

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORKAn Electron Diffraction Study of the Structures of NF_2 and N_2F_4

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The structures of tetrafluorohydrazine and the difluoramino radical have been determined by electron diffraction. The bond distances and bond angles are: $\text{N-F} = 1.363 \pm 0.008$ Å and $\angle \text{FNF} = 102.5 \pm 0.9^\circ$ for NF_2 and $\text{N-F} = 1.393 \pm 0.008$ Å, $\text{N-N} = 1.53 \pm 0.02$ Å, and $\angle \text{FNF} = 103.7 \pm 0.9^\circ$ for N_2F_4 . The dihedral angle is considerably less in N_2F_4 ($70 \pm 3^\circ$) than in N_2H_4 . The structural differences between NF_2 's when free and as part of stable molecules are briefly discussed, as is also the observation that the dihedral angles in hydrazine and hydrogen peroxide are smaller when fluorine atoms are substituted for hydrogen.

Introduction

The chemical and physical properties of tetrafluorohydrazine and of the difluoramino radical have received considerable attention during the past 5 years.¹ The heat of dissociation of tetrafluorohydrazine is 19.8 ± 0.8 kcal/mole,² and its entropy of dissociation is 38.6 eu.³ The infrared spectrum of NF_2 has been recorded, and a frequency has been unambiguously assigned to the symmetric stretching mode, ν_1 .⁴ From the rotational fine structure of this band and an assumed NF distance of 1.37 Å, an estimate (104.2°) was obtained for $\angle \text{FNF}$. The microwave spectrum of N_2F_4 has been observed and moments of inertia have been derived.⁵ Assuming $r_{\text{NN}} = 1.47$ Å (as in N_2H_4) and $r_{\text{NF}} = 1.37$ Å (as in NF_3), Lide and Mann deduced $\angle \text{FNF} = 108 \pm 3^\circ$, $\angle \text{NNF} = 104 \pm 3^\circ$, and a dihedral angle of $65 \pm 3^\circ$. The C_2 symmetry for N_2F_4 found in that study has been confirmed by infrared⁶ and Raman⁷ spectral studies.

At room temperature and 5 mm pressure, N_2F_4 is 0.7% dissociated, while at 225° and 5 mm total pressure, the degree of dissociation rises to 0.99. By controlling the temperature of the sample and nozzle it is thus possible to study independently the structures of the undissociated and the dissociated species by electron diffraction. Prior to this study there was not sufficient information on N_2F_4 and NF_2 to show the differences in the structural parameters of NF_2 in the dimer and monomer.

Experimental Section

The sample of N_2F_4 was obtained from Dr. Charles B. Colburn. Its reported composition was: $\text{N}_2\text{F}_4 > 99\%$, $\text{N}_2\text{O} \sim 0.2\%$, and $\text{NO} \sim 0.6\%$. For the electron diffraction photographs of N_2F_4 , the sample was maintained at about 5 mm pressure in a 6-l. glass bulb which was attached to the nozzle tube of the diffraction apparatus. The gas-handling system was preseasoned with small

samples of tetrafluorohydrazine, which were discarded. Kel-F grease was used on all stopcocks. The pressure was measured with a polychlorotrifluoroethylene oil manometer. Sector electron diffraction photographs were taken with the apparatus previously described.⁸ A small sector was used with an electron beam energy of 25 keV to record the scattering region of $12 \leq q \leq 50$. [$q = (40/\lambda) \sin(\phi/2)$, where λ is the wavelength of the electrons and ϕ is the scattering angle.] A larger sector was also used with a 50-keV electron beam for $25 \leq q$.

Diffraction photographs of NF_2 were obtained by heating the N_2F_4 sample container, the tube connecting this flask to the diffraction nozzle, and the nozzle to 225° . We were not successful in obtaining any indication of NF_2 when using the gas dynamic nozzle⁹ even when heated to $\sim 200^\circ$; a conventional nozzle had to be used. This we interpret as evidence for the very rapid association of two NF_2 's in the cooling jet which is developed by the gas dynamic nozzle.

