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Transmission of Substituent Effects Through the Nitrogen–Silicon–Nitrogen System[1]

BY C. H. YODER AND J. J. ZUCKERMAN

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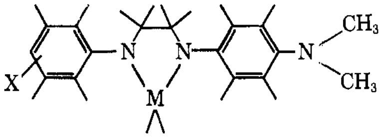
Transmission of substituent effects as determined by nmr chemical shifts is used to test the hypothesis of (p → d)–π bonding in the N–Si–N system. Unsymmetrically substituted N,N′-*p*- and -*m*-diphenylimidazolidines and -diphenylsilaimidazolidines were chosen for this study as such molecules satisfy the requirement that the substituents be held relatively far from one another on the scale of molecular dimensions, thus minimizing inductive and direct electrostatic field effects as well as magnetic anisotropy which might alter the chemical shift of the protons under examination. Studies were carried out in mixtures of the compound with the N-*p*-nitrophenyl,N′-*p*-dimethylaminophenylimidazolidine as a reference in each case [M = C, Si; X = *p*-NO_2, *p*-OCH_3, *p*-Cl, *m*-NO_2, and *p*-$N(CH_3)_2$] and chemical shifts extrapolated to infinite dilution in chloroform to eliminate bulk magnetic susceptibility effects. Chemical shift differences in the dimethylamino group could be measured to better than ±0.1 cps in this way. Transmission across analogous N,N′-diphenylethylenediamines is negligible. Shifts for a variety of organic N,N′-substituted diphenylimidazolidines are shown to correlate with the Hammett σ constant for each substituent. Shifts for the analogous silicon series are found to fall on the same linear plot against the Hammett σ constant for each substituent. Consequences of this finding on the possibility for (p → d)–π interactions in the N–Si–N system are discussed.



Pauling's classic paper on the hybridization of atomic orbitals in molecule formation[2a] neglected consideration of π-bond formation involving d orbitals. Craig, Maccoll, Nyholm, Orgel, and Sutton[2b] calculated overlap integrals for various σ and π combinations of s, p, and d orbitals and from their arguments it followed that overlap was possible between an oxygen or nitrogen p orbital holding a lone pair of electrons and the empty d orbital of an element of the next row or lower in the periodic table. Experimental evidence capable of being interpreted in terms of (p → d)–π interactions between silicon and neighboring atoms holding lone pairs of electrons exists in great abundance and has been reviewed in several excellent books.[3]

We offer in this paper the results of experiments designed as a test of (p → d)–π interactions in the silicon–nitrogen bond. Nmr spectroscopy presents a method for determining the transmission of substituent effects in ground-state neutral molecules. Such spectroscopic measurements are free from the complications inherent in the use of chemical reactions as a test of substituent effects, although results from nmr studies do parallel those from chemical studies on similar systems. Thus the effect of a substituent on the chemical shift of a *para*-spin nucleus in disubstituted benzenes is paralleled by its effect on the acidity of benzoic acids.[4-9] It appears that these chemical shifts are a function primarily of π-electron density distributions at the spin nucleus as affected by the *para* substituents,[4,10] and the good over-all correlation among chemical shifts of N^{15}, C^{13}, and F^{19} nuclei in *para*-substituted benzenes lends support to the suggestion that similar factors are operative in determining the chemical shifts in all cases.[7]

Three mechanisms exist in our current model of the chemical bond by which a substituent can influence a distant reaction center in the ground state of a molecule: (i) inductive (through σ bonds), (ii) field or direct electrostatic (through space), and (iii) π effect (resonance or mesomeric through π bonds). A distinguishing feature of the delocalized π system is the ability to transmit substituent electrical effects to a greater extent than a saturated system of comparable length. This has been tested with reference to benzoic acid dissociation constants for three saturated systems which hold the reactive center and the substituent in a rigid way at an equivalent distance: 4-substituted *trans*-cyclohexanecarboxylic acids,[11] 4-substituted bi-

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[1] A preliminary report of this work was presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[2] (a) L. Pauling, *J. Am. Chem. Soc.*, **53**, 1367 (1931); (b) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332, 354 (1954).

