BORON-11 CHEMICAL SHIFTS IN THE DETERMINATION OF DONOR-ACCEPTOR STRENGTHS—VII

PYRIDINE—BORANE AND PHENYLBORANE COMPLEXES[1]

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Abstract—The ^{1}H and ^{11}B spectra of a series of pyridine- and substituted pyridine–borane and phenyl-borane (Py, BH$_3$ and Py, PhBH$_2$) complexes have been measured. The ^{14}N chemical shifts of pyridine, 2-, 3- and 4-methyl and 4-ethyl-pyridines and the borane complexes and the hydrochlorides have also been determined.

The ^{11}B chemical shifts have been related to the donor strengths of the pyridines and, as for the boron trihalide complexes, the order of donor strengths was found to be 2-alkyl- > 4-alkyl- > 3-alkyl-pyridines and pyridine, an order contrary to thermochemical correlations. The merits of using the ^{11}B chemical shifts to determine donor-acceptor interaction are considered.

INTRODUCTION

PREVIOUS papers in this series[2] have clearly demonstrated that the boron-11 shifts may be correlated with the donor-acceptor properties of Lewis acid-base systems. On this basis it has been shown[3] that, in the boron trihalide complexes, the donor strengths of the 2-methyl- and 2-ethyl pyridines were unexpectedly greater than those of the corresponding 4-methyl- and 4-ethyl-pyridines. On the basis of Brown's F-strain theory[4] the presence of the 2-alkyl groups could cause a "face-to-face" interaction between the pyridine and the boron trihalide resulting in a reduction in the apparent basic strength of the 2-alkyl pyridine. In view of these anomalous results, found in the boron trihalide system, we have now investigated the complexes of pyridine and substituted pyridines with borane and phenylborane.

EXPERIMENTAL

Preparation of pyridine–borane complexes. A steady stream of diborane was bubbled through a solution of the pyridine in pentane to afford the complex (Table 1). The diborane was conveniently prepared by the addition of diethyl ether–boron trifluoride to sodium borohydride suspended in the minimum of "diglyme". It was originally claimed[5] that the reverse order of addition was obligatory for the formation of diborane.

Preparation of pyridine–phenylboranes. The complexes (Table 2) were prepared by the method of Hawthorne[6] who had previously described pyridine–phenylborane. In the case of the complexes of the 2,6-dimethyl and 2,4,6-trimethyl-pyridines no water was added to decompose the excess lithium aluminium hydride, since the addition of water resulted in the decomposition of the complex.

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3. E. J. McLauchlan and E. F. Mooney, *Spectrochim. Acta* **23A**, 1227 (1967).
4. H. C. Brown, *J. Chem. Soc.* 1248 (1956).
5. H. C. Brown and P. A. Tierney, *J. Am. chem. Soc.* **80** 1552 (1958).
6. M. Hawthorne, *Chemy. Ind.* 1243 (1957); *J. Am. chem. Soc.* **80** 4291 (1958).

Table 1. Pyridine–borane complexes – Py, BH_3

Substituent	Yield (%)	m.p.	Analysis: found			Formula	Analysis: calculated		
			C (%)	H (%)	N (%)		C (%)	H (%)	N (%)
Unsubstituted	95·1	*	64·9	8·7	15·3	C_5H_8BN	64·6	8·7	15·1
2-Me	93·9	50°	67·3	9·5	13·4				
3-Me	95·5	*	67·1	9·2	13·3	$C_6H_{10}BN$	67·4	9·4	13·1
4-Me	96·0	72·5°	67·6	9·5	13·4				
2-Et	92·0	50–51°	69·5	9·9	11·8				
3-Et	92·8	*	69·6	9·7	11·4	$C_7H_{12}BN$	69·5	10·0	11·6
4-Et	93·5	*	68·4	10·2	11·5				
2-Pr^n	75·3	*	71·2	10·5	10·4	$C_8H_{14}BN$	71·2	10·5	10·4
2-Phenyl	76·4	56–58°	78·2	7·1	8·2	$C_{11}H_{12}BN$	78·2	7·2	8·3
4-Phenyl	85·3	102–103°	78·0	7·3	8·3				
2,6-Di Me	49·5	106–107°	69·2	10·0	11·9	$C_7H_{12}BN$	69·5	10·0	11·6
2,4,6-Tri Me	80·7	99–100°	68·5	10·4	10·0	$C_8H_{14}BN$	71·2	10·5	10·4

*Liquids which decompose violently on attempting to distill.

