

ton donors even in the absence of electronegative substituents.<sup>6,9</sup> In compounds  $R_2C=CHX$ , X and at least one of the R groups have to be strongly electron withdrawing for the molecule to give a well detectable hydrogen bond. Benzene needs three such substituents to be a proton donor, since the grouping  $=CHX$  is impossible. In  $C(sp^3)-H$  compounds at least two substituents X in  $CHX_2$  have to be strongly activating in order for the compound to exhibit proton donor characteristics. The effectiveness of activation by electron-withdrawing substituents, as measured by the infrared spectral shift criterion, is:  $CN \gg CCl_2Cl_3 > CBr_3 > CCl_3 > Br > I > CHClCHCl_2 \sim Cl > F > COOCH_3 > CHBr_2 > CHCl_2$ . Each of these substituents can be assigned a "spectral shift increment" for a given proton acceptor; in compounds  $CHXYZ$  the sum of individual contributions for each group X, Y and Z can be used to predict  $\Delta\nu$ 's accurately. This additivity relationship is reminiscent of that observed for  $^{13}C-H$  n.m.r. coupling constants in the same compounds; the magnitudes of such coupling constants are used to estimate the hybridization of carbon.<sup>54</sup> However, the infrared and n.m.r. additivity

increments agree only in a very general way suggesting that hybridization of carbon cannot be the only significant factor in determining infrared spectral shifts. The spectral shifts of C-H proton donors do not appear to correlate with the enthalpy of hydrogen bonding.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND MATERIALS RESEARCH CENTER, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

## The Hydrogen Bonding Propensities of the Haloforms

BY C. J. CRESWELL AND A. L. ALLRED

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Thermodynamic constants for the association of tetrahydrofuran with fluoroform, chloroform, bromoform and iodoform were measured by nuclear magnetic resonance techniques. The magnitudes of the enthalpy of association decrease in the order chloroform > bromoform  $\approx$  fluoroform > iodoform.

### Introduction

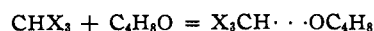
Conflicting results were obtained in previous studies of the relative strengths of hydrogen bonds formed by the haloforms. From dielectric polarizations of solutions of haloforms in various donors, the following orders of complex formation are indicated<sup>1</sup>

Acetone: chloroform > bromoform > iodoform  
Diethyl ether: chloroform = bromoform > iodoform  
Diisopropyl ether: chloroform > bromoform  
Quinoline: chloroform > bromoform > iodoform

The heat of mixing is slightly greater for the addition of a given donor solvent to chloroform than to bromoform.<sup>2,3</sup> It may also be noted<sup>2</sup> that, for a given donor, heats of mixing decrease in the order methylene chloride > methylene bromide  $\gg$  methylene iodide where hydrogen bonding is probably much less important. The heats of mixing for the systems chloroform-ethylene glycol dimethyl ether, dichlorofluoromethane-ethylene glycol dimethyl ether, chloroform-tetraethylene glycol dimethyl ether and dichlorofluoromethane-tetraethylene glycol dimethyl ether have been presented<sup>4</sup> for a wide range of concentrations. The maxima of the corresponding heat of mixing-composition curves for chloroform and dichlorofluoromethane were reported to be the same within experimental error. The solubilities of chloroform, dichlorofluoromethane and chlorodifluoromethane in several ethers were found to increase in the order given, and it was concluded<sup>5</sup>

that the hydrogen bonding ability of the  $\begin{array}{c} \diagup \\ C-H \\ \diagdown \end{array}$  group is increased as fluorine atoms are substituted for the chlorine atoms of chloroform. With the recent appearance<sup>6-9</sup> of considerable evidence for only limited validity of the Badger-Bauer rule<sup>10</sup> which relates spectral shifts in the infrared to the energies of hydrogen bonds, the earlier conflicting interpretations of spectral shifts<sup>11,12</sup> can be understood.

