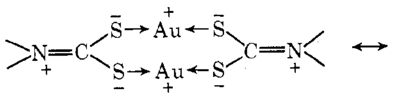
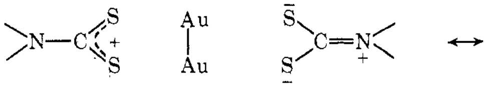
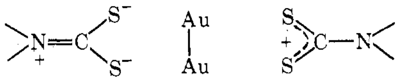

IV


V

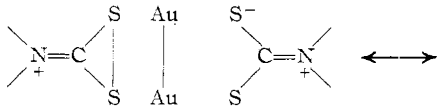

VI

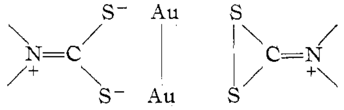
stant, 1.95 mdyn/Å, is nearly as large as that of $\mathrm{Au_2}^0$ and might have been taken to suggest a full Au–Au bond. However, force constants for cyclic molecules are not comparable with those for acyclic molecules, because of the extra redundancies among internal coordinates in the former. The Au–Au force constant in $\mathrm{Au_2(S_2CN(C_4H_9)_2)_2}$ contains indeterminate contributions from ring angles which have been neglected in the normal-coordinate analysis: S–Au–Au and S–Au–S. It has previously been noted that metal–metal force constants in weakly interacting polynuclear complexes are much higher than the strength of the interaction would suggest.[2,3]

Contributions of resonance forms V and VI should also lower the bond order of the Au–S bonds below that expected for a mononuclear complex. Raman intensities for metal–sulfur bonds have not been previously reported, so there is no reference point for comparing the present $(n/2)_{\mathrm{Au-S}}$ values, 0.24 or 0.25. For several metal–carbon bonds, $n/2$ ranges between 0.5 and 0.7.[2,4]

Because of the extensive mixing of C–S stretching and S–C–S bending, $\bar{\alpha}'_{\mathrm{C-S}}$ and $\bar{\alpha}'_{\mathrm{S-C-S}}$ are less well determined than $\bar{\alpha}'_{\mathrm{Au-S}}$ and $\bar{\alpha}'_{\mathrm{Au-Au}}$. In connection with the C–S bond order estimate, there is not much to choose between set 1 and set 2. Both suggest a bond order substantially in excess of unity. While the proposed 25% contribution from resonance forms V and VI would raise the theoretical C–S bond order to 1.12 and contributions from forms I and II would raise it slightly more, the $n/2$ values seem much too high, especially since they normally underestimate the theoretical bond order. For example $(n/2)_{\mathrm{C-C}}$ in ethane is 0.5 or 0.7.[16] Excessive $n/2$ values have previously been found[20,21] in π-delocalized systems where coordinate mixing is extensive, a situation which obtains here. The effect has been ascribed to cooperative contributions to the molecular polarizability derivative, which are not taken into account in eq 1.

This effect may also explain the high $\bar{\alpha}'_{\mathrm{S-C-S}}$ values reported here. In the Wolkenstein bond polarizability theory, bond bending is assumed not to contribute to molecular polarizability derivatives. Consistent with this assumption, measured values of $\bar{\alpha}'_{\mathrm{bend}}$ have usually been quite small.[14] Values as high as 0.84 (set 1), let alone 1.21 (set 2), are unprecedented. Aside from the delocalization effect, such values might be taken to imply a degree of sulfur–sulfur interaction, since S–C–S bending is approximately equivalent to the stretching of a hypothetical S–S bond. Indeed it is not unreasonable to write the following resonance forms as alternatives to V and VI


VII


VIII

It must be admitted, however, that, in contrast to the Au–Au distance, the S–S distance, at 3.05 Å, gives no support for the idea of a bonding interaction. On the other hand, this distance is largely determined by the C–S bond length and the hybridization ($\mathrm{sp^2}$) at the carbon atom.

