A Direct Low-temperature Carbon-13 and Fluorine-19 Nuclear Magnetic Resonance Study of Boron Trifluoride Complexes with Pyridines

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Complexes of boron trifluoride with a series of substituted pyridines have been studied using a direct, low-temperature ^{13}C and ^{19}F n.m.r. technique. At temperatures from 0 to −40 °C, ligand exchange is slow enough to permit the observation of separate ^{13}C n.m.r. signals for bulk and co-ordinated pyridine molecules. The co-ordinated pyridine shift displacements are interpreted in terms of ligand polarization and a paramagnetic effect at the nitrogen atom. The BF_3 ^{19}F n.m.r. chemical shifts were correlated with calorimetric data in several cases, and in general provide a measure of the strength of the interaction but not of ligand basicity. Comparative complexing abilities were evaluated by studying several pyridine mixtures.

Complexes of boron trihalide with organic ligands have been studied by a variety of thermodynamic and spectroscopic techniques to evaluate heats of complex formation, structural features (such as steric hindrance and stoicheiometry), and relative base strengths.[1-15] Gas-phase experiments provide the best measure of basicities, since steric hindrance is precluded.[16-20] However, in solution, steric hindrance often is of major importance when solvation is possible and when the acid molecule is large.[21-24]

The applicability of n.m.r. spectroscopy to studies of acid–base systems, including metal-ion solvation[25-29] and boron trihalide complexes,[30-37] has been amply demonstrated. At temperatures low enough to slow exchange, separate resonance signals are observed for the boron trihalide complex and free (unbound) ligand. Information about electron density changes in the boron trifluoride and at sites throughout the base molecule is provided by ^1H, ^{13}C, and ^{19}F chemical shifts, and ^1H and ^{19}F signal area measurements lead to the determination of the composition of the complex and the relative complexing abilities of ligands. Carbon-13 n.m.r. spectroscopy is particularly useful in that even non-protonated functional groups can be studied, and carbon nuclei are sensitive to electron density changes induced by complex formation.[35-39] In the present study, ^{13}C and ^{19}F n.m.r. measurements were made with BF_3 complexes of several pyridines containing substituents varying in size, location, and electron-donating ability, to evaluate the features discussed above.

Methods

Dichloromethane and all pyridines were reagent grade and were dried over $CaSO_4$ before use. Matheson CP grade boron trifluoride was fractionated at −110 °C and condensed *in vacuo* into the n.m.r. sample tube (Wilmad 504PP) in liquid nitrogen. Sample tubes were sealed, warmed (solid CO_2–acetone) to dissolve all components, and stored in liquid nitrogen until the spectra were to be recorded. The absence of extraneous ^{13}C and ^{19}F n.m.r. signals confirmed the purity of the samples and the lack of decomposition.

The ^{19}F n.m.r. spectra were recorded with a Varian HA-100 spectrometer operating at 94.1 MHz. The ^{13}C n.m.r. spectra were obtained at 22.6 MHz using a Bruker HX-90-E Fourier transform spectrometer, equipped with a Bruker–Nicolet B-NC-12 data system. Pulses of about 3µs width (7 µs produces a 90° tip angle) were applied at 1 s intervals. Usually 2 000—4 000 pulses were required for sufficient signal intensity. As in previous studies,[35-37] calibration-type ^{13}C n.m.r. experiments using a relatively small number of pulses were carried out to verify the slow-exchange condition. The final spectra were recorded at the temperature yielding maximum signal intensity and resolution.