The present paper reports the determination of the thermodynamic constants for the association of tetrahydrofuran with fluoroform, chloroform, bromoform



and iodoform in the solvent cyclohexane.

### Experimental

**Preparation of Compounds and Solutions.**—Fluoroform was prepared from the reaction of trifluoromethyl iodide with potassium hydroxide in the solvent acetone.<sup>13</sup> The fluoroform was separated from impurities by bulb-to-bulb distillation and shown to be pure by hydrogen and fluorine nuclear magnetic resonance (n.m.r.).

Chloroform was washed with concentrated sulfuric acid, dilute sodium hydroxide and ice-water.<sup>14</sup> The chloroform was then

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TABLE I

OBSERVED PROTON CHEMICAL SHIFTS OF FLUOROFORM IN SOLUTIONS CONTAINING 0.02 MOLE FRACTION (M.F.) FLUOROFORM, THE SPECIFIED M.F. (B) OF TETRAHYDROFURAN AND (1.00 - 0.02 - B) M.F. OF CYCLOHEXANE PLUS HEXAFLUORO-2,2,3,3-TETRACHLOROBUTANE<sup>17</sup>

B	$\delta_{\text{obsd}}$ (p.p.m.; reference, cyclohexane)							
	-8.3°	-6.5°	2.9°	7.2°	8.9°	26.7°	27.7°	38.3°
0.000	-4.815	-4.815	-4.810	-4.813	-4.813	-4.800	-4.800	-4.800
.049	-5.000	-4.995	-4.995	-4.957	-4.950	.....	-4.917	-4.896
.098	-5.103	-5.107	-5.060	-5.052	-5.050	-5.002	-5.000	-4.975
.147	-5.175	-5.167	-5.120	-5.113	-5.117	-5.063	-5.061	-5.028
.196	-5.218	-5.213	-5.168	-5.173	-5.160	-5.115	-5.106	-5.076
.245	-5.283	-5.277	-5.217	-5.207	-5.213	-5.147	-5.152	-5.117
$K$ (m.f.) <sup>-1</sup>	7.60	7.86	6.17	5.83	5.33	4.93	4.56	3.57

dried over potassium carbonate and distilled (b.p. 61.0°) shortly before use.

Bromoform (b.p. 149.3°) was purified by the procedure used for chloroform.

Iodoform was prepared by the reaction of potassium iodide, acetone and sodium hypochlorite.<sup>15</sup> The crude iodoform was purified by recrystallization from methanol.

Tetrahydrofuran was dried over sodium wire and distilled (b.p. 66°) from lithium aluminum hydride.

Cyclohexane was distilled (b.p. 81.3°) and dried over sodium wire.

**N.m.r. Measurements.**—All n.m.r. spectra were observed with a Varian Associates, Inc., high-resolution spectrometer operating at 60.0 Mc./sec. for hydrogen resonance and 56.45 Mc./sec. for fluorine resonance. In all samples the 5-mm. o.d. Pyrex sample tubes were filled to a height of at least 7 cm. For fluoroform-containing samples, the tubes were filled to a height which allowed 2 cm. of dead space. Chemical shift measurements were made by the side band technique with a standard deviation of approximately 0.005 p.p.m. Chemical shifts are reported in p.p.m., a negative shift indicating resonance at an applied field lower than that required for the internal reference, cyclohexane. The samples were thermostated<sup>16</sup> to within  $\pm 0.3^\circ$ .

