leads to a vanishing of the exchange integral. Another possible promotion is from the non-bonding level to a σ^*-antibonding state. This promotion should lead to a non-vanishing of the exchange integral. A comparison of the nitrogen splitting in NH_2 with that of NH_3^+, recently observed by Cole,[13] however, indicates that this contribution is small. Karplus and Fraenkel have pointed out that the spin polarization of the 1s electrons will also contribute to Q_1 of equation 1. No value for this contribution is available at the present time for nitrogen atoms in heterocyclic molecules.

Conclusion.—The use of equation 1 in relating spin densities and coupling constants of nitrogen atoms in heterocyclic negative ions appears to be substantiated. The Hückel theory is a reasonable approximation for these ions.

Acknowledgment.—I wish to thank Professor A. Streitwieser for helpful discussions.

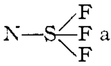
(13) T. Cole, *J. Chem. Phys.*, **35**, 1169 (1961).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE, MASS.]

The Microwave Spectrum and Structure of NSF_3[1a]

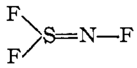
BY WILLIAM H. KIRCHHOFF[1b] AND E. BRIGHT WILSON, JR.

RECEIVED AUGUST 25, 1961

The action of AgF_2 on S_4N_4 in CCl_4 produces a gaseous compound, NSF_3, the structure of which has been in some doubt. A pure sample was prepared. Fragments in the mass spectrum show that the molecular structure is probably  as most recently claimed by Glemser. The microwave spectrum was studied in the region 8000 to 60,000 mc. with a conventional Stark modulated spectrograph. The spectrum has the simplicity and first order Stark effects characteristic of a symmetric top. From lines assigned to the normal and also to the ^{34}S and ^{15}N species occurring in natural abundance, the following set of structural parameters was obtained: $d(S–N) = 1.416$ Å., $d(S–F) = 1.552$ Å. and $<FSF = 94° 2'$. The above structure is thus confirmed and made quantitative. In addition, the dipole moment was measured and found to be 1.91 ± 0.03 Debye. The quadrupole coupling constant of the ^{14}N nucleus is $+1.19 \pm 0.05$ mc.

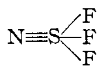
Introduction

The compound NSF_3 was first reported by Glemser and Schroeder[2] who initially proposed the structure



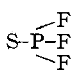
(A)

on the basis of hydrolysis experiments. After the present work was initiated, Richert and Glemser[2b] interpreted infrared and fluorine nuclear magnetic resonance data in favor of the structure

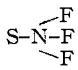


(B)

The compound PSF_3 is also known and has the structure[3]



so that the possibility



(C)

existed. The microwave spectrum of NSF_3 was investigated in order to determine the structure unambiguously and quantitatively. As shown below, the form (B) was confirmed.

Experimental

The Preparation of NSF_3.—NSF_3 is formed by the action of AgF_2 on S_4N_4 in an inert solvent. The preparation of S_4N_4 has been described by Arnold, Hugill and Hutson[4] and by Brauer.[5,6] A freshly prepared sample of S_4N_4 was dissolved in carbon tetrachloride which had been dried over phosphorus pentoxide. This solution was poured into a two-necked copper reaction flask which was fitted with a copper reflux condenser. The reflux condenser was followed by two U-traps which were both cooled by liquid nitrogen. The whole system was kept under an atmosphere of dry nitrogen.

The solution in the copper flask was then heated and, as it began to reflux, enough AgF_2 was added so that the reaction mixture contained twelve moles of AgF_2 for each mole of S_4N_4. The mixture then was refluxed for approximately 3 hr. The first trap contained the reaction products which consisted of SO_2, SOF_2, CCl_3F and SiF_4 in addition to the main product NSF_3. The use of a copper flask, as suggested by Dr. Glemser, rather than Pyrex substantially reduced the formation of these side products.

The reaction products were distilled *in vacuo* through three cold traps. The first was cooled by a toluene slush (−96°), the second by a methylcyclohexane slush (−126°) and the third by liquid nitrogen (−196°). The fraction trapped at −126° was collected for further purification. This sample still contained small amounts of SO_2, SOF_2 and CCl_3F. Further purification was achieved by the use of gas chromatography. The separation of NSF_3 from the impure reaction product was carried out in a conventional gas chromatographic apparatus using fifty grams of tricresyl phosphate per hundred grams of Chromosorb (manufactured by the Johns–Manville Co.) for a stationary phase and helium for the moving phase. The separation was quite clean and the resulting sample was at least 99% pure NSF_3. The purity of the sample was estimated from the mass spectrum.