Gold foil diffraction patterns were taken with each set of data to provide a scale factor. The diffraction photographs were scanned with a Leeds and Northrup microphotometer. The plates were rapidly oscillated about an axis through the center of the pattern, as they were scanned. Kodak lantern slide medium plates were used. Optical densities were converted to relative intensities by a method described elsewhere.¹⁰

Reduction of Data

An experimental $M(q)$ function was obtained

$$M_{\text{exptl}}(q) = Pq[T(q)/B(q) - 1] \quad (1)$$

where P is $\sum_k (Z_k^2 + Z_k)$, $T(q)$ is the observed total intensity, $B(q)$ is the background intensity, and Z_k is the atomic number. In the absence of extraneous scattering this corresponds to

$$M(q) = M_0(q) + N(q) \quad (2)$$

with

$$M_0(q) = \sum'_{ij} (Z_i Z_j / r_{ij}) \exp(-\pi^2 l_{ij}^2 q^2 / 200) \sin(\pi q r_{ij} / 10) \quad (3)$$

Here $N(q)$ is a correction for nonnuclear scattering,¹¹ l_{ij} the rms amplitude, and r_{ij} the interatomic distance between atoms i and j . The observed intensities are corrected according to

$$M_{0,\text{expt}}(q) = Y^{-1} M_{\text{expt}}(q) - N(q) \quad (4)$$

(8) J. M. Hastings and S. H. Bauer, *J. Chem. Phys.*, **18**, 13 (1950).

(9) R. B. Harvey, P. A. Keidel, and S. H. Bauer, *J. Appl. Phys.*, **21**, 860 (1950).

(10) K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 317 (1963).

(11) L. S. Bartell, L. O. Brockway, and R. H. Schwendemann, *ibid.*, **23**, 1854 (1955).

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(2) L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, **35**, 1481 (1961).

(3) C. B. Colburn and F. A. Johnson, *ibid.*, **33**, 1869 (1960).

(4) M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, Jr., and D. E. Mann, *ibid.*, **35**, 1129 (1961).

(5) D. R. Lide, Jr., and D. E. Mann, *ibid.*, **31**, 1129 (1959).

(6) J. R. Durig and R. C. Lord, *Spectrochim. Acta*, **19**, 1877 (1963).

(7) Yu. L. Kotov and V. M. Tatevskii, *Opt. i Spektroskopiya*, **14**, 443 (1963).

where Y is the inverse of the index of resolution, and $N(q)$ is computed for some acceptable model. A radial distribution function is then calculated according to

$$f(r) = \sum_{q=1}^{q_{\max}} [M_0(q < q_{\min}) + M_{0,\text{expt}}(q \geq q_{\min})] \times \exp(-\gamma q^2) \sin(\pi q r / 10) \quad (5)$$

q_{\min} and q_{\max} are the extremes of the range of observed scattering angle and γ is a damping factor calculated from $\exp(-\gamma q_{\max}^2) = 0.1$. Were the data available for the complete range of q and accurate, the assumed model correct, and the vibrational motions harmonic, $f(r)$ would consist of a superposition of Gaussian functions

$$f(r)_{\text{theor}} = 5 \sum_{ij} (Z_i Z_j / r_{ij}) (H_{ij} / \pi)^{1/2} \exp[-H_{ij}(r - r_{ij})^2] \quad (6)$$

with

$$H_{ij} = 1 / (2l_{ij}^2 + 400\gamma / \pi^2) \quad (7)$$

All extended calculations were made with a CDC 1604 digital computer. A structure was obtained after a series of successive refinements using criteria of a smooth background intensity and a zero-valued $f(r)$ for distances sufficiently far from any interatomic distance. This structure was used as the starting model for a least-squares analysis of the molecular intensity function based on a program developed by Seip.¹²

Results

NF_2 .—The derived $M_{0,\text{expt}}(q)$ function is shown in Figure 1 along with the theoretical $M_0(q)$ for the best model. Figure 2 shows the final radial distribution curve computed using a damping factor $\gamma = 0.00022$. For the first peak the mean amplitude of vibration is 0.054 Å. The ratio of the experimental area to the theoretical is 183:185. The second peak is assigned to the $\text{F}\cdots\text{F}$ nonbonded pair at a distance of 2.127 Å with a mean amplitude of 0.065 Å. The ratio of the experimental area to the theoretical is 77:76. The lower curve of Figure 2 shows the difference between the experimental radial distribution function and the theoretical function calculated using the distances and amplitudes given above.

Five parameters—the two distances, their amplitudes of vibration, and an amplitude scale—were refined simultaneously by the least-squares procedure. The final structural parameters for NF_2 are summarized in Table I. The standard deviations calculated by the least-squares program are shown. The estimated error for a distance is the square root of the sums of the squares of three times the standard deviation and an estimated linear scale error of 0.5%. The estimated error for each vibrational amplitude and bond angle is three times the standard deviation since these parameters are nearly independent of scale errors.

(12) A. Almenningen, O. Bastiansen, R. Seip, and H. Seip, *Acta Chem. Scand.*, **18**, 2115 (1964).