### Results

In Tables I, II, III and IV are presented the observed chemical shifts,  $\delta_{\text{obsd}}$ , of the protons of fluoroform, chloroform, bromoform and iodoform, respectively, for solutions containing cyclohexane,<sup>17</sup> either 0.01 or 0.02 mole fraction (m.f.), of haloform, and the specified mole fraction of tetrahydrofuran. The proton resonance of fluoroform was a quartet with  $J = 79.5$  c./sec. The treatment of comparable data has been discussed elsewhere<sup>19</sup> and will be outlined only briefly here. Equilibrium constants, in (m.f.)<sup>-1</sup> units, were calculated from eq. 1 and 2<sup>20</sup> where  $\delta_{\text{free}}$  is the proton chemical shift of unassociated haloform,  $\Delta$  is the "hydrogen bond shift" ( $\delta_{\text{complex}} - \delta_{\text{free}}$ ),  $\delta_{\text{complex}}$

$$K = \frac{C(A + B + S - C)}{(A - C)(B - C)} \quad (1)$$

$$\delta_{\text{obsd}} = \frac{C}{A} \Delta + \delta_{\text{free}} \quad (2)$$

is the chemical shift of complexed haloform,  $C$  is the number of moles of complex at equilibrium, and  $A$ ,  $B$  and  $S$  are the initial numbers of moles of haloform, tetrahydrofuran and solvent. Only the correct value of  $K$ , selected after repeated trial and error involving least-squares plots, gives a linear variation of  $\delta_{\text{obsd}}$  with calculated  $C/A$  values. The concentration of haloform was limited to either 0.01 or 0.02 m.f. to eliminate the effect of self-association. The concentration of

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(17) The fluoroform samples also contained 0.049 m.f. hexafluoro-2,2,3,3-tetrachlorobutane, the reference compound for a separate determination of equilibrium constants at various temperatures by fluorine magnetic resonance. The concentration of cyclohexane in the fluoroform samples is (1.000 - 0.020 - 0.049 - B) m.f. The fluorine shift data are listed in ref. 18, and the corresponding  $\Delta H$  value is compared in the Discussion section with the results from proton magnetic resonance spectroscopy.

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TABLE II

OBSERVED CHEMICAL SHIFTS OF CHLOROFORM IN SOLUTIONS CONTAINING 0.01 M.F. CHLOROFORM, THE SPECIFIED M.F. (B) OF TETRAHYDROFURAN AND (1.00 - 0.01 - B) M.F. OF CYCLOHEXANE

B	$\delta_{\text{obsd}}$				
	2.9°	26.7°	37.0°	44.3°	55.6°
0.0000	-5.653	-5.653	-5.653	-5.653	-5.653
.0495	-5.897	-5.812	-5.800	-5.783	-5.763
.0990	-6.043	-5.948	-5.927	-5.895	-5.863
.1485	-6.113	-6.022	-5.992	-5.960	-5.927
.1980	-6.178	-6.080	-6.057	-6.023	-5.985
.2475	-6.220	-6.127	-6.115	-6.067	-6.033
$K$ (m.f.) <sup>-1</sup>	9.32	5.44	4.43	4.14	3.20

TABLE III

OBSERVED CHEMICAL SHIFTS OF BROMOFORM IN SOLUTIONS CONTAINING 0.01 M.F. BROMOFORM, THE SPECIFIED M.F. (B) OF TETRAHYDROFURAN AND (1.00 - 0.01 - B) M.F. OF CYCLOHEXANE

B	$\delta_{\text{obsd}}$					
	2.9°	15.3°	33.0°	37.0°	44.3°	55.6°
0.0000	-5.257	-5.257	-5.257	-5.257	-5.257	-5.257
.0495	-5.455	-5.437	-5.402	-5.388	-5.373	-5.365
.0990	-5.580	-5.555	-5.498	-5.492	-5.472	-5.447
.1485	-5.663	-5.640	-5.573	-5.572	-5.555	-5.510
.1980	-5.733	-5.702	-5.635	-5.617	-5.603	-5.568
.2475	-5.767	-5.750	-5.688	-5.670	-5.647	-5.610
$K$ (m.f.) <sup>-1</sup>	6.66	5.59	4.09	4.19	3.62	3.14

TABLE IV

OBSERVED CHEMICAL SHIFTS OF IODOFORM IN SOLUTIONS CONTAINING 0.01 M.F. IODOFORM, THE SPECIFIED M.F. (B) OF TETRAHYDROFURAN AND (1.00 - 0.01 - B) M.F. OF CYCLOHEXANE