Results

Since ^1H n.m.r measurements had been completed previously for several of these pyridines,[32-34] most of this work involved ^{13}C and ^{19}F n.m.r. experiments. However, ^1H n.m.r. chemical shift and area measurements conclusively demonstrated the existence of 1 : 1 BF_3–pyridine complexes in all systems. In Table 1, the ^{19}F and ^{13}C n.m.r. chemical shift data for BF_3 complexes with a series of substituted pyridines are listed. The ^{19}F δ values represent the resonance positions, all downfield, of the complexed BF_3 with respect to internal C_6F_6, [*i.e.* $\delta(BF_3) - \delta(C_6F_6)$]. For comparison with $CFCl_3$, the reference value of +162.3 p.p.m. should be taken for $\delta(CFCl_3) - \delta(C_6F_6)$.[40] The ^{19}F and ^{13}C δ values are consistent with complexing at the pyridine nitrogen lone pair in all cases. For example, the ^{19}F δ values were about 11.1 p.p.m. for the complexes of pyridine and all 3- and 4-substituted pyridines. The ^{13}C δ values (to be discussed later) also did not depend significantly on the nature of the 3-, 4-, or 5-*C*-substituent. The BF_3 signals show BF_3 coupling, broadened by quadrupolar interaction and complexing.

The ^{13}C δ values in Table 1 are those of the bulk (B), unco-ordinated pyridines; the displacements resulting from co-ordination, $\delta_C - \delta_B$, are shown in parentheses, with a positive sign indicating a low-field shift of the signal of the complex. The ^{13}C signals were identified unambiguously in most spectra, though overlap sometimes occurred. In those cases in which a comparison could be made with the literature,[41-44] the δ_B values agreed within less than 0.2—1 p.p.m.; the difference can be attributed to solvent and temperature effects. Signal assignments for 2-vinyl-, 3-n-propyl-, 3-fluoro-, 2,4-dimethyl-, and 2,5-dimethyl-pyridine are not available in the literature, so they were made by analogy with other members of the series.

In Table 2, ^{19}F n.m.r. signal area data are given for BF_3 complexes with mixtures of pyridines. The ^{19}F chemical shifts of the complexes are not included since they agree almost exactly with those in Table 1. Rather than making an exhaustive study of all possible combinations, we made an attempt to select mixtures of pyridines which would permit a general comparison of complexing abilities. With the exception of the 2-vinylpyridine–2-n-propylpyridine mixtures, the choices avoided the problem of signal overlap.

Table 1. Carbon-13 and fluorine-19 chemical shifts for BF_3 complexes of pyridines