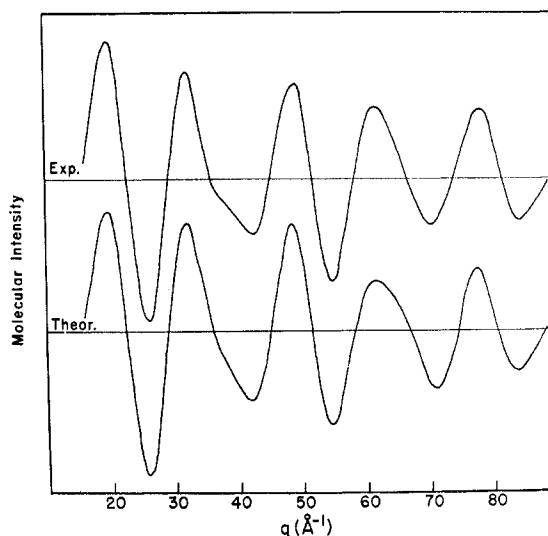


Figure 1.—The reduced experimental intensity curve for NF_2 compared with that calculated for the best model.

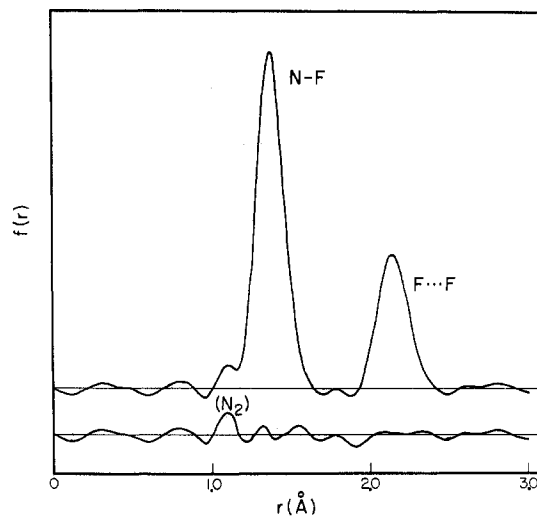


Figure 2.—The experimental radial distribution curve for NF_2 . The lower curve shows the difference between the experimental curve and that calculated for the best model. The small peak at 1.09 Å is due to N_2 produced during heating; the corresponding fluorine reacted with the tube walls.

N_2F_4 .—The derived $M_{0,\text{expt}}(q)$ is plotted in Figure 3 along with the theoretical $M_0(q)$ for the best model. Figure 4 shows the final radial distribution curve computed with a damping factor $\gamma = 0.00022$. The peak at 1.40 Å was resolved into two Gaussian contributions. The first corresponds to the four bonded N-F distances of 1.393 Å with a mean vibrational amplitude of 0.050 Å. The second corresponds to the N-N bond distance of 1.53 Å with an amplitude of 0.05 Å. The ratio of the observed area to the theoretical is 433:429. The small peak at 3.4 Å has an area of 42. The theoretical area for a single $\text{F}\cdots\text{F}$ distance at 3.38 Å is 47 while two would give an area of 94. Hence, there is only a single $\text{F}\cdots\text{F}$ distance at 3.38 Å and the molecular configuration therefore is not *trans*. This $\text{F}\cdots\text{F}$ distance has a mean amplitude of 0.05 Å.

The complex peak at 2.2 Å is shown on an expanded

TABLE I
 STRUCTURAL PARAMETERS FOR N_2F_4

		Estd error	Std dev	l_{ij}	Estd error	Std dev	Infrared results ^a
N-F, A	1.3631	± 0.008	0.0013	0.0536	± 0.005	0.0018	1.37 (assumed)
F...F, A	2.1267	± 0.016	0.0039	0.0647	± 0.011	0.0036	104.2 (NF = 1.37 A)
$\angle \text{N-F}$, deg	102.53	± 0.9	0.30				103.8 (NF = 1.363 A)

^a M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **35**, 1129 (1961).

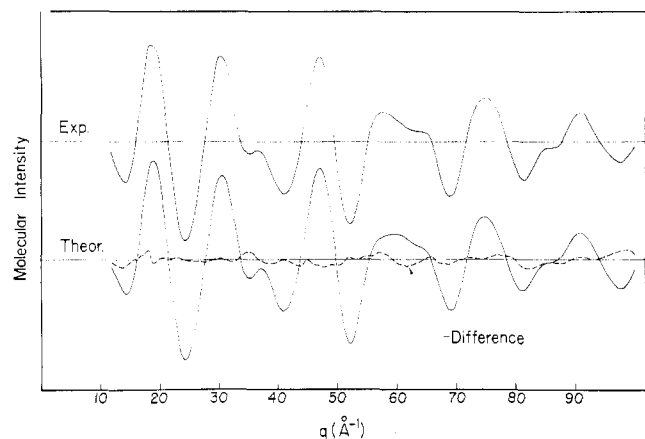


Figure 3.—The reduced experimental intensity curve for N_2F_4 compared with that calculated for the best model.