B	$\delta_{\text{obsd}}$					
	2.9°	26.7°	27.0°	37.9°	48.8°	55.6°
0.0000	-3.383	-3.383	-3.383	-3.383	-3.383	-3.383
.0495	-3.483	-3.468	-3.472	-3.462	-3.452	-3.450
.0990	-3.548	-3.525	-3.525	-3.512	-3.503	-3.495
.1980	-3.622	-3.597	-3.595	-3.582	-3.568	-3.562
.2475	-3.648	-3.622	-3.633	-3.612	-3.591	-3.587
$K$ (m.f.) <sup>-1</sup>	6.30	5.18	5.02	4.46	4.35	3.80

tetrahydrofuran was kept less than 0.25 m.f. to minimize the solvent effects discussed in ref. 19 and 21. Values of  $K$ , with probable errors of 0.05-0.3 (m.f.)<sup>-1</sup>, at various temperatures are presented in Tables I-IV. Due to the small range of concentration of tetrahydrofuran and to the low values of  $\Delta$ , a slight error in the measurement of  $\delta_{\text{obsd}}$  produces an appreciable error in the calculation of  $K$ . In Table V are presented the average values of the hydrogen bond shifts of the haloforms. Values of  $\Delta H$ , obtained from least-squares plots of  $\log K$  vs.  $1/T$ , of  $\Delta G_{25^\circ}$  and of  $\Delta S$  are listed in Table V also.

### Discussion

The magnitudes of the  $\Delta H$  values in Table V decrease in the order: chloroform > bromoform  $\approx$

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TABLE V

THERMODYNAMIC CONSTANTS FOR HYDROGEN BOND FORMATION BETWEEN THE HALOFORMS AND TETRAHYDROFURAN IN CYCLOHEXANE AND RELATED CHEMICAL SHIFT DATA

	CHF <sub>3</sub>	CHCl <sub>3</sub>	CHBr <sub>3</sub>	CHI <sub>3</sub>
$\Delta H$ , kcal. mole <sup>-1</sup>	-2.4 ± 0.2	-3.6 ± 0.4	-2.6 ± 0.2	-1.6 ± 0.4
$\Delta G_{25^\circ}$ , kcal. mole <sup>-1</sup>	-0.90	-1.04	-0.93	-0.91
$\Delta S_{25^\circ}$ , cal. mole <sup>-1</sup> deg. <sup>-1</sup>	-5.2 ± 0.6	-8.6 ± 0.4	-5.6 ± 0.4	-2.3 ± 0.6
Av. $\Delta$ for X <sub>3</sub> CH...OC <sub>4</sub> H <sub>8</sub> , p.p.m.	-0.69 ± 0.03	-0.85 ± 0.03	-0.83 ± 0.02	-0.43 ± 0.03
$\delta_{\text{CHX}}$ , dilute, <sup>a</sup> p.p.m.	-4.800	-5.653	-5.257	-3.383

<sup>a</sup> Chemical shift with C<sub>6</sub>H<sub>12</sub> serving as both the internal reference and the solvent.

fluoroform > iodoform. The relative electronegativities<sup>22,23</sup> of the halogens leads to the prediction, based on only inductive effects, that hydrogen bond strengths would decrease in the order: fluoroform > chloroform > bromoform > iodoform. The magnitudes of the dissociation constants of the trihaloacetic acids do decrease in the order: CF<sub>3</sub>COOH > CCl<sub>3</sub>COOH = CBr<sub>3</sub>COOH > CI<sub>3</sub>COOH. In the following paragraphs, various properties of the haloforms will be surveyed and additional evidence will be presented for the order of hydrogen-bonding propensities determined from the enthalpy values in Table V. It has been shown<sup>24</sup> that for the same type of hydrogen bonds, the decrease in entropy is proportional to the strength of the hydrogen bonds. The order of decreasing entropy of association for the haloform-tetrahydrofuran interactions is chloroform > bromoform  $\approx$  fluoroform > iodoform.