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A Fluorine-19 Nuclear Magnetic Resonance Study of Some Boron Trifluoride Adducts

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A fluorine-19 nuclear magnetic resonance study of some substituted aromatic amine 1-oxide adducts of boron trifluoride was conducted. The $^{11}\mathrm{B}$–$^{19}\mathrm{F}$ spin–spin coupling constant is found to be negative in chloroacetonitrile. It is illustrated from the nmr data that variations in chemical shift are due primarily to steric factors.

Introduction

Inquiry into the $^{11}\mathrm{B}$–$^{19}\mathrm{F}$ spin–spin coupling constant in the tetrafluoroborate anion began several years ago with the studies of Kuhlman and Grant[2] and was later expanded by Gillespie and coworkers.[3] $J_{^{11}\mathrm{B}-^{19}\mathrm{F}}$ was

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[1] National Defense Education Trainee, 1967–1968, 1970–1972.

[2] K. Kuhlman and D. M. Grant, *J. Phys. Chem.*, **68**, 3208 (1964).

[3] R. J. Gillespie, J. S. Hartman, and M. Parekh, *Can. J. Chem.*, **46**, 1601 (1969).

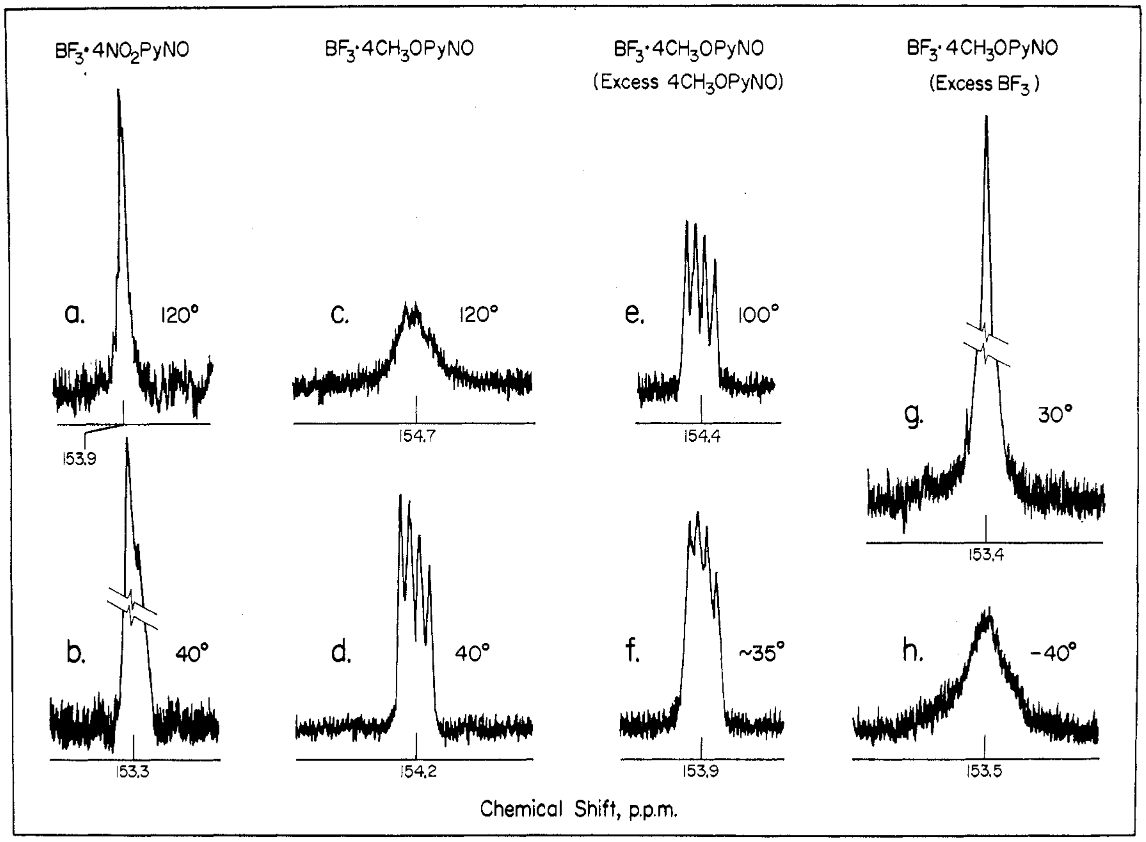

Figure 1.—Selected ^{19}F nmr spectra of some boron trifluoride adducts of pyridine 1-oxides (pyNO).