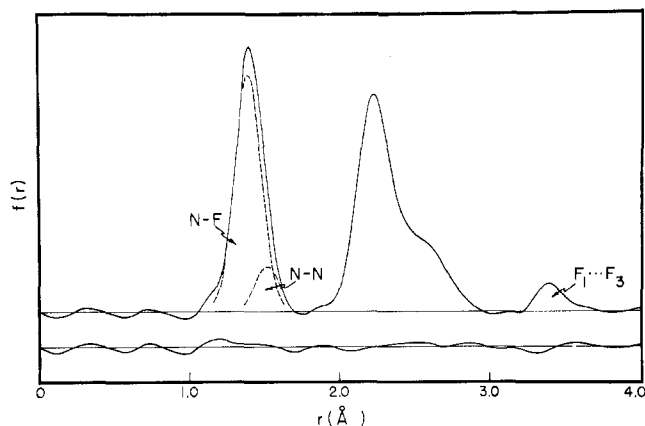


Figure 4.—The experimental radial distribution curve for N_2F_4 . The lower curve shows the difference between the experimental curve and that calculated for the best model.

scale in Figure 5. This peak was resolved into five Gaussians. The first component was assigned to the two nonbonded distances $\text{F}_1 \cdots \text{F}_2$ and $\text{F}_3 \cdots \text{F}_4$, separated by 2.192 Å with a mean amplitude of 0.054 Å. A diagram of the model is shown in Figure 6. The component Gaussian at 2.591 Å is well defined and has a mean amplitude of 0.11 Å. This was assigned to the two distances $\text{F}_1 \cdots \text{F}_4$ and $\text{F}_2 \cdots \text{F}_3$. In order for the sum of the components to appear as a peak with a pronounced shoulder (rather than as two distinct peaks), it is necessary that one distance be at 2.35 Å. A peak has been assigned to $\text{F}_2 \cdots \text{F}_4$ at a distance of 2.35 Å with an amplitude of 0.15. The latter two distances and the assigned N-F and N-N bond distances impose a restriction on the NNF angles (99 and 104°). The remaining components were assigned to the two

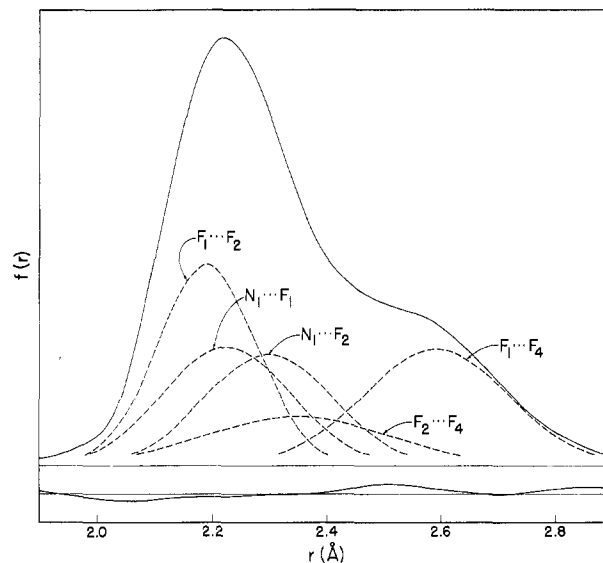


Figure 5.—The radial distribution curve for N_2F_4 in the region 2.0-2.8 Å. The dotted lines show the resolved peaks for individual atom pairs. The lower curve shows the difference between the experimental curve and the curve calculated from the best model.

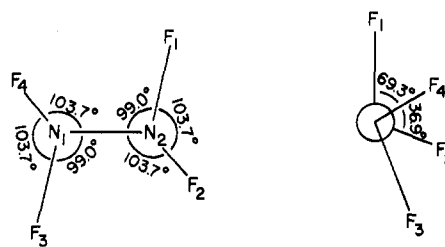


Figure 6.—Projections of the structure of N_2F_4 .

pairs $\text{N}_1 \cdots \text{F}_1$ and $\text{N}_2 \cdots \text{F}_3$ at 2.225 Å and to two pairs $\text{N}_1 \cdots \text{F}_2$ and $\text{N}_2 \cdots \text{F}_4$ at 2.30 Å. The amplitudes of vibration were assumed to be equal and have the value 0.09 Å. The ratio of the observed to the calculated area is 566:564. The lower curves in Figures 4 and 5 show the difference between the experimental radial distribution functions and the curves calculated using the parameters given above.