[3] (a) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. Ltd., London, 1960; (b) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press Ltd., London, 1963; (c) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[4] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); G. F. Maciel and J. J. Natterstad, *ibid.*, **42**, 2427 (1965), and references therein.

[5] R. W. Taft, Jr., *J. Am. Chem. Soc.*, **85**, 3146 (1963), and references therein.

[6] H. C. Beachell and D. W. Beistel, *Inorg. Chem.*, **3**, 1028 (1964).

[7] D. T. Clark and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 745 (1966).

[8] S. H. Marcus, W. F. Reynolds, and S. I. Miller, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; *J. Org. Chem.*, **31**, 1872 (1966).

[9] R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **40**, 1071 (1962).

[10] T. K. Wu and B. P. Dailey, *J. Chem. Phys.*, **41**, 2796 (1964).

[11] S. Siegel and J. M. Komarmy, *J. Am. Chem. Soc.*, **82**, 2547 (1960).

cyclo[2.2.2.]octane-1-carboxylic acids,[12] and 1,3-adamantanes.[13] It is found in these cases that those substituents which are capable of strong interaction with the π system of the benzene ring (in the *para* position) have a more powerful effect on the acidity of benzoic acids than on the acidity of saturated acids.

Thus it should be possible to test the hypothesis of (p → d)–π interaction in the silicon–nitrogen bond by measuring the extent of transmission of electrical effects through such a system with respect to the saturated carbon–nitrogen case. In considering the design of a suitable test molecule, we included the requirement that the substituents be held relatively far removed from one another on the scale of molecular dimensions. In this way both the inductive transmission of charge through the chain of atoms and the direct electrostatic field effect would be minimized, as well as any through-space effect which might alter the magnetic environment of the protons of interest.

Such requirements are nicely met by the imidazolidine ring system depicted in Figure 1. We have investigated the stereochemistry of the imidazolidine ring system by nmr where a single, sharp resonance was reported for the methylene bridge protons of the M = silicon ring.[14] A similar resonance is found in the symmetrically substituted spiro derivatives (M = silicon, germanium)[15] and the monocyclic carbon,[16] silicon,[17] and germanium[18] imidazolidines and can be interpreted as indicating either planarity of the ring or rapid inversion about tetrahedral nitrogen. In either case the phenyl substituents are held apart by being attached to 1,3 positions on the ring and magnetic anisotropy effects should be constant through both (M = C, Si) series of compounds. Substituent X was varied in each series p-NO_2, m-NO_2, p-Cl, p-OCH_3, and p-$N(CH_3)_2$. The effect of changing X on the proton nmr chemical shift of the dimethylamino group was taken as a measure of the transmission of substituent effects across the ring. We have as a preliminary to this study investigated the transmission of substituent effects in the unsymmetrically substituted N,N′-diphenylethylenediamines themselves,[19] where we find an only barely measurable change in chemical shift for N-*p*-nitrophenyl,N′-*p*-methoxyphenyl- as against N,N′-bis(*p*-methoxyphenyl)ethylenediamine, the pair of compounds expected to exhibit the greatest effect.

By utilizing the N-*p*-nitrophenyl,N′-*p*-dimethylaminophenylimidazolidine compounds as a reference system in each case (M = carbon, silicon) and by measuring all N-dimethylaminophenyl chemical shifts relative to the N-dimethylaminophenyl chemical shift in these compounds in mixtures in chloroform of the reference compound with the compound holding substituent X, the change in chemical shift could be measured to better than ±0.1 cps. The shifts were extrapolated to infinite dilution to eliminate bulk magnetic susceptibility effects.

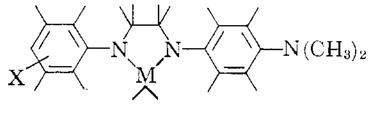


Figure 1.

Results

Table I lists chemical shift differences, Δ, in cps for N-*p*- and N-*m*-nitrophenyl organic imidazolidines unsymmetrically substituted with various N′-aryl groups as against the analogous symmetrically disubstituted N,N′-bis compounds. Measured shifts in these organic *m*- and *p*-imidazolidine series roughly parallel the Hammett σ constants for the respective substituents as shown in Figure 2. No resolvable Δ could be measured for N-*p*-dimethylaminophenyl,N′-*p*-methoxyphenylimidazolidines as against their N,N-bis(*p*-methoxyphenyl) analogs in either the M = carbon or M = silicon case. The half-height widths for the broadened methoxy proton resonances are recorded in Table I.