found to be unusually small, between 1 and 5 Hz, and to be dependent on the concentration of the ions and the nature of the cation, as well as the solvent. It was suggested that the anomolously low magnitude of $J_{^{11}B-^{19}F}$ is the result of two opposing coupling mechanisms of nearly equal magnitude. This is a result predicted by the molecular orbital calculations of Pople and Santry[4] for the interaction between small nuclei, such as boron and fluorine.

Since BF_4^- can be considered a fluoride adduct of BF_3 and viewing the results of both Kuhlman and Grant and Gillespie and workers, it became interesting to investigate other adducts of BF_3. Choosing aromatic amine 1-oxides (where Z-pyNO, Z-QNO, and ANO represent the substituted pyridine 1-oxides, quinoline *N*-oxides, and acridine *N*-oxide, respectively) as the ligands provided not only the opportunity to study solvent and concentration effects but also to investigate any changes in $J_{^{11}B-^{19}F}$ due to differing donor basicity. Since all the complexes are neutral, there was no need to be concerned with cation effects.

Experimental Section

All of the complexes were prepared by bubbling boron trifluoride (Matheson) through a chloroform solution of the desired aromatic amine 1-oxide;[5-7] in some cases the complex precipitated immediately; in most, an oil formed. In all instances, however, the chloroform was removed with a rotary evaporator and anhydrous diethyl ether was added, often with slight trituration, to effect crystallization. The complexes were then filtered, washed with ether, and dried *in vacuo*. The complexes were not found to be overly water sensitive. Only the reaction was carried out under dry nitrogen; all other manipulations were performed with no special precautions. The preparation of the pyridine 1-oxide and 4-methylpyridine 1-oxide adducts of BF_3 have been previously reported.[8]

Representative compounds were analyzed by Alfred Bernhardt Laboratorium, Mülheim, Germany. These data are given in Table I. Comparison of the infrared and nmr spectra of the compounds not analyzed with the spectra of those analyzed indicate the formation of 1:1 adducts in all cases.

TABLE I
ELEMENTAL ANALYSES FOR SOME REPRESENTATIVE AROMATIC AMINE OXIDE ADDUCTS OF BORON TRIFLUORIDE

	% C		% H		% N	
	Calcd	Found	Calcd	Found	Calcd	Found
BF_3·4-CH_3OpyNO	37.4	37.0	3.7	3.6	7.3	7.2
BF_3·4-CH_3pyNO	40.7	40.9	4.0	4.0	7.9	8.1
BF_3·4-NO_2pyNO	28.9	29.4	1.9	2.0	13.5	12.7
BF_3·4-CH_3OQNO	49.4	48.9	3.7	3.4	5.8	6.0
BF_3·4-NO_2QNO	41.9	42.0	2.3	2.3	10.9	10.7

The ^{19}F nmr spectra were recorded at 56.4 MHz on a Varian Associates A56-60 spectrometer equipped with a variable-temperature probe.

Results and Discussion

The fluorine resonance assignable to $BF_3 \cdot D$ is the result of the overlap of the 1:1:1:1 quartet due to the ^{11}B isotope ($I = {}^3/_2$) and the septet arising from the coupling with ^{10}B ($I = 3$). Because of the 81.3% abundance of the ^{11}B isotope, the predominant structure will be the quartet. However, a 0.05-ppm downfield shift of the septet causes a noticeable asymmetry in the observed peak (Figure 1d).

Measurement of the $^{11}B-^{19}F$ coupling constant presented some obstacles. As the strength of the donor

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[4] J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

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[7] C. J. Popp, L. C. Nathan, T. E. McKean, and R. O. Ragsdal e, *J. Chem. Soc. A*, 2394 (1970).