The final structural parameters were obtained by a least-squares analysis of the molecular intensity curve. Fourteen independent parameters were refined: six interatomic distances, N-N, N-F (all assumed equal), $\text{N}_1 \cdots \text{F}_1$, $\text{N}_1 \cdots \text{F}_2$, $\text{F}_1 \cdots \text{F}_2$, and $\text{F}_1 \cdots \text{F}_4$; seven vibrational amplitudes (the vibrational amplitudes of $\text{N}_1 \cdots \text{F}_1$ and $\text{N}_1 \cdots \text{F}_2$ were assumed equal); and an amplitude scale. The remaining two distances were

TABLE II
STRUCTURAL PARAMETERS FOR N_2F_4

	This work						Microwave results ^a
		Estd error	Std dev	l_{ij}	Estd error	Std dev	
N-F, A	1.3933	±0.008	0.0011	0.0499	±0.006	0.0016	1.37 (assumed)
N-N, A	1.5302	±0.027	0.0065	0.0475	±0.030	0.0074	1.47 (assumed)
F ₁ ···F ₂ , A	2.1920	±0.015	0.0027	0.0543	±0.010	0.0024	
N ₁ ···F ₁ , A	2.2249	±0.024	0.0053	0.0897	±0.015	0.0038	
N ₁ ···F ₂ , A	2.2979	±0.029	0.0066				
F ₂ ···F ₄ , A	2.3470			0.1485	±0.110	0.0276	
F ₁ ···F ₄ , A	2.5913	±0.037	0.0086	0.1070	±0.030	0.0076	
F ₁ ···F ₃ , A	3.3810			0.0540	±0.026	0.0064	
∠FNF, deg	103.73	±0.8	0.21				108 ± 3
∠NNF ₁ , deg	99.01	±1.8	0.45				104 ± 3
∠NNF ₂ , deg	103.53	±2.1	0.53				
Dihedral, deg	69.32	±4.7	1.18				65 ± 3

^a D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **31**, 1129 (1959).

calculated from the six independent distances. Shrinkage effects were not included. Attempts to refine all parameters simultaneously failed and it was necessary to carry out the refinement in an iterative manner. First, only distances were refined with amplitudes held fixed. The resulting distances were then held constant and the amplitudes refined. This iteration was continued until neither type of refinement changed any of the parameters. This was carried through for a number of different starting models to ensure that the final structure represented an absolute minimum of the least-squares criterion and not a local minimum. All starting models converged to the same final structure. The parameters obtained are given in Table II. The standard deviations of the distances are those obtained keeping all amplitudes constant. Similarly the standard deviations of the vibrational amplitudes were calculated holding the distances constant. They are unrealistically small because correlations between distances and amplitudes are absent. Therefore the estimated error of each distance is the square root of the sum of the squares of four times the standard deviation and an estimated linear scale error of 0.5%. The estimated error of each bond angle and amplitude is 4 times its standard deviation.

Discussion

The structure obtained by electron diffraction for NF_2 agrees well with that derived from the infrared data.⁴ The results for N_2F_4 likewise agree with the existing microwave values.⁵ Moments of inertia calculated from the structural parameters deduced in this work are compared in Table III with those derived from the microwave spectra.

The N-N bond length in tetrafluorohydrazine, 1.53 Å,

TABLE III
MOMENTS OF INERTIA OF TETRAFLUOROHYDRAZINE
(amu-Å²)

	This work	Microwave spectra ^a
I_a	91.9	90.68
I_b	161.8	158.6
I_c	177.4	179.8

^a Reference 5.

is longer than the corresponding bond length in hydrazine, 1.45 Å,^{13,14} and in dimethylhydrazine,¹⁵ and is considerably longer than the value found recently in $\text{N}_2(\text{CF}_3)_4$ by Bartell and Higginbotham¹⁶ (1.40 ± 0.02 Å). In contrast, the corresponding atoms in N_2O_4 are much farther apart, 1.75 Å.¹⁷ The corresponding >N-N< dissociation energies are 12.9 kcal/mole for N_2O_4 ,¹⁸ 19.8 kcal/mole for N_2F_4 , and approximately 60 kcal/mole in N_2H_4 (as derived from kinetic¹⁹ and mass spectral data²⁰). $\text{N}_2(\text{CF}_3)_4$ is so stable that it can be heated to 500° without extensive decomposition. It appears that methyl substitution affects the magnitude of the N-N bond dissociation energy. Gowenlock, *et al.*,²¹ estimated $D[\text{H}_2\text{N}-\text{N}(\text{CH}_3)_2]$ to be 38-44 kcal/mole and $D[(\text{CH}_3)_2\text{N}-\text{N}(\text{CH}_3)_2]$ to be 50 kcal/mole.