The magnitude of the "hydrogen bond shift",  $\Delta$ , has been employed<sup>25-27</sup> as a measure of hydrogen bond strength. The "hydrogen bond shifts" recorded in Table V for the haloform-tetrahydrofuran association decrease in the order: chloroform > bromoform > fluoroform > iodoform and thus qualitatively parallel the  $\Delta H$  values, although  $\Delta H$  and the hydrogen bond shift" are not linearly related.

The relative values, in Table V, of the chemical shifts of the unassociated haloforms in cyclohexane are not understood at present. However, it is interesting that the chemical shifts follow the order of  $\Delta H$  and the "hydrogen bond shifts."

As mentioned in the Introduction, the solubilities of chloroform, dichlorofluoromethane and chlorodifluoromethane in several high-boiling polyethers have been measured.<sup>5</sup> To the present authors, the earlier data indicate that association in the liquid phase with ethers probably *decreases* in the order chloroform > dichlorofluoromethane > chlorodifluoromethane since the greatest deviation from ideal behavior occurs with chloroform and the least deviation with chlorodifluoromethane. While differences in van der Waals forces may influence the relative solubilities, it appears that the propensity for hydrogen bond formation decreases in the order chloroform > dichlorofluoromethane > chlorodifluoromethane.

For the chloroform-ethylene glycol dimethyl ether, dichlorofluoromethane-ethylene glycol dimethyl ether, chloroform-tetraethylene glycol dimethyl ether, and dichlorofluoromethane-tetraethylene glycol dimethyl ether systems a total of 40 heats of mixing were measured.<sup>4</sup> Although the maxima of the corresponding heat of mixing-composition curves were stated<sup>4</sup> to be the same within experimental error, the published heat of

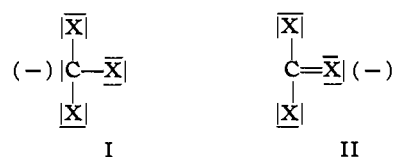
mixing curves are consistently higher over the reported range of concentrations for chloroform than for dichlorofluoromethane, and therefore the data may be interpreted as evidence for a slightly greater extent of hydrogen bond formation by chloroform than by dichlorofluoromethane.

The free energies of intramolecular hydrogen bonding in the 2,6-dihalophenols decrease<sup>28</sup> in the order Cl > Br > F > I. This order exactly parallels the order for intermolecular hydrogen bonding with the haloforms, although steric factors differ.

The association of fluoroform with tetrahydrofuran in cyclohexane has been measured also by fluorine n.m.r.<sup>17,18</sup> The results,  $K_{25^\circ} = 4.77 \pm 0.02$  (m.f.)<sup>-1</sup> and  $\Delta H = -2.593 \pm 0.024$  kcal./mole, agree well with the values in Tables I and IV. The relatively high accuracy from fluorine n.m.r. is a consequence of the large value of  $\Delta$ , 1.480 p.p.m., for fluorine resonance.

The present systems are probably not appreciably complicated by the presence of charge-transfer complexes since an interaction involving the large transfer or "contact interaction" is "either non-existent or hardly observable in the case of the diethyl ether-carbon tetrachloride system."<sup>29</sup>

The order of hydrogen-deuterium exchange rates of the trihalomethanes was attributed<sup>30</sup> to some combination of inductive effect, polarizability and *d*-orbital resonance. The involvement of the *d*-orbitals of chlorine, bromine or iodine, but not of fluorine, in bonding represented by resonance structures of type II *may* explain the lower reactivity of DCX<sub>3</sub> compounds where one or more of the halogens is fluorine.<sup>31</sup> The



contributions of hyperconjugative resonance structures comparable to type II for chloroform, bromoform or iodoform, but not fluoroform, involved in hydrogen bond formation is consistent with the  $\Delta H$  values for haloform-tetrahydrofuran association.