[8] N. Kulevsky and L. Sveum, *J. Inorg. Nucl. Chem.*, **27**, 2111 (1965).

molecule decreased, it became increasingly difficult and finally impossible to measure the coupling constants directly. For example, compare the spectra of $BF_3 \cdot 4\text{-}CH_3OpyNO$ and $BF_3 \cdot 4NO_2pyNO$ (Figure 1b, d). The collapse and loss of fine structure of the multiplet could be attributed to nuclear quadrupole broadening but the most important mechanism is probably due to ligand exchange which will be considered later. The width of the multiplet can be approximated by the equation $W = 3J + \Delta\nu$ where $\Delta\nu$ is the width of a single member of the quartet. When $\Delta\nu \simeq J$, as is the case with the series of BF_3 complexes, $W \simeq 4J$ or $J \simeq W/4$. In analyzing the spectrum of $BF_3 \cdot 4\text{-}CH_3OpyNO$ where the coupling constant is easily determined, it was found that the separation of the two most upfield peaks of the quartet taken as the best measure of $J_{^{11}B-^{19}F}$ (this separation is least affected by $J_{^{10}B-^{19}F}$) compared favorably to the measurment of one-fourth of the peak width at half-height ($W/4$). This verified the assumption that $\Delta\nu \simeq J$ and allowed $J_{^{11}B-^{19}F}$ to be represented by $W/4$. Boron–fluorine coupling constants in BF_4^- in various solvents have previously been determined by taking the width of the multiplet.[3] $J_{^{11}B-^{19}F}$ could be determined directly in approximately 60% of the spectra (with satisfactory agreement between J and $W/4$); however, in this paper $W/4$ is reported even in those instances where $J_{^{11}B-^{19}F}$ could be measured to ensure a more uniform comparison. The coupling constants reported in Table II represent the average of three to five determinations. All of the results listed in Table II were obtained from saturated chloroacetonitrile solutions of the adducts. To ascertain any effect the solvent could be having, the spectrum of $BF_3 \cdot 4CH_3\text{-}OpyNO$ was recorded using three other solvents: acetonitrile, dichloromethane, and acetone. Within experimental error, no differences in the data were found. Due to the varying solubilities of each of the adducts and the fact that saturated solutions were being studied, a series of 0.2 *M* solutions of the 4-substituted pyridine 1-oxide adducts was prepared. The spectra of these solutions gave chemical shift and coupling constant data comparable to the saturated solutions; no concentration effects were observed. Consequently, and since better spectra were obtained from the saturated solutions, all subsequent experiments were conducted on saturated solutions.

TABLE II

^{19}F CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] FOR SOME SUBSTITUTED AROMATIC AMINE OXIDE ADDUCTS OF BORON TRIFLUORIDE

	Z-pyNO		Z-QNO		Z-ANO	
Z	δ, ppm	$J_{^{11}B-^{19}F}$, Hz	δ, ppm	$J_{^{11}B-^{19}F}$, Hz	δ, ppm	$J_{^{11}B-^{19}F}$, Hz
4-CH_3O	154.3	5.0	153.1	5.3		
4-CH_3	153.7	4.5	152.6	4.8		
4-H	153.6	4.3	152.7	4.6	149.8	5.5[c]
4-Cl	153.8	4.3	152.9	4.1		
4-$CH_3OC(O)$	153.6	3.8				
4-CN	153.5	3.5	152.6	3.4		
4-NO_2	153.5	3.3	152.6	3.3		
2-CH_3	152.5	4.7				
2-CH_2CH_3	152.1	4.5				
2,4-$(CH_3)_2$	152.5	5.2				
2,6-$(CH_3)_2$	149.1	4.9				
3,5-$(CH_3)_2$	153.7	4.6				

[a] Internal $CFCl_3$ reference, ±0.5 ppm. [b] Estimated from peak width at half-height, ±0.2 Hz. [c] Deviation ±0.5 Hz.

As previously stated, both Grant[2] and Gillespie[3] suggested that the small coupling constant was the result of two opposing mechanisms of nearly equivalent magnitude. It was further suggested that any small perturbation in one of these mechanisms would cause a relatively large effect in the observed coupling constant. A plot of $W/4$ *vs.* the σ_{pyNO} constants[9] for the 4-substituted pyridine 1-oxides shows a marked decrease in the absolute magnitude of $W/4$ (J) as the basicity of the donor decreases (Figure 2). From these data it was possible to determine the sign of $J_{^{11}B-^{19}F}$ for BF_3 in this system. Two different approaches were taken, one based on bond polarity and the other on the hybridization of the boron in the B–F bond.