According to a theoretical analysis presented about 30 years ago by Penney and Sutherland²² of the structure of N_2H_4 , the interaction of the two electronic clouds associated with the nonbonding electron pairs on the nitrogen atoms is the dominant factor in determining the orientation of one NH_2 group relative to the other; all other interactions, generally referred to as steric and van der Waals, are of lesser importance. The energy calculated as a function of rotational angle about the N-N bond is lowest at a dihedral angle of 90-100°. Recently, the dihedral angle in hydrazine was found to be 90-95°¹³ confirming this theoretical prediction. Penney and Sutherland's arguments may be extended to N_2F_4 . However, it appears that the F···F repulsions in N_2F_4 are greater than the H···H repulsions in N_2H_4 since potential minima occur, not at 90 and 270°

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TABLE IV
 SUMMARY OF OBSERVED NF BOND PROPERTIES

Molecule	r_{NF} , Å	$\angle FNX$, deg	Sym NF str freq, cm^{-1}
NF	(1.35) ^a		1115 ^a
NO ₂ F	1.35 ^b	117.5 (assumed)	
NF ₂	1.363 ± 0.008 ^c	102.5 ± 1.0	1074 ^d
NF ₃	1.371 ^e	102.1	1031 ^f
NF ₂ Cl	1.38 ± 0.01 ^g	103 ± 1 ($\angle FNF$) 104.5 ± 1 ($\angle FNCl$)	925 ^h
N ₂ F ₄	1.393 ± 0.008 ^c	103.7 ± 0.8 ($\angle FNF$) 101.3 ± 3 ($\angle FNN$, av)	998 ^b
N ₂ F ₂ (<i>trans</i>)	1.396 ± 0.008 ⁱ	105.5 ± 1.0	1010 ^j
HNF ₂	1.400 ± 0.002 ^k	99.8 ± 0.2 ($\angle FHN$) 102.9 ± 0.2 ($\angle FNF$)	972 ^l
N ₂ F ₂ (<i>cis</i>)	1.410 ± 0.009 ⁱ 1.384 ± 0.010 ^m	114.4 ± 1.0 ($\angle NNF$) 114.5 ± 0.5	896 ^j
FN ₃	(1.435) ^o		869 ^a
NF ₄ ⁺ (in NF ₄ ⁺ AsF ₆ ⁻)	(1.48) ^o		813 ^m
FNO	1.52 ^p	110	766 ^q
H ₃ CNF ₂	1.413 ± 0.005 ^r	104 38' ± 20' ($\angle CNF$) 110 59' ± 20' ($\angle FNF$)	858 ^s

^a D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **40**, 2461 (1964). ^b D. F. Smith and D. W. Magnuson, *Phys. Rev.*, **87**, 2264 (1952). ^c This work. ^d Reference 4. ^e J. Sheridan and W. Gordy, *Phys. Rev.*, **79**, 513 (1950). ^f E. L. Pace and L. Pierce, *J. Chem. Phys.*, **23**, 1248 (1955). ^g L. V. Vilkov and I. I. Zitovtcheva, private communication. ^h Reference 6. ⁱ R. K. Bohn and S. H. Bauer, *Inorg. Chem.*, **6**, 309 (1967). ^j R. H. Sanborn, *J. Chem. Phys.*, **33**, 1855 (1960); R. E. Ettinger and F. A. Johnson, *ibid.*, **34**, 2187 (1961); R. H. Sanborn, *ibid.*, **34**, 2188 (1961). ^k D. R. Lide, Jr., *ibid.*, **38**, 456 (1963). ^l J. J. Comeford, D. E. Mann, L. J. Schoen, and D. R. Lide, Jr., *ibid.*, **38**, 461 (1963). ^m R. L. Kuczkowski and E. B. Wilson, Jr., *ibid.*, **39**, 1030 (1963). ⁿ R. Ettinger, *ibid.*, **38**, 2427 (1963). ^o Estimated from distance-frequency correlation. ^p D. W. Magnuson, *ibid.*, **19**, 1071 (1961). ^q P. J. H. Woltz, E. A. Jones, and A. H. Nielson, *ibid.*, **20**, 378 (1952). ^r L. Pierce, R. G. Hayes, and J. F. Beecher, private communication of AEC Document No. COO-38-497. ^s R. H. Atalla, A. D. Craig, and J. A. Gailey, *J. Chem. Phys.*, **45**, 423 (1966).