Spectroscopic measurements. The ^1H spectra were recorded in methylene dichloride using a Varian A60 spectrometer; the solvent was used as the internal standard. The ^{11}B and the ^{14}N spectra were recorded in methylene dichloride solution at 12·83 and 4·34 Mc/s. respectively using Perkin-Elmer R 10 Spectrometer; a Northern Scientific 544 C.A.T. was used for the ^{14}N measurements. The accuracy of the ^{11}B chemical shifts is ±0·05 ppm, while that of the broader ^{14}N signals is ±0·1 ppm.

RESULTS

The ^{11}B chemical shifts, in ppm from dimethyl ether–boron trifluoride, and the shifts, in c/s of the methyl and the methylene groups on complex formation are shown in Tables 3 and 4. As, has already been discussed[7] the ^{11}B shifts of the uncomplexed and complexed borane cannot be compared because of the dimeric nature of free "borane", i.e. diborane. The ^{11}B—^1H coupling constants are within the general range normally expected in borane complexes. An interesting point is that, in these pyridine–borane complexes, no ^1H resonance signals of the BH_3 group have been observed; a similar situation was found in phosphite–borane[7] and in dialkylaminoboranes[8]. The difficulty in observing the ^1H resonance of the B—H protons cannot be due to exchange, since the ^{11}B resonance signals were sharp and the ^{11}B—^1H coupling constants were readily determined. The chemical shifts and the coupling constants of the ring protons of the free and complexed pyridine bases were calculated using the LAOCOON II iterative programme[9], which had been modified for use on the University KDF 9 computer.

DISCUSSION

Using the criterion of the ^{11}B chemical shifts as a measure of the strength of the co-ordinate bond it can be seen that in the pyridine–borane complexes the donor strengths of the pyridines are in the order: 2,4,6-trimethyl > 2,6-dimethyl > 2-ethyl > 2-methyl ≈ 2-*n*-propyl ≈ 2-*n*-butyl > 2-phenyl > 4-

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8. E. F. Mooney and B. S. Thornhill, Unpublished work.
9. S. Castellano and A. A. Bothner-By, *J. chem. Phys.* **41**, 3863 (1964).

Table 2. Pyridine–phenylborane complexes – Py, $PhBH_2$

Substituent	yield (%)	m.p.	Analysis: found				Formula	Analysis: calculated			
			C (%)	H (%)	B (%)	N (%)		C (%)	H (%)	B (%)	N (%)
Unsubstituted	84·3	78·0†	78·0	6·9	6·4	8·2	$C_{11}H_{12}BN$	78·2	7·2	6·3	8·3
2-Me	87·6	64·5	78·5	7·6	5·6	7·3	$C_{12}H_{14}BN$	78·7	7·7	5·9	7·7
3-Me	95·0	46–47	78·7	7·9	6·2	7·4					
4-Me	95·0	49–49·5°	78·8	7·7	6·1	7·5					
2-Et	43·4	105–107°	79·3	8·0	5·7	7·1					
3-Et	45·2	†	79·3	8·5	—	7·2	$C_{13}H_{16}BN$	79·2	8·2	5·5	7·1
4-Et	46·2	28–30°	79·1	8·2	—	7·2					
2-Pr^n	84·3	25–27°	79·8	8·5	—	6·6	$C_{14}H_{18}BN$	79·7	8·6	—	6·6
2,6-Di Me	65·7	40–43°	79·3	8·5	—	—	$C_{13}H_{16}BN$	79·2	8·2	—	—
2,4,6-Tri Me	60·8	(decomp.)	79·5	8·4	—	6·3	$C_{14}H_{18}BN$	79·7	8·6	—	6·6

†Hawthorne[6], quotes 83–85°.