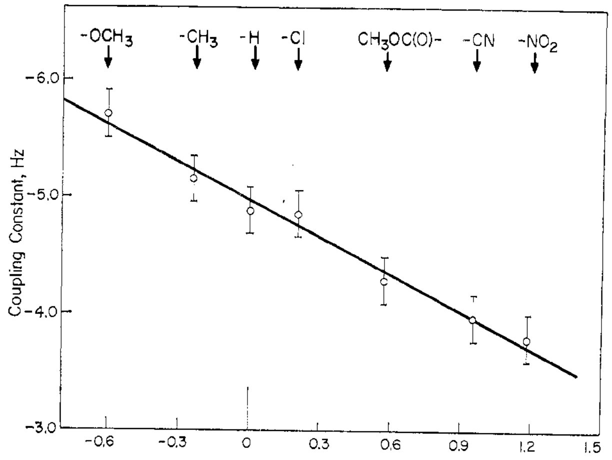

Figure 2.—A plot of peak width at half-height *vs.* σ_{pyNO} for some boron trifluoride adducts of pyridine 1-oxides.

It has been suggested that the negative contribution to $J_{^{11}B-^{19}F}$ decreases as the bond polarity increases.[3] In examining the adducts, it would be expected that the more positive the boron atom, the more polar the B–F bond should be. Since 4-nitropyridine 1-oxide is a weaker donor than 4-methoxypyridine 1-oxide, the electrons from the oxygen are much more strongly felt by the boron in the methoxy than in the nitro complex. That is, relative to each other, the boron is more positive and the B–F bond more polar in the nitro complex than in the corresponding methoxy complex. Since the absolute value of the coupling constant can decrease as the bond polarity increases (fom the methoxy to the nitro complex) only if the coupling constant is negative, it must be concluded that $J_{^{11}B-^{19}F}$ is indeed negative.

The second approach deals, as stated, with the hybridization of the boron when complexed. In these adducts the s contribution will lie somewhere between the 33% characteristic of sp^2 in BF_3 and the 25% characteristic of sp^3 in BF_4^-. The amount of s character will depend on the strength of the boron-donor bond. In the 4-nitropyridine 1-oxide complex the B–O bond is weaker than in the 4-methoxypyridine 1-oxide complex. This indicates that, relative to the methoxy complex, the B–F bonds in the nitro complex have more s character (more sp^2-like). It has been demonstrated that as the s character decreases (from nitro to methoxy), the positive contribution to the coupling constant in-

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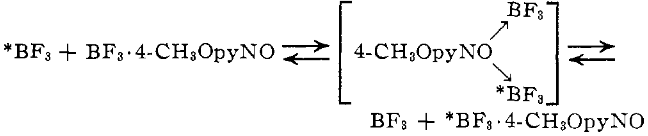
(9) J. H. Nelson, R. G. Garvey, and R. O. Ragsdale, *J. Heterocycl. Chem.*, **4**, 591 (1967).

creases.[4,10] Again, the conclusion must be that $J_{^{11}B-^{19}F}$ is negative.

These discussions should not be misconstrued to suggest that the differences in hybridization and bond polarity are large, but, rather, the fact that such very small effects can result in such large relative differences in the coupling only reinforces the idea that two very large opposing mechanisms are operative.