The Mass Spectrum of NSF_3.—The mass spectrum of NSF_3 was useful not only in giving an estimate of the purity of the sample but also in revealing evidence for the possible structure of NSF_3. The mass spectrum contained peaks at the mass numbers of the following fragments: NSF_3, SF_3, NSF_2, SF_2, NSF, NS, S, F and N. No mass peaks

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(1) (a) This research was supported by a contract with Harvard University from the Office of Naval Research. (b) National Institutes of Health Fellow, 1959–1962.

(2) (a) O. Glemser and H. Schroeder, *Z. Anorg. u. Allgem. Chem.*, **284**, 97 (1956). (b) H. Richert and O. Glemser, *ibid.*, **307**, 328 (1961).

(3) Q. Williams, J. Sheridan and W. Gordy, *J. Chem. Phys.*, **20**, 164 (1952).

(4) M. H. M. Arnold, J. A. C. Hugill and J. H. Hutson, *J. Chem. Soc.*, 1645 (1936).

(5) G. Brauer, "Handbuch der Praeparativen Anorganischen Chemie," Ferdinand Enke, Stuttgart, 1954, p. 316–318.

(6) G. Brauer, *ibid.*, 1960, p. 368–369.

were observed which could be assigned to NF, NF_2 or NF_3. This pattern suggested structure (B) mentioned above.

The Microwave Spectrum of NSF_3.—A conventional Stark modulated spectrometer[7] was used for measuring the absorption transitions of NSF_3 in the region 8,000 mc to 60,000 mc. For the regions 25,000 to 37,000 mc. and 48,000 to 60,000 mc., backward wave oscillators were used for the generation of the microwave radiation. The frequency measurements were made with crystal driven frequency standards which were monitored by a signal from an atomicron in the Cruft Laboratory of Harvard University. Frequencies were measured by sweeping over each line in both directions and then taking an average value.

The spectrum observed consisted of a regularly spaced series of groups of lines. All lines except those assigned to the $1 \leftarrow 0$ transitions showed first order Stark effects. This type of spectrum is characteristic of a symmetric top. The most intense line of each group was assigned to the transition of the normal isotopic species in the ground vibrational state. The remaining lines in each group consisted of transitions due to other isotopic species and to vibrationally excited states. In order to assign various transitions to isotopic species, several of the vibrational satellites were excluded by locating the second and third harmonics. The ^{34}S and ^{33}S species were identified by the temperature dependence of their intensities and by the fact that they give a consistent value for the distance of the sulfur atom from the center of mass. The ^{15}N species was identified by the temperature dependence of its intensity. All isotopic species observed occurred in natural abundance. The observed and calculated frequencies of the ground vibrational state lines are listed in Table I. The calculated spectrum is based on the rotational constants given in Table II.

TABLE I

OBSERVED AND CALCULATED TRANSITIONS FOR THE GROUND VIBRATIONAL STATE OF NSF_3

Isotopic species	Transition	Obsd. frequency, mc.	Calcd. frequency, mc.
$^{14}N^{32}SF_3$	$1 \leftarrow 0$	9,272.56	9,272.48
	$2 \leftarrow 1$	18,545.10	18,544.96
	$3 \leftarrow 2$	27,817.67	27,817.44
	$6 \leftarrow 5$	55,633.94	55,634.88
$^{14}N^{33}SF_3$	$3 \leftarrow 2$	27,799.71	27,799.44
	$6 \leftarrow 5$	55,598.35	55,598.88
$^{14}N^{34}SF_3$	$2 \leftarrow 1$	18,521.34	18,521.24
	$3 \leftarrow 2$	27,782.10	27,781.86
	$6 \leftarrow 5$	55,563.27	55,563.72
$^{15}N^{32}SF_3$	$3 \leftarrow 2$	27,121.49	27,121.20
	$6 \leftarrow 5$	54,241.76	54,242.40

TABLE II

ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA[a]

Isotopic species	B_0, mc.	I, amu. Å.^{2}
$^{14}N^{32}SF_3$	4636.24	109.039
$^{14}N^{33}SF_3$	4633.24	109.110
$^{14}N^{34}SF_3$	4630.31	109.179
$^{15}N^{32}SF_3$	4520.20	111.838

[a] Conversion factor 505, 531 mc. amu. Å^2.