Table 3. Chemical shifts of pyridine–borane complexes

| | $\delta^{11}B$† | $J^{11}B-^1H$ | Shift of alkyl resonances* | |
			$\delta(CH_3)c/s$	$\delta(CH_2)c/s$
Unsubstituted	+12·95	104·3	—	—
2-Me	+14·40	104·4	−13·5	—
3-Me	+12·30	104·3	−5·5	—
4-Me	+13·20	102·65	−20·0	—
2-Et	+14·80	103·9	−1·5	−22·5
3-Et	+12·50	103·0	−3·0	−9·5
4-Et	+13·25	102·9	−0·5	−6·0
2-Pr^n	+14·40	104·45	+3·0	−19·0‡
2-Bu^n	+14·40	104·7	+1·0	−21·0‡
2-Phenyl	+13·90	108·4	—	—
4-Phenyl	+13·80	105·2	—	—
2,6-Di Me	+19·00	103·3	−19·5§	
2,4,6-Tri Me	+19·50	100·3	{−25·5§ {−19·5‖	

*Shifts of the CH_3 and CH_2 resonances of the alkyl pyridines to low (−) or high (+) field on complex formation.

†ppm to high field of external Me_2O, BF_3.

‡α-CH_2 resonance.

§2,6-Methyl resonances.

‖4-Methyl resonance.

Table 4. Chemical shifts of pyridine–phenylborane complexes

| | $\delta^{11}B$* | $J^{11}B-^1H$ | Shift of alkyl resonance† | |
			$\delta(CH_3)c/s$	$\delta(CH_2)c/s$
Unsubstituted	+3·30	102·65	—	—
2-Me	+5·85	103·65	−11·5	—
3-Me	+3·65	94·60	−9·75	—
4-Me	+4·00	92·40	−17·25	—
2-Et	+6·15	102·65	0·00	−23·0
3-Et	+3·65	98·80	−12·8	−15·0
4-Et	+4·60	105·85	−10·0	−15·5
2-Pr^n	+6·80	102·65	−3·5	{−28·0‡ {−19·0§

*ppm to high field of external Me_2O, BF_3.

†Shifts of the CH_3 and CH_2 resonances of the alkyl pyridines to low-field on complex formation.

‡α-CH_2 resonance.

§β-CH_2 resonance.

phenyl > 4-ethyl ≈ 4-methyl > pyridine > 3-ethyl > 3-methyl. Surprisingly the highly substituted pyridines are the best donors despite the face-strain which might have been expected between the 2- and 6-methyl groups and the hydrogen atoms of the BH_3 group. Even the presence of the bulky 2-*n*-butyl and 2-phenyl groups does not appreciably reduce the donor strength of the base as both of these substituted pyridines are better donors than pyridine.

In the case of the pyridine–phenylborane complexes the [11]B chemical shifts give the donor strengths of the pyridines as decreasing in the order 2-*n*-propyl > 2-ethyl > 2-methyl > 4-ethyl > 4-methyl > 3-ethyl ≈ 3-methyl > pyridine. The data for the 2,4,6-trimethyl- and 2,6-dimethyl-pyridine phenylboranes are not available as both of these complexes decomposed very quickly on resolution. However in both the borane and phenylborane complexes the order of donor strength of the pyridines decreased in the order: 2-alkyl- > 4-alkyl- > 3-alkyl-pyridines and pyridine. The present results confirm the rather surprising observation, previously found in the study of pyridine–boron trihalide complexes[3], that the donor strengths of the 2-alkyl pyridines are greater than those of the 4-alkyl pyridines. The order of donor strengths found in these investigations do not correlate with the pKa values of the free pyridines for, on the bases of these values, the donor strengths would be expected to decrease in the order 4-alkyl- > 2-alkyl- > 3-alkyl-pyridines > pyridine. The point which warrents some comment is that the order of donor strengths, based upon the [11]B shifts, found in both the cases in which borane and phenylborane are the acceptor molecules and that using the boron trihalides as the acceptors, is in contradiction to the order found by Brown and his co-workers. Both in the earlier work of Brown with pyridines and boron trihalides[10], and in a more recent study[11], of alkyl pyridines and the deuterated derivatives with boron trifluoride, nitrobenzene was used as the solvent for the reaction of the pyridine with the boron trihalide or borane. Brown and Holmes[12] had previously described the isolation of the complexes of nitrobenzene with the boron trihalides which, with the exception of that with boron tribromide, were fairly stable. In a recent investigation[1] we have measured the [11]B and ^{14}N chemical shifts of the nitrobenzene complexes and the order of acceptor strengths of the boron trihalides as determined from the chemical shift measurements is in complete agreement with that obtained earlier[12]. However if we consider the donor strength of nitrobenzene in relationship to other bases we find, from the Δ^{11}B values and considering for example boron trifluoride as the standard Lewis acid, that the basic strength of nitrobenzene is slightly less than that of benzophenone, while benzophenone is in turn a weaker donor than pentafluoronitrobenzene. It is thus clear that using the heats of reaction of the boron trihalide with nitrobenzene solutions of the pyridines for the determination of donor-acceptor strengths is liable to error as no consideration of exchange reactions, or equilibrium, of the type