Examination of the chemical shift data (Table II) for the 4-substituted pyridine 1-oxides shows that there is essentially no difference in the chemical shift arising from a difference in basicity. In going from 4-methoxy- to 4-nitropyridine 1-oxide there is only a 0.8-ppm change in chemical shift, whereas the change in pK_a is 3.8.[9] This same constancy in chemical shift is observable for 3,5-dimethylpyridine 1-oxide, as well as the series of 4-substituted quinoline 1-oxides. However, δ for the quinoline 1-oxides is about 1 ppm lower than the corresponding pyridine 1-oxides but is about the same as δ for the 2-substituted pyridine 1-oxides. This is not a surprising result, since quinoline 1-oxides are essentially "2-substituted" pyridine 1-oxides. Referring to Table II once more, δ for acridine 1-oxide is very nearly equal to δ for 2,6-dimethylpyridine 1-oxide; again the positions substituted are the same. Consequently, the chemical shift appears to be a reflection of the bulky nature of the ligand and its interaction with the fluorines.

The spectra represented in Figure 1 show a definite temperature dependence. Rapid exchange of fluorine among the boron atoms is occurring since there is a collapse of the quartet at high temperatures (Figure 1c, d). A possible mechanism for the fluorine exchange is a simple dissociation of the complex and, for discussion, is exemplified by use of the 4-CH_3OpyNO complex, $BF_3\cdot 4\text{-}CH_3OpyNO \rightleftharpoons BF_3 + 4\text{-}CH_3OpyNO$. Addition of excess ligand causes the quartet structure to be maintained, even at high temperatures (Figure 1e, f). With added BF_3 the same result might be expected; however, the quartet is collapsed even at low temperatures. As a result, in addition to the above mechanism, it is suggested that the following mechanism is also operative



$$*BF_3 + BF_3\cdot 4\text{-}CH_3OpyNO \rightleftharpoons \left[4\text{-}CH_3OpyNO \begin{array}{l} \nearrow BF_3 \\ \searrow *BF_3 \end{array} \right] \rightleftharpoons BF_3 + *BF_3\cdot 4\text{-}CH_3OpyNO$$

The proposed 1-oxide bridge intermediate is not without precedent. It has been demonstrated through X-ray studies that a bridging oxygen is involved in the copper complex of pyridine 1-oxide.[11]

Further support for the proposed exchange mechanisms can be gained from the following considerations. It was not possible to measure the boron–fluorine coupling constant directly for the aromatic amine 1-oxide–boron trifluoride adducts where the donor molecule had deactivating substituents such as the nitro or cyano groups. It was also necessary to estimate J for the adducts which involved the bulky ligands: 2,6-dimethylpyridine 1-oxide, the quinoline N-oxides, and acridine N-oxide. For the dissociation $BF_3\cdot\text{base} \rightleftharpoons BF_3 + \text{base}$, the equilibrium constant would be larger for the weaker bases and the bulky donor molecules. A larger equilibrium constant would enhance the rate of exchange and would account for the loss of fine structure in the fluorine spectra of the above complexes.

In all the spectra recorded a small, broad singlet appeared (150.5–151.0 ppm). The magnitude of this peak is dependent on the strength of the base being used, the largest for the strongest base. A possible explanation for this observation is dehydrofluorination, resulting in a reduced fluorine-containing species.

Acknowledgment.—Support of this work by th Reesearch Corp. is gratefully acknowledged.

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Isotopic Labeling for Mössbauer Studies. An Application to the Iron Cyanides[1]

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The overlapping resonance absorption peaks in the Mössbauer spectra for iron atoms in the iron cyanides have been simplified by selective labeling with Mössbauer-inactive isotopes and with enriched, Mössbauer-active ^{57}Fe. The spectra for each of the three iron environments in Turnbull's and Prussian blues have been shown independently of each other, and in all cases the spectra for the two blues are the same. This isotopic labeling technique may be applied to any compounds containing a Mössbauer-active element in more than one chemical environment if suitable labeling techniques may be derived.

Mössbauer spectroscopy has been applied to the studies of solid compounds of iron, tin, etc., and has been a great aid in attaining a better understanding of the nature of the compounds studied. However, in compounds containing an element in more than one chemical environment, *e.g.*, mixed oxidation states, the interpretations of the Mössbauer spectra are not always clear-cut because of difficulties in interpreting the overlapping absorption peaks. Milligan, *et al.*,[2] have used selective isotope labeling with Mössbauer-active,

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[1] Presented in part to the South Carolina Academy of Sciences, Columbia, S. C., April 24, 1970.

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