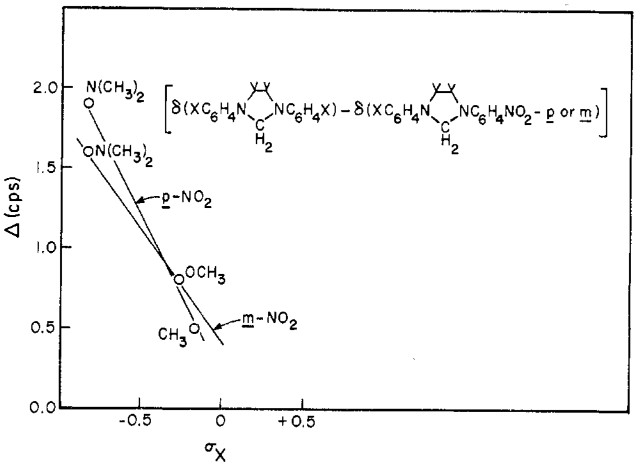
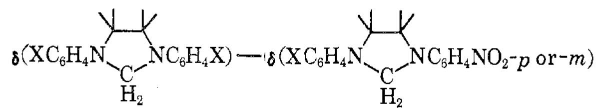


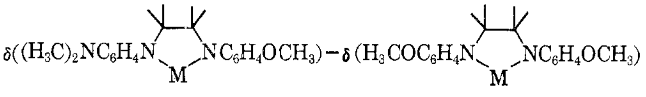
Figure 2.

Table I



$\delta(XC_6H_4N\,\underset{H_2}{C}\,NC_6H_4X)-\delta(XC_6H_4N\,\underset{H_2}{C}\,NC_6H_4NO_2\text{-}p \text{ or-}m)$

X	Δ ± 0.07, cps
p-NO_2	
$N(CH_3)_2$	1.9
OCH_3	0.8
CH_3	*ca.* 0.5 (hhw = 2.3)
m-NO_2	
$N(CH_3)_2$	1.6
OCH_3	0.8



$\delta((H_3C)_2NC_6H_4N\,\underset{M}{}\,NC_6H_4OCH_3)-\delta(H_3COC_6H_4N\,\underset{M}{}\,NC_6H_4OCH_3)$

M = CH_2	M = $Si(CH_3)_2$
hhw = 0.6	hhw = 0.5

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(12) J. D. Roberts and W. T. Moreland, Jr., *J. Am. Chem. Soc.*, **75**, 2167 (1953); H. D. Holtz and L. M. Stock, *ibid.*, **86**, 5188 (1964).

(13) H. Stetter and J. Mayer, *Chem. Ber.*, **95**, 667 (1962).

(14) D. Kummer and J. D. Baldeschwieler, *J. Phys. Chem.*, **67**, 98 (1963).

(15) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **3**, 1329 (1964).

(16) C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 4831 (1966).

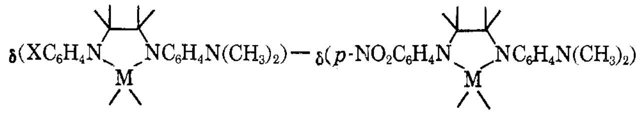
(17) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **4**, 116 (1965).

(18) C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 2170 (1966).

(19) C. H. Yoder and J. J. Zuckerman, *J. Med. Chem.*, in press.

Table II lists the measured difference Δ in cps between the dimethylamino proton resonance in the reference N-*p*-nitrophenyl,N′-*p*-dimethylaminophenylimidazolidines (M = carbon, silicon) and the dimethylamino proton resonance in the unsymmetrically substituted analogs where the *p*-nitro group is replaced by various *para* and *meta* substituents X. We find little difference between the values obtained for the M = carbon and M = silicon series. Organic Δ values in fact appear to be somewhat larger. These data are plotted against the substituent Hammett σ constant in Figure 3.