$$\phi NO_2, BX_3 + Py \rightleftharpoons \phi NO_2 + Py, BX_3$$
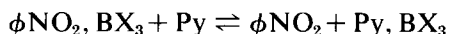
was made.

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11. H. C. Brown, M. E. Azzaro, J. G. Koelling and G. J. McDonald, *J. Am. chem. Soc.* **88**, 2520 (1966).
12. H. C. Brown and R. R. Holmes, *J. Am. chem. Soc.* **78**, 2173 (1956).

We believe that our method of using the differences in the ^{11}B chemical shifts is a particularly useful parameter for the investigation of donor-acceptor strengths since all our investigations have been carried out in methylene dichloride solution and the chemical shifts reflects the presence of any dissociation or exchange. If the exchange (1) occurs slowly then separate resonance signals of the free and complexed boron compounds would be observed, while if the exchange was rapid a time-average shift of the free and complexed boron halide would be recorded. In this latter instance the recorded shift will be lower than that of the undissociated complex, thus the use of the ^{11}B parameter is valid since it does truely reflect the stability of the complex.

$$Py, L \rightleftharpoons Py + L.$$

(1)

Furthermore this particular type of measurement does ensure that we are observing the species in which we are interested. An example of this is seen in the study of complexes of di-n-butyl ether with boron trichloride in which a ^{11}B resonance signal at $-21 \cdot 0$ is first observed due to the complex Bu_2O, BCl_3 but a new signal at $-31 \cdot 3$ very quickly appears at the expense of the high-field signal, and finally within 20 min only the low-field signal is observed. This new signal results from the formation of the n-butyl dichloroborinate due to the decomposition of the complex; the shift is in good agreement with that previously recorded by us for the borinate[13]. An additional example of the value of this type of investigation was apparent during our study of pyridine–boron trihalide complexes. It was found[14] that mixing 2,6-dimethylpyridine and boron tribromide in 1 : 1 molar proportions in chloroform solution resulted in the formation of four separate ^{11}B resonance signals at $+1 \cdot 5$, $+8 \cdot 9$, $+12 \cdot 0$ and at $+25 \cdot 1$ ppm to high field of Me_2O, BF_3. The signal at $+8 \cdot 9$ almost certainly corresponds to the 1 : 1 complex while the high-field signal at $+25 \cdot 1$ is due to the presence of the tetrabromo-borate ion (the shift has been given[15] as $+23 \cdot 9$ ppm with respect to Et_2O, BF_3). These two examples illustrate that thermochemical measurements for the determination of donor-acceptor strengths could lead to erroneous results.

As has previously been observed[16] there is no correlation between the shifts of the ring protons and the ring alkyl substituents, on complex formation, and the donor property of the pyridine. Examination of the proton shifts recorded in Tables 3–5 clearly show that there is no definite pattern. It is not surprising that, for example, the shift of the methyl group resonance in the 2-, 3-, 4-, 2,6- and 2,4,6-substituted pyridines cannot be related. The anistropy of the co-ordinate $N \rightarrow B$ bond would affect the chemical shifts of the alkyl substituents of the pyridine ring, and the extent of deshielding will depend upon the relative position of the alkyl group with respect to the $N \rightarrow B$ bond and is determined by the function θr^{-3}, where $r =$ distance of alkyl group protons from the $N \rightarrow B$ bond

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Table 5. Shifts* of the ring protons of alkyl pyridines on formation of the borane complexes

	δ_2	δ_6	δ_3	δ_5	δ_4
2-Me	—	−8·7	−18·9	−20·1	−16·75
3-Me	+4·05	+2·4	—	−18·15	−19·35
4-Me	+2·85	+2·85	−20·15	−20·15	—
2-Et	—	−10·35	−21·8	−22·05	−23·2
3-Et	+1·3	−1·0	—	−22·7	−24·5
4-Et	+7·7	+7·7	−12·45	−12·45	—
2,6-Di Me	—	—	−22·85	−22·85	−18·2
2,4,6-Tri Me	—	—	−33·0	−33·0	—

*Shifts are expressed in c/s to low (−) or high (+) field on complex formation with borane.

and θ = angle subtended by the alkyl protons with respect to the N → B bond.