The association of chloroform with tetrahydrofuran exhibits a smaller entropy change than the corresponding association ( $\Delta H = -4.15$  kcal. mole<sup>-1</sup> and  $\Delta S = -11.0$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>)<sup>19</sup> with triethylamine. For the chloroform-triethylamine system, the larger change in enthalpy implies stronger hydrogen bonding, greater order due to a more restricted configuration, and hence

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(25) C. M. Huggins, G. C. Pimentel and J. N. Shoolery, *J. Phys. Chem.*, **60**, 1311 (1956).

(26) L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **35**, 251 (1957).

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a larger decrease in entropy. An additional factor which contributes to a lower change in entropy for the chloroform-tetrahydrofuran system is the availability of two unshared pairs of electrons in tetrahydrofuran. Since there is available only one pair of electrons in triethylamine, the association is more probable in the case of tetrahydrofuran. The change of free energy for the association of chloroform and tetrahydrofuran is thus larger than that of the association of chloroform and triethylamine.

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## The Microwave Spectrum and Structure of NSF<sup>1a</sup>

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The microwave spectrum of the compound reported to be NSF was investigated in order to remove the uncertainty regarding its structure. The compound was found, contrary to previous notions, to have the (bent) structure N≡S—F with the molecular dimensions:  $d_{SF} = 1.646 \pm 0.01 \text{ \AA}$ ,  $d_{SN} = 1.446 \pm 0.01 \text{ \AA}$ , and  $\angle NSF = 116^\circ 52' \pm 15'$ . These dimensions are compatible with the force constants of the bonds as determined from previous infrared work. The quadrupole coupling constants are  $eq_a Q = -1.66 \pm 0.05 \text{ Mc}$ . and  $\eta = +5.86 \pm 0.05$ . The hydrolysis of NSF to give HNSO was also confirmed.

### Introduction

In 1955, Glemser, Schröder and Haeseler reported the preparation of a mixture of SNF and SN<sub>2</sub>F<sub>2</sub> by the action of AgF<sub>2</sub> on S<sub>4</sub>N<sub>4</sub> but were unable to obtain pure SNF<sup>2</sup>; in the following year, the preparation of the isomer NSF was reported as arising from the thermal decomposition of SN<sub>2</sub>F<sub>2</sub>.<sup>2b</sup> NSF was described as being quite stable with a boiling point of 4.8° and a melting point of -79°. The hydrolysis of NSF was interpreted as favoring the structure N≡S—F. In 1961, Glemser and Richert reported the isolation of SNF and gave its boiling point as  $0.4 \pm 2^\circ$  and its melting point as -89°.<sup>3</sup> In addition they obtained the infrared spectrum and the fluorine nuclear magnetic resonance spectrum of SNF and interpreted their results in favor of the structure S=N—F.<sup>4</sup> However, they were unable to repeat the preparation of SN<sub>2</sub>F<sub>2</sub> and were led to the conclusion that this compound did not exist. Since NSF was reported as arising from the decomposition of SN<sub>2</sub>F<sub>2</sub>, its existence would also be in some doubt.

Also in 1961, Rogowski, presumably working with a sample supplied by Glemser,<sup>5</sup> determined the structure of SNF by means of electron diffraction studies.<sup>6</sup> He obtained the molecular parameters:  $d_{SN} = 1.62 \pm 0.03 \text{ \AA}$ ,  $d_{NF} = 1.42 \pm 0.03 \text{ \AA}$ , and  $\angle SNF = 122 \pm 3^\circ$ .