as in hydrazine, but at 70 and 290°. Also, since atoms F₂ and F₄ (see Figure 6) are each repelled by two fluorine atoms on the adjacent nitrogen atom, while atoms F₁ and F₃ experience only a single strong repulsion, $\angle F_2NN$ is greater than $\angle F_1NN$. The height of the central maximum above the adjacent minima is 3.1 ± 0.1 kcal/mole in hydrazine;²³ in tetrafluorohydrazine the best estimates give this barrier height as greater than 3 kcal/mole.⁵ The large amplitude of vibration for the F₂···F₄ and F₁···F₃ distances, 0.15 and 0.11 Å, respectively, indicate considerable torsional motion. The dihedral angle in N₂(CF₃)₄ could not be established with precision; it appears to be $88 \pm 4^\circ$. The effect of fluorine substitution on the magnitude of the dihedral angle is in the same direction but of a larger magnitude for the peroxide system than for the hydrazine system. In F₂O₂ the dihedral angle is 87.5° whereas in hydrogen peroxide it is 119.8°.²⁴

A summary of NF bond properties is given in Table IV. Although the NF bond length and stretching frequencies vary over a wide range, there is a good correlation between the two sets of data; the longer the bond the lower the frequency associated with the corresponding stretching mode (Figure 7). This correlation permits one to estimate the NF bond lengths in NF, FN₃, and NF₄⁺ as 1.35, 1.44, and 1.48 Å, respectively.

The relation between various N-H bond lengths and the corresponding bond angles on the nitrogen has been discussed by Dressler and Ramsay.²⁵ Thus, NH₂ in the

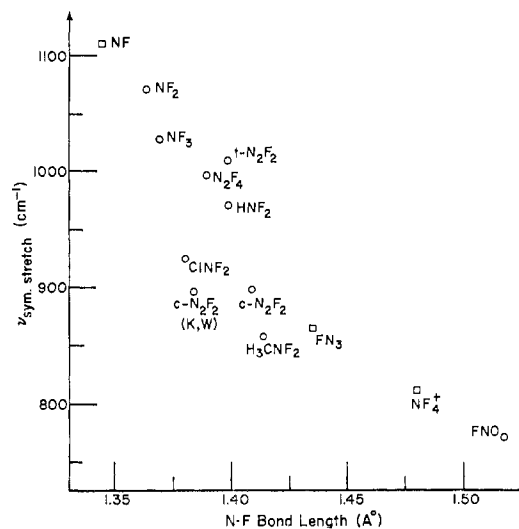


Figure 7.—Comparison between N-F bond distances and the assigned symmetric stretching frequencies. The N-F separations in NF, NF₄⁺, and FN₃ were estimated, as indicated.

²A₁Π_u state has a bond angle of 180° and an NH distance of 0.975 Å, and the bonding can be represented by an sp hybrid. In the ground state NH₂(²B₁) has a bond angle of 103° and an NH separation of 1.024 Å, which corresponds mostly to p-type bonding with a small amount of sp hybridization. The data in Table IV indicate that a similar correlation does not exist among the F-substituted molecules. Those molecules which have only single bonds show F-N-X bond angles of about 103° but bond lengths which vary between 1.365 and 1.400 Å. In the NF systems pπ-pπ bonding interactions may occur with fluorine which are not

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possible with hydrogen. The shorter NF separations in NF₂ compared with those in N₂F₄ or HNF₂ may be explained by postulating a significant contribution of π bonding in NF₂. Kaufman's modified "extended Hückel" procedure for calculating bond overlap populations²⁶ leads to values which correlate well with the observed N-F distances and with the corresponding bond-stretching force constants. In carbon-fluorine compounds it has been observed that the C-F bond lengths shorten with increasing fluorine substitution.²⁷ By analogy, it would be expected that NF₃ should have shorter NF bond lengths than does HNF₂ or N₂F₄, as observed. The CF systems also show wide variations in C-F separations but have nearly constant F-C-F bond angles. For example, the C-F distance in F₂CO is 1.312 ± 0.010 Å;²⁸ in F₂C=CH₂ it is 1.323 Å;²⁷ and in F₂CH₂ it is 1.358 Å.²⁹ The corresponding F-C-F bond angles are 108.0 ± 0.5 , 109.1 , and 108.3° , respectively.