On the basis of the large reduction of the electron density of the nitrogen atom on complex formation we would have anticipated that the ring protons in the 2- and 6- positions could have experienced the greatest degree of deshielding. However Table 5 shows that this is not the case and in the absence of a 2-alkyl substituent the 2- and 6-ring protons are usually shielded. There have been several instances now of the study of solvent effects upon the chemical shifts of the ring protons of substituted pyridines. The most recent investigation using phosphorus and arsenic trichlorides, liquid sulphur dioxide and trifluoroacetic acid as solvents has confirmed that the β- and γ-protons experience greater deshielding than those of the α- positions[17]. Baldeschwieler and Randall[18] have explained both the low-field ^{14}N resonance of pyridine and the insensitivity of the shift of the α-protons in terms of a paramagnetic contribution from the nitrogen atom. In a more detailed consideration of this Gill and Murrell[19] have shown that the low-field resonance of the α-proton is due to both the magnetic anistropy of the nitrogen atom and the local dipole moment associated with the nitrogen line pair. We therefore suggest that the shielding of the α-protons observed in the present work is due to the removal of the paramagnetic effect of the nitrogen and to the effect of the localised dipole of the $B^{\delta-} \leftarrow N^{\delta+}$ co-ordinate bond; such a large dipole is not present in the pyridinium ion in which the $\overset{+}{N}$—H bond is essentially covalent.

Nitrogen-14 *chemical shifts*

To attempt to elicidate these effects more clearly we have measured the ^{14}N shifts of pyridine and the 2-, 3- and 4-methyl and 4-ethyl pyridines and the corresponding hydrochlorides and borane derivatives, and these results are shown in Table 6. There is by no means such a large shift to high field in the pyridine–borane complexes as occurs in the pyridine hydrochlorides which suggests that there may still be a paramagnetic contribution arising from the nitrogen atom, although this seems unlikely since in the borane complexes the nitrogen lone-pair

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19. V. M. S. Gill and J. N. Murrell, *Trans. Faraday Soc.* **60** 248 (1964).

Table 6. Nitrogen-14 shifts of pyridine, alkyl-pyridines and of the hydrochlorides
and borane-complexes

Pyridine	Free base* δ‡	Hydrochloride† δ‡	Δ	Borane-complex* δ‡	Δ
Unsubstituted	+59·3	+166·6	+107·7	+122·0	+62·7
2-Methyl	+59·4	+162·3	+102·9	+123·8	+64·4
3-Methyl	+59·2	+163·3	+104·1	+114·5	+55·3
4-Methyl	+60·3	+168·6	+108·3	+119·5	+59·2
4-Ethyl	+60·2	+169·0	+108·8	+122·8	+62·6

*Recorded in methylene dichloride solution.

†Recorded in conc. hydrochloride acid solution to prevent hydrolysis.

‡Shifts in ppm to high-field of the nitrate resonance of external ammonium nitrate solution; Δ represents the shift to high-field on formation of the pyridinium ion or of the complex.

is used in forming the co-ordinate bond. Our experience of the variation of ^{14}N shifts in amine complexes is too limited at present to draw any definite conclusions but it seems possible that shielding of the nitrogen nucleus and of the α-protons could arise from a common source, namely the anisotropy of the co-ordinate bond.

The i.r. spectra

The i.r. spectra of all the complexes have been examined in the range of 4000–400 cm^{-1} and vibrational assignments made. We were unable to assign the B ← N stretching frequency and, apart from the general observation that the ν(C—C, C—N) modes in the region 1450–1330 cm^{-1} fell to lower frequency on complex formation, there was little effect upon the pyridine vibrations. In the pyridine-copper(II) halide complexes the ν(C—C, C—N) modes increased slightly in frequency (2–10 cm^{-1})[20], and in this case, as in the present work, we considered that the frequency changes of the fundamental vibrations of the pyridine ring are insufficient to be of any reliable value in accessing donor-acceptor interaction.

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