TABLE II



$\delta(XC_6H_4N\underset{M}{\quad}NC_6H_4N(CH_3)_2) - \delta(p\text{-}NO_2C_6H_4N\underset{M}{\quad}NC_6H_4N(CH_3)_2)$

	Δ ± 0.07, cps	
X	M = CH₂	M = Si(CH₃)₂
p-N(CH$_3$)$_2$	1.9	. . .
p-OCH$_3$	1.45	1.15
p-Cl	. . .	0.9
m-NO$_2$	hhw = 0.9	hhw = 0.7
p-NO$_2$	0	0

Discussion

According to the hypothesis outlined in the introduction, our results are compatible with two limiting possiblities: (i) no (p → d)–π interaction in the silicon–nitrogen bond or (ii) (p → d)–π overlap in the N–Si–N linkage such that a nodal plane exists in the system. The latter possibility could arise through two two-center π bonds involving orthogonal d orbitals at the silicon atom. We shall discuss (ii) in detail first.

In the limit of strong π overlap between silicon and nitrogen in the imidazolidines, a nitrogen pure p orbital would combine with a silicon d orbital of appropriate symmetry. The nitrogen σ bonds in this case would be hybridized sp² and the five-membered ring system would be planar. By definition the π bonds between silicon and nitrogen must be antisymmetric with respect to reflection in the *xy* plane. Thus, the d orbitals of appropriate symmetry for overlap are the d_{xz} and d_{yz}, but not the d_{z^2}. Orientations of the d_{xz} and d_{yz} orbitals are shown in Figure 4 where the top portion of both sets of lobes can be seen. The extent of overlap between the p orbital of nitrogen and each of these d orbitals of silicon depends upon their relative orientations, sizes, and energies. Overlap with the silicon d_{yz} orbital would result in a three-center π system of the type $\mathrm{N}\stackrel{\cdots}{-}\mathrm{Si}\stackrel{\cdots}{-}\mathrm{N}$, contrary to our results. Overlap with the d_{xz} orbital would give rise to two two-center π bonds insulated from one another by a node at the silicon atom in the *yz* plane of the coordinate system as drawn in Figure 4(a).

Alternatively, linear combination of the d_{xz} and d_{yz} orbitals would form two equivalent, orthogonal d orbitals, rotated from d_{xz} and d_{yz} by 45° as shown in Figue 4(b). These two orbitals can now overlap with the nitrogen p orbitals to form separate, noninteracting (p → d)–π systems. Where ∠N–Si–N = 90° no interaction between these two π bonds is possible. In fact the actual N–Si–N bond angle is probably somewhat larger than 90°, although no structural data for the imidazolidine ring are available. This treatment of (p → d)–π overlap has been applied to the cyclic phosphonitrilic trimer where suggestions for both the three-center overlap[20] and the localized two-center (p → d)–π bonds[21] have been put forward.

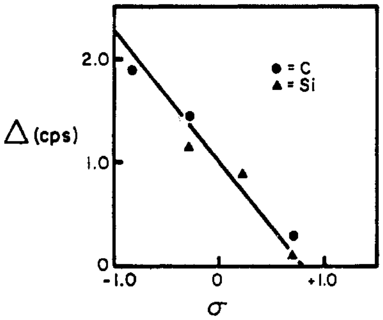


Figure 3.—Correlation of N(CH₃)₂ shift with Hammett's σ constants.

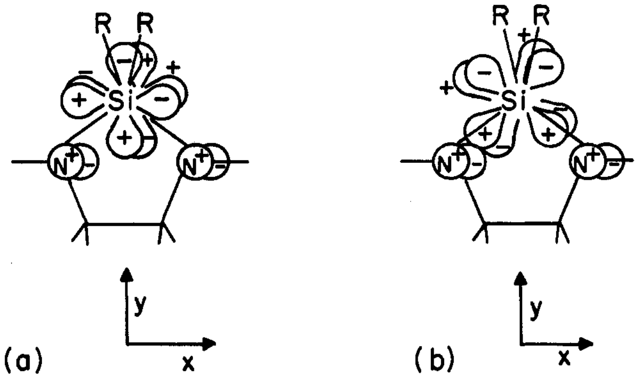


Figure 4.

