81
$C_6H_4O_2BC_6H_5$	163.23	122.62	137.98	122.23	148.27	25.64	13.79	1.88	29.00	3.36

[a] Cl_3CD solvent. [b] q, $^3J_{CF}$ 5.8 Hz. [c] q, $^4J_{CF}$ 3.8 Hz.

Table 5. Hydrogen-1 chemical shifts and i.r. data for several boron Lewis acid complexes of 2-ethylpyridine

Lewis	^{1}H δ						δ/cm^{-1}
acid	H-3	H-4	H-5	H-6	CH_2	CH_3	N ⟶ B
BF_3	7.70	8.35	7.80	8.90	3.30	1.45	1 069
$C_6H_4O_2BOC_6H_5$	7.20	7.50	7.20	8.85	3.35	1.30	1 068
BH_3	7.50	8.00	7.40	8.81	3.24	1.35	1 086
$B(OC_6H_5)_3$	7.20	7.65	7.20	8.45	2.80	1.20	1 069
$B(C_6H_5)_3$	7.30	7.80	7.30	8.65	2.80	0.82	1 053
$C_6H_5BO_2C_6H_4$	7.40	8.00	7.40	8.55	2.85	1.30	1 069

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