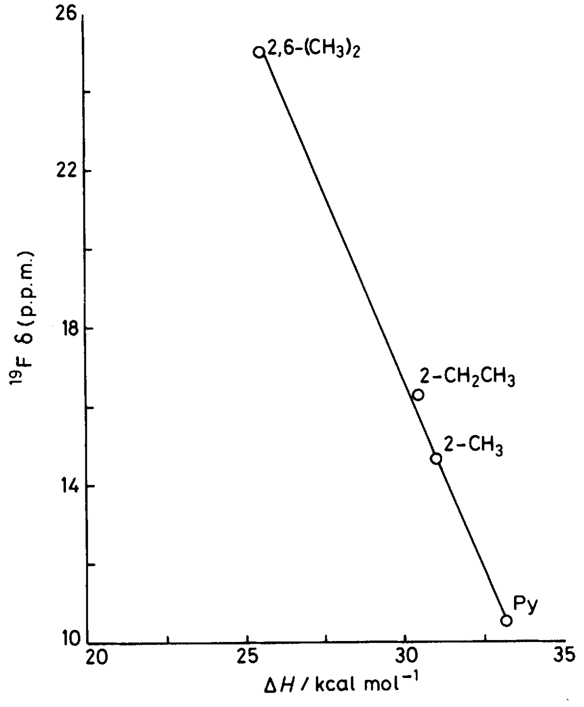
Pyridine[a,b]	θ/°C[c]	δ ^{19}F (p.p.m.)[d]	δ ^{13}C (p.p.m.)[e,f]							
			2-C	3-C	4-C	5-C	6-C	CH_2	CH_3	Other
Pyridine	−40	11.1	150.2	124.4	136.9	124.4	150.2			
			(−6.6)	(+2.5)	(+7.6)	(+2.5)	(−6.6)			
2-CH_3	−40	14.7	158.7	124.0	137.2	121.5	149.1		24.4	
			(−1.4)	(+5.4)	(+6.7)	(+2.2)	(−4.9)		(−3.1)	
2-CH_2CH_3	−40	16.3	163.5	123.1	138.0	122.0	148.7	31.2	14.4	
			(−1.0)	(+4.6)	(+6.0)[j]	(+1.7)	(−4.7)[j]	(−4.0)	*ca.* 0	
2-$CH_2CH_2CH_3$	−40	16.4	160.9	123.6	138.1	121.6	147.1	α, 39.3	14.0	β, 23.7
			(−0.5)	(+4.0)	(+5.0)	(+1.5)	(−4.0)	(−3.4)	(+0.4)	(+0.3)
2-CH=CH_2	−40	16.8	155.2	123.1	137.4	122.0	149.3	118.7		136.6
			(−2.0)	(+1.3)	(+6.3)[j]	(+3.0)	(−5.6)[j]	(+6.4)		(−5.5)
2-OCH_3	0	13.7	164.4	110.9	140.9	117.7	146.4		53.4	
	(−40)		(−0.7)	(−1.0)	(+6.3)	(+0.3)	(−3.5)		(+4.3)	
2-CN[g]	0	14.4								
2-F[h]	−15	14.7	163.9	110.0	141.9	121.8	147.7			
	(0)		(−2.1)	(+3.7)	(+0.5)	(+1.1)	(+2.3)			
2-Cl	−20	15.1	151.2	125.3	139.5	123.1	150.5			
	(0)		(−2.8)	(+4.8)	(+6.6)	(+1.6)	(−3.6)			
2-Br	0	15.2	142.5	128.9	139.5	123.5	150.8			
			(−4.7)	(+5.5)	(+7.7)	(+2.0)	(−5.8)			
3-CH_3	−40	11.0	150.7	133.8	136.9	123.6	147.3		18.6	
			(−7.3)	(+3.9)	(+3.8)	(+2.6)	(−2.7)		*ca.* 0	
3-CH_2CH_3	−40	11.0	149.9	140.3	136.1	124.1	147.5	26.4	16.0	
			(−8.6)	(+3.8)	(+7.7)	(+2.6)	(−4.6)	*ca.* 0	(−0.9)	
3-F[i]	−30	11.3	123.1	160.0	138.0	125.7	145.7			
	(0)		(+8.3)	(+0.6)	(−4.5)	(+3.0)	(−5.0)			
3-Cl	−40	11.2	148.9	132.9	136.6	125.2	148.0			
			(−5.7)	(−3.1)	(+7.6)	(+2.7)	(−5.7)			
3-Br	−30	11.2	151.2	121.4	139.2	125.6	148.4			
	(0)		(−5.8)	(+1.1)	(+3.3)	(+2.4)	(−1.4)			
3-I	−10	11.2	155.7	94.2	144.9	125.9	148.2			
			(−6.0)	(−0.6)	(+7.3)	(+1.8)	(−5.7)			
4-CH_3	−40	11.0	146.9	126.2	151.9	126.2	146.9		21.5	
			(−4.3)	(+1.2)	(+5.8)	(+1.2)	(−4.3)		(+0.4)	
4-CH_2CH_3	−40	10.9	150.1	124.0	153.2	124.0	150.1	29.0	14.8	
			(−7.1)	(+2.3)	(+9.8)	(+2.3)	(−7.1)	(−0.5)	(−0.8)	
4-$C(CH_3)_3$	0	10.9	148.8	121.0	160.4	121.0	148.8		30.4	34.9
	(−20)		(−6.1)	(+2.3)	(+8.3)	(+2.3)	(−6.1)		(−0.4)	(+0.6)
4-CH=CH_2	0	11.0	150.7	121.3	143.9[j]	121.3	150.7	119.0		135.3
	(−10)		(−6.8)	(+4.2)	(+8.5)	(+4.2)	(−6.8)[j]	(+4.5)		(−2.2)
2,4-$(CH_3)_2$	0	14.6	157.9	124.1[j]	147.5	121.8	148.5		(2)	(4)
	(−30)		(−1.6)	(+5.1)	(+8.2)	(+2.3)[j]	(−5.5)		24.1	20.9
									(−3.1)	(+0.5)
2,5-$(CH_3)_2$	0	14.5	155.0	122.6	136.9	130.1	149.0		(2)	(5)
	(−30)		(−1.3)	(+5.7)	(+6.6)	(+3.5)	(−5.5)		23.7	17.9
									(−3.1)	+0.2
2,6-$(CH_3)_2$	−10	25.0	156.3	121.2	138.5	121.2	156.3		23.2	
			(+1.4)	(+5.4)	(+3.3)	(+5.4)	(+1.4)		(+0.8)	
3,5-$(CH_3)_2$	−40	10.8	147.7	133.2	137.7	133.2	147.7		18.5	
			(−6.9)	(+4.0)	(+7.5)	(+4.0)	(−6.9)		(−6.8)	