The Structure of NSF_3.—The microwave spectrum shows that NSF_3 is a symmetric top. Therefore there are only three parameters necessary to give the molecular dimensions. The distances of the sulfur and the nitrogen atoms from the center of mass of the normal species were obtained directly from isotopic changes in the moments of inertia.[8,9]

$$Z_i^2 = \frac{M + \Delta m_i}{M \Delta m_i} \Delta I$$

where Δm_i is the difference in the mass of the isotopes of atom i, M is the total molecular mass of the normal species, and ΔI is the increase in the moment of inertia due to the isotopic substitution at atom i. This yields

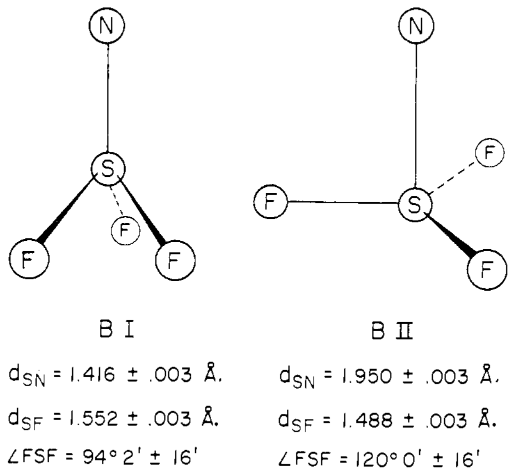

Fig. 1.

$$Z_S = \pm 0.2670 \pm 0.0031 \text{ Å.}$$

and

$$Z_N = \pm 1.6833 \pm 0.0010 \text{ Å.}^{10}$$

Thus, corresponding to the arbitrary choice of sign for Z_S and Z_N two possible values were obtained for the SN distance

$$d_{SN} = 1.4163 \pm 0.0033 \text{ Å.}$$

or

$$d_{SN} = 1.9503 \pm 0.0033 \text{ Å.}$$

To obtain the FSF angle and the SF bond distance, the first moment condition and the moment of inertia for the normal isotopic species were used. From these two equations, two structures corresponding to the two values of d_{SN} were obtained. They are shown in Fig. 1. These two structures are the only ones which will give the observed moments of inertia. However, in order to choose which of the two structures is the correct one, a comparison must be made with other compounds containing SN and SF bonds. The structures of several molecules containing SF bonds are listed in Table III. The SF bond length does not differ much in going from one molecule to another and this fact would support structure BI.

TABLE III

SOME OBSERVED SF BOND DISTANCES[11]

Molecule	SF bond distance, Å.
SF_2O_2	1.53 ± 0.01
SOF_2	1.585 ± .001
SF_6	1.56 ± .02
	or
	1.58 ± .03
S_2F_{10}	1.56 ± .02
$S_2F_{10}O_2$	1.56 ± .02
NSF_3	1.552 ± 0.003 or 1.488 ± 0.003

Comparison of the SN bond length with other existing bond lengths is more difficult. If nitrogen is to have a covalency number of three and sulfur a covalency number of six, then the nitrogen must be triply bonded to the sulfur. Indeed, Glemser and Richert have calculated a bond order of 2.7 for the SN bond in NSF_3 from their infrared work.[2] However, no other SN triple bonds have been reported. Sutton lists the following SN bond lengths: 1.79 Å. in $SN_2O_5^{--}$ (single bond) and 1.62 Å. in S_4N_4 (bond order 1.5). This immediately suggests that the model with 1.950 Å. is

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[7] K. B. McAfee, R. H. Hughes and E. B. Wilson Jr., *Rev. Sci. Instr.*, **20**, 821 (1949).

[8] J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953); C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

[9] For atomic masses used, see C. H. Townes and A. L. Shawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 644.

[10] All values for the error in the various calculated quantities are based on an estimated error of 0.1 mc. in the rotational constants.

[11] L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958, pp. 72–76; SF_2O_2: D. R. Lide, D. E. Mann and R. M. Fristrom, *J. Chsm. Phys.*, **26**, 734 (1957).

unreasonable and that structure BI (SN bond distance 1.416 Å.) is the correct one.

If one assumes, as has been proposed,[12] that the bond order is linearly related to the inverse square of the bond distance for a given pair of atoms, *i.e.*, if

$$N = \frac{a}{R^2} + b$$

where N is the bond order, R is the bond distance and a and b are constants which depend only on the chosen pair of nuclei, then a and b may be evaluated from knowledge of single and double bonded covalent radii by use of the Schomaker–Stevenson rule as modified by Gordy to include double bonds. This was done using the single and double bonded covalent radii of nitrogen as given by Gordy[13] and the single and double bonded covalent radii of sulfur as given by Pauling.[14] The single and double bond distances were calculated and, using these distances, the constants a and b were evaluated. The constants a and b were used in turn to calculate the bond distances of bonds of order 1, 1.5 and 2.7.

$$R(1) = 1.74 \text{ Å.}$$
$$R(1.5) = 1.63 \text{ Å.}$$
$$R(2.7) = 1.42 \text{ Å.}$$

The first two are in reasonable agreement with the observed values for $SN_2O_5^{--}$ and S_4N_4. While the calculated value of the SN distance for a bond of order 2.7 is no doubt fortuitously close to the observed distance for structure B I of NSF_3, this calculation in addition to the observed values for known SN and SF distances leads to the conclusion that structure B I is the correct structure for NSF_3.