With regard to the effect of dimerization on the structure of the monomer, electron diffraction studies of the

(26) J. J. Kaufman, *J. Chem. Phys.*, **37**, 759 (1962); J. J. Kaufmann, L. A. Burnelle, and J. R. Haman, *Advances in Chemistry Series*, American Chemical Society, Washington, D. C., in press; presented at the 148th National Meeting of the American Chemical Society, Division of Fluorine Chemistry, Chicago, Ill., Aug 1964.

(27) V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, **38**, 2693 (1963).

(28) V. W. Laurie, D. T. Pence, and R. H. Jackson, *ibid.*, **37**, 2995 (1962).

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planar molecule N₂O₄¹⁷ indicate that the NO₂ group has nearly the same dimensions in the dimer as in the free molecule:³⁰ N-O = 1.180 Å and \angle ONO = 133.7° in N₂O₄, compared with N-O = 1.188 Å and \angle ONO = 134.1° in NO₂. Similarly, the N-H bond length is nearly the same in N₂H₄ and NH₂, 1.022 Å¹⁴ and 1.024 Å,²⁵ respectively. The significance of the difference in the N-F bond distances in N₂F₄ and NF₂ may be that the odd electron in NF₂ is in a π orbital and can be utilized in NF π bonding; also refer to ref 26.³¹

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(31) NOTE ADDED IN PROOF.—After this paper was submitted for publication we were informed of the nmr study of tetrafluorohydrazine by Colburn, *et al.* [C. B. Colburn, F. A. Johnson, and C. Haney, *J. Chem. Phys.*, **43**, 4526 (1965)]. They concluded that the *trans* configuration was 100–200 cal more stable than the staggered conformations. Since the radial distribution curve (Figure 4) shows a peak at 3.4 Å with an area of 42 units only, the electron diffraction data exclude the *trans* form as the dominant structure. Some other explanation must be found for the observed single strong line ascribed to this species.

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An Electron Diffraction Study of the Structures of *cis*- and *trans*-N₂F₂

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The structures of *cis*- and *trans*-difluorodiazine were determined from electron diffraction measurements, using sectored-microdensitometer data. The geometric configurations and interatomic distances were found to be essentially those previously estimated on the basis of the visual technique. The major structural difference between the two isomers is the smaller NNF bond angle in the *trans* isomer. In the *cis* compound, the N=N bond length appears to be shorter and the N-F bonds longer than in the *trans* isomer. It is suggested that these differences are related to the greater thermodynamic stability of the *cis* compound relative to the *trans*.

Introduction

It has been known for a long time that more than one isomer of N₂F₂ exists. Meager electron diffraction data¹ on samples prepared by Haller² were interpreted in terms of a mixture of the *cis* and *trans* isomers of FN=NF, to obtain N-F = 1.44 ± 0.04 Å, N=N = 1.25 ± 0.04 Å, and \angle NNF = $115 \pm 5^\circ$. The possibility of a 1,1-difluorodiazine configuration, however, could not be ruled out.

In recent years interest in these compounds has been renewed and several reviews have been published.³

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(2) J. F. Haller, Thesis, Cornell University, 1942.

(3) C. J. Hoffman and R. G. Neville, *Chem. Rev.*, **62**, 1 (1962); C. B. Colburn, *Advan. Fluorine Chem.*, **3**, 92 (1963); A. V. Pankratov, *Russ. Chem. Rev.*, **32**, 157 (1963).

It has been established that there are indeed two isomers of N₂F₂. In view of the infrared and nmr spectra and the absence of a measurable dipole moment the lower boiling isomer (bp -111.4°) must be *trans*-N₂F₂. However, there has been considerable controversy regarding the configuration of the higher boiling isomer (bp -105.7°). This material is much more reactive and has a significantly different mass spectrum, a dipole moment sufficient to produce a microwave absorption spectrum, and a relatively complex infrared spectrum. To account for the latter, Sanborn proposed for it the 1,1 structure.⁴ However, Armstrong and Marantz⁵ argued that the heat of formation and

(4) R. H. Sanborn, *J. Chem. Phys.*, **33**, 1855 (1960); R. Ettinger and F. A. Johnson, *ibid.*, **34**, 2187 (1961); R. H. Sanborn, *ibid.*, **34**, 2188 (1961).

(5) C. T. Armstrong and S. Marantz, *ibid.*, **38**, 169 (1963).