[a] Solvent dichloromethane. [b] Within less than 5%, the molar ratios (BF_3–pyridine–CH_2Cl_2) were 1 : 2.25 : 11.5. [c] Temperatures listed for the ^{13}C n.m.r. measurements; when the ^{13}C and ^{19}F n.m.r. measurements were made at different temperatures, the latter are shown in parentheses. [d] The ^{19}F chemical shifts were measured with respect to internal C_6F_6, which appeared to higher field in all spectra. [e] The ^{13}C chemical shifts were measured with respect to internal tetramethylsilane, which appeared to higher field in all spectra. [f] The δ values are for the bulk (unbound) pyridine signals. The values in parentheses are the chemical shift differences in p.p.m. between the co-ordinated and bulk ligand signals ($\delta_C - \delta_B$); a positive sign indicates a signal displacement to lower field in the complex. [g] The BF_3 complex solubility was too low to permit ^{13}C measurements. [h] The signals are all doublets, with coupling constants of 10.6 (12.7), 1.6 (1.1), 0.3 (br), 0.2 (br), and 0.6 (0.5), respectively, for the 2-, 3-, 4-, 5-, and 6-C signals of the bulk and co-ordinated (in parentheses) pyridine; the δ values are averages. [i] The signals are all doublets with coupling constants of 0.8 (0.8), 11.3 (11.3), 1.0 (1.5), 0.2 (0.2), and 0.1 (0.1) p.p.m., respectively, for the 2-, 3-, 4-, 5-, and 6-C signals of the bulk and co-ordinated (in parentheses) pyridine; the δ values are averages. [j] The ^{13}C signals overlapped.

Table 2. BF_3 fractions complexed by pyridines

Mixtures[a,b] (A)	Mixtures[a,b] (B)	θ/°C	BF_3 fractions complexed (A)	BF_3 fractions complexed (B)
2-CH=CH_2	Pyridine	−40	—	1.00
	2-CH_3	−40	0.20	0.80
	$2\text{-CH}_2\text{CH}_2\text{CH}_3$	−40	(0.40)[c]	(0.60)[c]
	2-OCH_3	−40	0.47	0.53
	3-CH_3	−40	0.49	0.51
	$3\text{-CH}_2\text{CH}_3$	−40	0.56	0.44
	3-F	−40	0.34	0.66
	3-Cl	−30	0.46	0.54
	3-Br	−40	0.48	0.52
	3-I	−40	0.20	0.80
	$4\text{-CH}_2\text{CH}_3$	−40	0.34	0.66
$2\text{-CH}_2\text{CH}_3$	2-OCH_3	−40	0.34	0.66
	$3\text{-CH}_2\text{CH}_3$	−30	0.53	0.47
	3-F	−30	0.37	0.63
	3-Cl	−30	0.53	0.47
	4-CH_3	−30	0.40	0.60
	$4\text{-C(CH}_3)_3$	−30	0.50	0.50

[a] Of components A and B; solvent dichloromethane. [b] Within 5%, the molar ratios [BF_3–(A)–(B)–CH_2Cl_2] were 1 : 1.10 : 1.10 : 11.0. [c] Signal overlap present.