The Dipole Moment of NSF_3.—The dipole moment was obtained by measuring the displacement of the $M = \pm 1$ and $M = 0$ second order Stark lobes of the $2 \leftarrow 1$ transition as a function of the square of the applied Stark modulating voltage. The spectrometer was calibrated by measuring the displacement of the $M = \pm 1$ and $M = 0$ Stark lobes for the $2 \leftarrow 1$ transition of OCS. The dipole moment of OCS was taken to be 0.7124 Debye.[15] The data were fitted by least squares to give

$$\mu = 1.91 \pm 0.03 \text{ Debye}$$

The ^{14}N Quadrupole Coupling Constant of NSF_3.—Hyperfine structure due to the ^{14}N electric quadrupole was observed at low pressures for the $1 \leftarrow 0$ transition. Given in Table IV are the observed and calculated frequencies for the hyperfine structure. The calculated values are based on a coupling constant of $eqQ = +1.19 \pm 0.05$ mc. and $\nu_0 = 2B = 9{,}272.48$ mc. Since the three components were not completely resolved, it was difficult to obtain meaningful relative intensities, but semi-quantitatively, the calculated and observed intensities were in good agreement.

TABLE IV

CALCULATED AND OBSERVED QUADRUPOLE HYPERFINE STRUCTURE FOR THE $1 \leftarrow 0$ TRANSITION OF NSF_3

F_1	F_f	Obsd. frequency, mc.	Calcd. frequency, mc.
1	0	9271.90	9271.88
1	2	9272.42	9272.42
1	1	9272.79	9272.78

Discussion

The confirmed structure of NSF_3 may be considered naïvely as a derivative of SF_6 with three of the fluorine atoms replaced by a triply bonded nitrogen atom. The FSF angle has been increased by only four degrees and the SF distance has been diminished slightly. The SN distance agrees well with the expected value for a covalent nitrogen–sulfur triple bond. It should be mentioned that NSF_3 appears to be the first reported example of a molecule containing a nitrogen–sulfur triple bond. On the other hand, the triple bond in NSF_3 differs markedly from the triple bond in the cyanides with respect to the quadrupole coupling constant of the nitrogen atom since, in the cyanides, eQq ranges from -2.5 to -5 mc. Indeed, the only previously reported examples of a positive coupling constant have been in molecules where the nitrogen bonds are not cylindrically symmetrical or where the nitrogen atom has more than three bonds.[16] However, in all of the reported cases the nitrogen atom has been bonded exclusively to elements of the first row of the periodic table. Thus it appears that the 3s, 3p and 3d orbitals of the sulfur atom have a pronounced effect on the electronic distribution in the vicinity of the nitrogen nucleus.

Acknowledgments.—The authors wish to thank Dr. T. S. Piper for calling their attention to this compound and for supplying an early sample and Professor R. M. Badger for his helpful suggestions concerning the preparation.

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[12] W. Gordy, *J. Chem. Phys.*, **15**, 305 (1947).

[13] W. Gordy, *ibid.*, **15**, 81 (1947).

[14] L. Pauling, "Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 224.

[15] S. A. Marshall and J. Weber, *Phys. Rev.*, **105**, 1502 (1950).

[16] For a list of many of the N-14 coupling constants which have been measured, see C. H. Townes an d A. L. Shawlow, ref. 9, pp. 613–642.

[CONTRIBUTION OF DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY, ATLANTA 22, GA.]

N.m.r. Studies of Pyrimidine, Imidazole and their Monomethyl Derivatives

BY G. S. REDDY, R. T. HOBGOOD, JR., AND J. H. GOLDSTEIN

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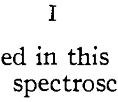
Pyrimidine, imidazole and their monomethyl derivatives have been studied by n.m.r. techniques. In all cases the spectra were simple patterns, easily analyzable by first-order theory. Additional information for pyrimidine itself was obtained from its C^{13}–H spectrum. The results are discussed in relation to the structures and bonding aspects of the ring systems.

Introduction

Various derivatives of pyrimidine (1) and imidazole (II) are of great importance in biological chemistry and have received considerable attention in recent years.[1] Among the newer techniques to be applied in this area, nuclear magnetic resonance (n.m.r.) spectroscopy gives promise of providing



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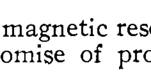

II

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[1] See, for example, A. Albert, "Heterocyclic Chemistry," University of London, The Athlone Press, London, 1959.