Still another approach to understanding the data of Table II is to assume that the magnetic and electrical environments of the N-dimethylaminophenyl protons of the silicon imidazolidines are insensitive to the presence of delocalized (p → d)–π bonding in the N–Si–N system. Valence bond structures depicting charge delocalization from the N-dimethylaminophenyl group to the N′-*p*-nitrophenyl group across the center ring involve unfavorable charge separation. Thus these two groups may find themselves in what is electronically equivalent to the *meta* relationship in a disubstituted benzene. In this case not even strong N–Si–N (p → d)–π delocalization will greatly influence the N-dimethylaminophenyl chemical shift.[21a]

The imidazolidine ring is probably not planar,[22]

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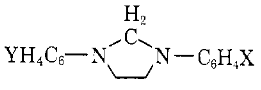
(20) D. P. Craig and N. L. Paddock, *Nature*, **181**, 1052 (1958); D. P. Craig, *J. Chem. Soc.*, 997 (1959); see also D. P. Craig and N. L. Paddock, *ibid.*, 4118 (1962).

(21) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *ibid.*, 2423 (1960); D. P. Craig and K. A. R. Mitchell, *ibid.*, 4682 (1965).

(21a) NOTE ADDED IN PROOF.—We have tested this possibility by synthesizing the analogous asymmetrically disubstituted boron imidazolidines. Preliminary investigations indicate that the $\mathrm{N}\stackrel{\cdots}{-}\mathrm{B}\stackrel{\cdots}{-}\mathrm{N}$ system affords large across-ring shifts [D. E. Fenton, C. H. Yoder, and J. J. Zuckerman, unpublished results].

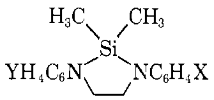
(22) Electric dipole moment studies suggest the organic imidazolidines are nonplanar: E. Fischer, *J. Chem. Phys.*, **19**, 395 (1951); E. D. Bergmann, E. Fischer, E. Zimkin, and S. Pinchas, *Rec. Trav. Chim.*, **71**, 213 (1952).

Table III



X	Y	Mp (uncor), °C		Analyses			
				% C	% H	% N	Mol wt
p-N(CH$_3$)$_2$	p-NO$_2$	202–204	Found	65.26	6.53	17.18	
			Calcd	65.38	6.45	17.93	
p-N(CH$_3$)$_2$	m-NO$_2$	170–172	Found	65.08	6.66	18.01	
			Calcd	65.38	6.45	17.93	
p-N(CH$_3$)$_2$	p-Cl	230.5–232.0	Found	67.79	6.69	13.55	
			Calcd	67.66	6.68	13.92	
p-N(CH$_3$)$_2$	p-OCH$_3$	212–213	Found	72.50	7.79	14.06	301
			Calcd	72.70	7.79	14.13	297
p-N(CH$_3$)$_2$	p-N(CH$_3$)$_2$	231–233.5	Found	73.30	8.52	18.13	313
			Calcd	73.51	8.44	18.04	310
p-OCH$_3$	p-NO$_2$	167–168	Found	64.51	5.75		
			Calcd	64.22	5.73		
p-OCH$_3$	m-NO$_2$	141–141.5	Found	64.29	5.70	14.11	
			Calcd	64.22	5.73	14.04	
p-OCH$_3$	p-OCH$_3$	229–230.5	Found	72.05	7.17	10.17	
			Calcd	71.81	7.09	9.86	
p-CH$_3$	p-NO$_2$	181–182	Found	67.72	6.09	14.57	295
			Calcd	67.84	6.05	14.83	283
p-CH$_3$	p-CH$_3$	181–184	Found	80.92	8.06	11.08	266
			Calcd	80.90	7.99	11.10	252