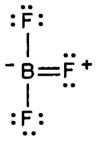
A plot of fluorine-19 chemical shift *versus* enthalpy of formation for several boron trifluoride–pyridine complexes; the point ' Py ' is actually a composite (see text); calorimetric data from ref. 2

Discussion

The variation of ^{19}F chemical shifts observed must reflect in some way the strengths of the BF_3–pyridine complexes. An illustration is provided by the observed correlation of the ^{19}F δ values of Table 1 with the enthalpies of complex formation.[2] A plot of the available data is shown in the Figure. The point labelled ' Py ' is actually a composite of the δ(11.0 ± 0.1 p.p.m.) and ΔH(33.2 ± 0.1 kcal mol^{-1}) values for pyridine and 3-methyl-, 3-ethyl-, 4-methyl-, 4-ethyl-, and 4-t-butylpyridine. With decreasing complex strength (ΔH), the BF_3 signal moves to lower field, with the greatest displacement for the bulky 2,6-dimethylpyridine. Consistent with this trend is the +35 p.p.m. displacement observed for unco-ordinated BF_3.[40] As in the calorimetric study, one may conclude that steric hindrance is the most important factor regulating the strength of the complex and, in this case, the BF_3 chemical shift.

It is not clear, however, why the intrinsic basic strength of the pyridines in comparable groups has only a minor effect on these BF_3 shifts, since it is reasonable to assume that complexing propensity must be related to this property. For example, the BF_3 complexes of pyridine itself and all 3- and 4-substituted pyridines exhibit resonance signals at about +11 p.p.m. from C_6F_6. This group includes compounds whose basicities, expressed as pK_{BH^+} ($BH^+ \rightleftharpoons B + H^+$), vary by several units. Pyridine and the 3- and 4-alkylpyridines have pK_{BH^+} values of +5 to +6, whereas those of the 3-halogenopyridines are *ca.* +3.[45–47] This behaviour is even more exaggerated with the BF_3 complexes of the 2-substituted pyridines, for which the ^{19}F δ values vary from about 14 to 17 p.p.m., a relatively small range. Here again, pK_{BH^+} varies significantly from 2-cyano- and the 2-halogeno-pyridines (<1) to the alkyl-substituted derivatives (*ca.* +6).[45–47] In fact the ^{19}F δ values of the 2-halogenopyridine complexes differ only slightly from that of the 2-methylpyridine complex.

These results may be related to the empirical observation that BF_3 is a weaker Lewis acid than BCl_3, whereas, considering relative electronegativities, one would predict the opposite. To explain this, resonance structures such as (1) have been proposed.[1,48] The back-bonding involved in this resonance form would make the boron atom less acidic, reduce diamagnetic shielding at the fluorine nuclei, and shift the unco-ordinated BF_3 ^{19}F resonance to lower magnetic field. Complexing with a base will diminish this effect and would be accompanied by an increased electron density and diamagnetic shielding at the fluorine nuclei, and, as observed here, ^{19}F resonance shifts to higher field. It is possible that the magnitude of these shifts is determined primarily by the BF_3–base bond length in the complex, and this would depend heavily on steric hindrance.