In their interpretation of the infrared spectrum of SNF based on the S=N—F model, Richert and Glemser calculated the force constants of the SN and the NF bonds. If one then uses Badger's rule<sup>7</sup> to estimate the bond distances from the force constants, the following bond distances are obtained:  $d_{SN} = 1.45 \text{ \AA}$ , and  $d_{NF} = 1.63 \text{ \AA}$ . The results of the infrared work and the electron diffraction work appear to be incompatible.<sup>8</sup> Furthermore, Glemser and Richert reported the preparation of SNF as also arising from the thermal decomposition of S<sub>4</sub>N<sub>4</sub>F<sub>4</sub> where the fluorine atoms are bonded

to the sulfur atoms. One would expect NSF to be formed from such a decomposition. These anomalies plus the uncertainty concerning the existence of NSF indicated that further studies of this system would be advisable.

Microwave spectroscopy is an ideal tool for dealing with systems which contain a number of compounds since the spectrum of each component of the mixture is quite distinct and separate from the spectrum of every other component. In addition, the microwave spectra of most of the side products have already been reported so transitions due to these species could easily be accounted for. As will be shown below, the compound claimed by Glemser and Richert to be SNF is in fact NSF and has the molecular parameters:  $d_{SF} = 1.646 \text{ \AA}$ ,  $d_{SN} = 1.446 \text{ \AA}$ , and  $\angle NSF = 116^\circ 52'$ .

### Description of the Experiments

**The Preparation of NSF.**—NSF is formed in the reaction of AgF<sub>2</sub> with S<sub>4</sub>N<sub>4</sub> in an inert solvent. The procedure followed was that outlined by Glemser and Richert.<sup>3</sup> The crude NSF was purified somewhat by the use of a low temperature fractional distillation apparatus. The sample thus obtained consisted of roughly 50% NSF, the major impurities being CCl<sub>3</sub>F, SO<sub>2</sub>, HNSO and SOF<sub>2</sub>. The composition of the sample was determined from the mass spectrum, the infrared spectrum and the fluorine nuclear magnetic resonance spectrum.

**The Microwave Spectrum of NSF.**—The microwave spectrum of the impure sample was investigated using a conventional Stark modulated spectrometer. Some of the observed transitions were assigned to NSF by relating the intensity of the transition to the amount of NSF present in the sample as determined from the mass spectrum. Some of these transitions had resolvable fine structure which was attributed to the coupling of the spin of the nitrogen nucleus to the over-all rotation of the molecule by means of the electrical quadrupole moment of the nitrogen nucleus. For certain transitions, resolvable Stark effects were observed, and these observations led to an assignment of the microwave spectrum of the normal isotopic species of NSF. The assignment of the rotational transitions was based upon measurement of the quadrupole splitting, the observed Stark effect, and upon the agreement of the observed frequency with the values calculated from a fitted rigid asymmetric rotor model.

The quadrupole coupling constants

$$eq_a Q = \partial^2 V / \partial a^2$$

and

$$\eta = \frac{\partial^2 V / \partial b^2 - \partial^2 V / \partial c^2}{\partial^2 V / \partial a^2}$$

where  $a$ ,  $b$  and  $c$  are coordinates located along the principal moments of inertia and  $V$  is the potential at the nitrogen nucleus due to all the external charge distribution, were calculated from

(1) (a) This research was supported by a grant extended to Harvard University by the Office of Naval Research. (b) NIH Fellow, 1959-1962.

(2) (a) O. Glemser, H. Schröder and H. Haeseler, *Z. anorg. allgem. Chem.*, **279**, 28 (1955); (b) O. Glemser and H. Haeseler, *ibid.*, **287**, 54 (1956).

(3) O. Glemser and H. Richert, *ibid.*, **307**, 313 (1961).

(4) O. Glemser and H. Richert, *ibid.*, **307**, 328 (1961).

(5) O. Glemser, H. Richert and F. Rogowski, *Naturwissenschaften*, **47**, 94 (1960).

(6) F. Rogowski, *Z. physik. Chem. (Frankfurt)*, **27**, 277 (1961).

(7) R. M. Badger, *J. Chem. Phys.*, **3**, 710 (1935).

(8) Prof. R. M. Badger suggested to one of us that there seemed to be a discrepancy for this molecule.