Table IV



X	Y	Mp (uncor), °C		Analyses			
				% C	% H	% N	% Si
p-N(CH$_3$)$_2$	p-NO$_2$	168–171	Found	61.95	6.68	15.05	8.12
			Calcd	60.64	6.78	15.71	7.88
p-N(CH$_3$)$_2$	m-NO$_2$	108–110	Found	60.93	6.67	15.78	7.70
			Calcd	60.64	6.78	15.71	7.88
p-N(CH$_3$)$_2$	p-Cl	163–169	Found	62.48	6.93	11.65	
			Calcd	62.50	6.99	12.15	
p-N(CH$_3$)$_2$	p-OCH$_3$	114–118	Found	67.61	8.10	13.00	8.88
			Calcd	66.82	7.97	12.30	8.23
p-OCH$_3$	m-NO$_2$	145–147	Found	59.56	6.25	12.17	7.84
			Calcd	59.45	6.16	12.24	8.18

although we have examined nmr spectra of organometallic imidazolidines in Freon solvents to $-100°$ without observing any broadening of the single, sharp methylene bridge resonance.[23] If the ring is indeed nonplanar, then the nmr results dictate that rapid inversion is taking place about pyramidal nitrogen atoms. The amount of (p $\rightarrow$ d)–π interaction between nitrogen lone-pair electrons and silicon d orbitals should be affected by the inversion process, making the silicon–nitrogen bonding situation time dependent. It is clear that, if such a dynamic situation exists in the molecules studied in this paper, then we are observing a time average over many molecular conformations in our experiments.

The molecules may be spending much of their time with nitrogen in a pyramidal geometry and with little (p $\rightarrow$ d)–π interaction in the silicon–nitrogen bond. Indeed the N^{15}–H^1 coupling constants for N-trimethylsilyl-,[24] N-trimethylgermyl-, and N-trimethylstannylaniline[25] recently measured in this laboratory would seem to support this suggestion. The N-trimethylsilylaniline molecule is the closest analog to the systems reported in this investigation where J(N^{15}–H^1) measurements are possible.

Experimental Section

The nmr measurements were carried out using a Varian A-60 spectrometer.

Preparation N,N'-Diarylimidazolidines.—The N,N'-diarylethylenediamine[19] is dissolved in a quantity of absolute methanol or ethanol just sufficient for solution. Approximately 0.5 ml of 1:1 acetic acid–water is added, and then, while stirring, a slight molar excess of aqueous formaldehyde is added dropwise. Usually the imidazolidine begins to precipitate within 10 min and after several hours the solution is filtered and the precipitate is recrystallized from ethanol. The more soluble nitro derivatives require heating and evaporation of some solvent to effect precipitation of the imidazolidine. Crude yields are in the 80–90% range. Physical properties and analytical data for the compounds are given in Table III. Molecular weights were determined by vapor phase osmometry in benzene.

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(23) A. J. R. Bourn, C. H. Yoder, and J. J. Zuckerman, unpublished results.

(24) E. W. Randall, J. J. Ellner, and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 622 (1966).

(25) E. W. Randall, J. J. Ellner, and J. J. Zuckerman, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

Preparation of N,N′-Diarylsilaimidazolidines.—Equimolar amounts of the N,N′-diarylethylenediamine and dimethylbis(diethylamino)silane are heated together with stirring in the presence of a small amount (<0.1 g) of ammonium sulfate. A temperature sufficient to melt the diamine is generally necessary. Liberated diethylamine is removed from the reaction vessel by a stream of nitrogen and can be collected in a cold trap if desired. After perhaps 5 hr of reaction time, the material is allowed to cool and then, after solidification, is recrystallized from benzene or benzene–hexane. Because the starting diamine and the product imidazolidine have similar solubilities, purification is difficult. Sublimation was attempted in several cases but did not markedly improve the purity. Yields after recrystallization were in the 20–50% range. Compounds were characterized by their nmr spectra and analytical data. Physical properties and analytical data are listed in Table IV.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
UNIVERSITY OF CALIFORNIA AND THE INORGANIC MATERIALS RESEARCH DIVISION OF THE LAWRENCE
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Adducts of Sulfur Nitride with Boron Trihalides and Antimony Pentachloride