(1)

The ^{19}F n.m.r. results summarized in Table 2 demonstrate both the utility of this technique for evaluating competitive complexing abilities of bases, and the care which must be taken when making generalizations. For any particular mixture, the ^{19}F signal areas provide an unambiguous measure of the BF_3 complexed and a measure of the relative complexing strength of the two components. For example, towards BF_3, pyridine is a much stronger base than the sterically hindered 2-vinylpyridine. Also, in spite of steric hindrance, it is not surprising that 2-vinyl- and 2-ethyl-pyridine are able to compete effectively for BF_3 in the presence of the much less basic 3-halogenopyridines. However, on the basis of the results with 2-vinyl- and 2-ethyl-pyridine, it is not correct to conclude that the 3- and 4-alkylpyridines in Table 2 are weaker bases than pyridine itself. In fact, in previous work, these alkylpyridines complexed more BF_3 than pyridine when these mixtures were studied.[33] Such direct studies of particular mixtures provide the most accurate measure of relative complexing abilities.

In view of the diversity of the pyridines studied, it would be surprising if the ^{13}C n.m.r. shift displacements upon complexing could be interpreted in terms of totally general statements. However, among members of a similar group, certain trends are evident. For example, for pyridine itself and the ten monosubstituted alkylpyridines (including 2- and 4-vinylpyridine), the average chemical shift displacements induced by complex formation for 3-C ($+3.4 \pm 1.0$), 4-C ($+7.0 \pm 1.4$), 5-C ($+2.5 \pm 0.5$), and 6-C (-5.3 ± 1.1) are similar throughout the series. On the other hand, the 2-C shift displacements for the 2-substituted pyridines (-1.2 ± 0.5) differ markedly from those observed with the remaining members of these groups (-7.1 ± 0.6). Furthermore the 2-C shift displacement in the BF_3 complex of 2,6-dimethylpyridine is +1.4 p.p.m. Table 1 shows that the BF_3 ^{19}F δ values for the complexes of 2,6-dimethylpyridine, 2-alkylpyridines, and the remaining group members are +25, +16, and +11 p.p.m., respectively. While the correlation is not perfectly linear, there is a definite relationship between the BF_3 ^{19}F and the 2-C ^{13}C δ values. Since the ^{19}F δ results reflect the strengths of the complexes, the same may be true of the 2-C δ results.

However, the observed signs of the chemical shift displacements for the five pyridine carbon atoms indicate that more than one molecular property must be operative, particularly at 2- and 6-C. Consider first that the ^{1}H and ^{13}C n.m.r. signals for the 2- and 6-CH nuclei of pure pyridine appear at lower field than the 3-, 4-, and 5-CH peaks.[41–44] Also, in prior ^{1}H n.m.r. studies of BF_3 and BCl_3 complexes of several pyridines, the low-field displacements of the 2- and 6-CH signals were significantly attenuated in comparison with the 3-, 4-, and 5-CH peaks of bound ligand.[32] Moreover, ^{1}H and ^{13}C chemical shift displacements induced by protonation of pyridine are analogous in sign and magnitude to those induced by BF_3 complexation.[49,50] For the 2- and 6-CH, 3- and 5-CH, and 4-CH signals, respectively, displacements of +4, +30, and +36 Hz (^{1}H)[49] and −7.8, +5.0, and +12.4 p.p.m. (^{13}C)[50] were measured. In all the prior studies, the 2- and 6-CH n.m.r. data were interpreted in terms of a so-called paramagnetic effect arising from the mixing of low-lying energy levels in the nitrogen atom. This effect could account for the 2- and 6-CH low-field ^{1}H and ^{13}C resonance positions. Also, the diminution of this effect by complex formation could explain the attenuated ^{1}H δ values and the upfield ^{13}C δ values observed here. Whereas polarization of the pyridine molecule by BF_3 may dominate at the 3-, 4-, and 5-C sites, producing low-field displacements, this additional paramagnetic effect may be of importance at the 2- and 6-carbon atoms.

With the exception of 2,6-dimethylpyridine, the chemical shift displacements of the co-ordinated dialkylpyridines were similar to those obtained with the monoalkylpyridines. In fact, even though the remaining compounds in Table 1 contain electron-withdrawing substituents which cause extensive changes in pyridine properties (basicity, for example), the shift displacements are similar in most cases to those discussed previously. This merely implies that, even in these cases, the same factors as discussed above are operative.

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