BY KENNETH J. WYNNE AND WILLIAM L. JOLLY

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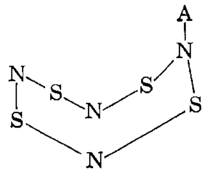
Sulfur nitride in methylene chloride reacts with BF_3 to form burgundy-colored crystals of $S_4N_4\cdot BF_3$ and with BCl_3 to form red-orange needles of $S_4N_4\cdot BCl_3$. The BF_3 adduct decomposes reversibly to S_4N_4 and BF_3 when heated, whereas the BCl_3 adduct sublimes with slight decomposition. The properties of the adducts are consistent with structures in which the Lewis acid is coordinated to a nitrogen atom of an S_4N_4 ring, as in $S_4N_4\cdot SbCl_5$. The boron trifluoride in $S_4N_4\cdot BF_3$ may be displaced by BCl_3 or $SbCl_5$. In an attempt to displace BCl_3 from $S_4N_4\cdot BCl_3$ with $SbCl_5$, the adduct $S_4N_4\cdot BCl_3\cdot SbCl_5$ formed. This reaction was unexpected because no diadducts were found in the reaction of S_4N_4 with either excess BCl_3 or $SbCl_5$. The conversion of $S_4N_4\cdot BCl_3$ to $S_4N_4\cdot SbCl_5$ may be effected by treating $S_4N_4\cdot BCl_3$ with $SbCl_5$ to give $S_4N_4\cdot BCl_3\cdot SbCl_5$, followed by heating this substance *in vacuo* at 90° to form $S_4N_4\cdot SbCl_5$ and BCl_3.

The following adducts of S_4N_4 with Lewis acids have been prepared: $S_4N_4\cdot SbCl_5$,[1,2] $2S_4N_4\cdot SnCl_4$,[1,2] $S_4N_4\cdot TiCl_4$,[1,2] $S_4N_4\cdot 2SO_3$,[3] $S_4N_4\cdot 4SO_3$,[3] $S_4N_4\cdot TeBr_4$,[4] $S_4N_4\cdot 4SbF_5$,[5] and $4S_4N_4\cdot BF_3$.[6] Only for $S_4N_4\cdot SbCl_5$ is definite structural information available. An X-ray study[7] has shown this adduct to have a structure of type I where A represents the coordinated Lewis acid.



I

The unusual stoichiometry reported for the BF_3 adduct, and the lack of information regarding the other boron trihalide adducts, led us to a systematic study of the reaction of S_4N_4 with the boron trihalides.

Experimental Section

General.—Moisture-sensitive materials were handled in a nitrogen-filled polyethylene glove bag or a standard vacuum line. Analyses were performed in the microanalytical laboratory of this department by V. Tashinian and F. Balistreri.

Infrared spectra were recorded in the 700–4000-cm^{-1} range with a Perkin-Elmer Infracord Model 137B, in the 400–700-cm^{-1} range with a Perkin-Elmer Infracord Model 137 equipped with a KBr prism, and in the 33–400-cm^{-1} range with a Beckman IR-11 grating spectrophotometer. Samples were generally prepared in a nitrogen atmosphere as Nujol mulls and then pressed between either KBr or polyethylene plates. Methylene chloride solution spectra were run in a 0.1-mm KBr cavity cell.

Methylene chloride was refluxed for 3–4 hr over P_2O_5, distilled, and stored in a nitrogen atmosphere. Sulfur nitride was prepared and purified according to the method described by Villena-Blanco and Jolly.[8]

Sulfur Nitride–Boron Trifluoride Adduct.—A slurry of 8.45 g of sulfur nitride and 135 ml of CH_2Cl_2 was prepared in a flask equipped with a gas inlet tube and an outlet protected with a $CaSO_4$ drying tube. While stirring with a magnetic stirrer, BF_3 was bubbled at *ca.* 4–6 bubbles/sec. The solution, initially red-orange, immediately turned dark burgundy. The BF_3 flow was terminated after 40 min, the gas bubbler was removed, and the slurry was filtered, yielding 7.89 g of dark burgundy-colored $S_4N_4\cdot BF_3$. A further yield of 3.07 g of relatively large crystals (*ca.* 3 × 1 × 1 mm) was obtained by cooling the filtrate to −15°; the total yield was 95%. On heating, the product became continually lighter in color above 90° until melting occurred at 145–147°.

Anal. Calcd for $S_4N_4\cdot BF_3$: S, 50.88; N, 22.23; formula weight, 252.1. Found: S, 50.22; N, 22.21; molecular weight, 259 (in $CHCl_3$, with vapor pressure osmometer).

The Nujol-mull infrared spectrum showed the following peaks[9]

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