possible with hydrogen. The shorter NF separations in NF_2 compared with those in N_2F_4 or HNF_2 may be explained by postulating a significant contribution of π bonding in NF_2. Kaufman's modified "extended Hückel" procedure for calculating bond overlap populations[26] 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 NF_3 should have shorter NF bond lengths than does HNF_2 or N_2F_4, 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 F_2CO is 1.312 ± 0.010 A;[28] in $F_2C{=}CH_2$ it is 1.323 A;[27] and in F_2CH_2 it is 1.358 A.[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 planar molecule N_2O_4[17] indicate that the NO_2 group has nearly the same dimensions in the dimer as in the free molecule:[30] N–O = 1.180 A and $\angle$ONO = 133.7° in N_2O_4, compared with N–O = 1.188 A and $\angle$ONO = 134.1° in NO_2. Similarly, the N–H bond length is nearly the same in N_2H_4 and NH_2, 1.022 A[14] and 1.024 A,[25] respectively. The significance of the difference in the N–F bond distances in N_2F_4 and NF_2 may be that the odd electron in NF_2 is in a π orbital and can be utilized in NF π bonding; also refer to ref 26.[31]

Acknowledgments.—The authors wish to thank Dr. Charles B. Colburn of the Rohm and Haas Co., Redstone Arsenal Research Division, Huntsville, Ala., for providing the sample of N_2F_4. Grateful acknowledgment is made for the support of this work by the Office of Naval Research (ARPA) under Contract No. Nonr-401 (41). R. K. B. received generous support from the National Science Foundation through cooperative graduate fellowships (1960–1962).

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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 A 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*-N_2F_2

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Received September 7, 1965

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 N_2F_2 exists. Meager electron diffraction data[1] on samples prepared by Haller[2] were interpreted in terms of a mixture of the *cis* and *trans* isomers of FN=NF, to obtain N—F = 1.44 ± 0.04 A, N=N = 1.25 ± 0.04 A, and $\angle$NNF = 115 ± 5°. 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] It has been established that there are indeed two isomers of N_2F_2. 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*-N_2F_2. 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 Marantz[5] argued that the heat of formation and

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[1] S. H. Bauer, *J. Am. Chem. Soc.*, **69**, 3104 (1947).

[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).

[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).

bond energy considerations favored a *cis* configuration. Herron and Dibeler[6] supported the *cis* structure on the basis of its mass spectrum. The relative intensities of the lines in the microwave spectrum of $^{14}N_2F_2$ and the deduced moments of inertia (Kuczkowski[7]) are compatible with a *cis* configuration. Double-resonance nmr spectra (Noggle, *et al.*[8]) favor a *cis* structure; these investigators suggested that the only significant dimensional difference between the *cis* and *trans* isomers would be the larger ∠NNF in the *cis* isomer. Finally, the preliminary report of this electron diffraction study[9] and a concurrent microwave investigation of $^{15}N^{14}NF_2$ by Kuczkowski and Wilson[10] conclusively established the *cis* structure of the higher boiling isomer.

Experimental Section

Samples of the two isomers of N_2F_2 were obtained from Dr. Frederick A. Johnson, who reported the composition in these two samples to be: sample I: 1.2% NO; 0.2% N_2O; 0.6% SiF_4; 98.0% N_2F_2 (approximately 2% *cis*, 98% *trans*); sample II: 1.7% CO_2; 1.0% SiF_4; 97.0% N_2F_2 (approximately 91% *cis*, 9% *trans*). Mass spectral analyses of these samples, made by Professor R. F. Porter in this laboratory, showed no significant differences in composition.

The apparatus, experimental conditions, and method of data reduction were the same as described in the preceding paper[11] on N_2F_4, except that in addition to N_2F_4, small amounts of N_2F_2 were used to preseason the gas-handling system.

Results

trans-$\mathbf{N_2F_2}$.—The reduced experimental intensity, $M_{0,\text{exptl}}(q)$, is plotted in Figure 1 for comparison with the theoretical $M_0(q)$ for the best model. Figure 2 shows the final radial distribution curve computed using a damping factor $\gamma = 0.00022$. The first peak at 1.40 A is resolved into two Gaussian peaks: one corresponds to an N═N distance at 1.230 A with a mean amplitude of 0.04 A, and the second corresponds to the two bonded N—F pairs at a distance of 1.396 A with a mean amplitude of 0.056 A. The peak at 2.1 A was assigned to the two nonbonded N···F pairs at 2.093 A with a mean amplitude of 0.070 A. The peak at 3.3 A is due to the nonbonded F···F pair at a distance of 3.339 A with a mean amplitude of 0.071 A. The lower curve in Figure 2 shows the difference between the experimental radial distribution and the theoretical distribution function calculated from the distances and amplitudes given above. The ratios of the observed areas to those calculated are 258:260 for the first peak, 119:120 for the second peak, and 47:48 for the third peak.

Eight independent parameters were refined simultaneously in the least-squares analysis of the molecular intensity curve. They are the N═N, N—F, and N···F distances, the four vibrational amplitudes, and a resolution factor. The F···F distance was calculated from the other three distances. The refined structural parameters for *trans*-N_2F_2, standard deviations, and estimated errors are summarized in Table I. Error limits were estimated as described in the preceding paper on the structure of NF_2.[11]

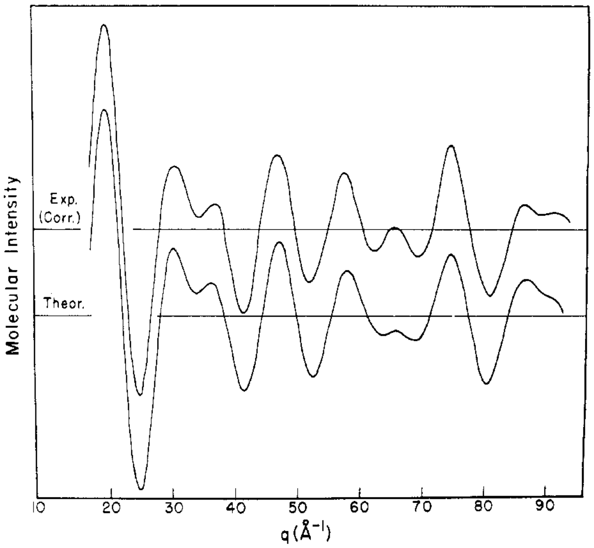

Figure 1.—The experimental $M_0(q)$ curve for *trans*-N_2F_2 compared with the calculated $M_0(q)$ curve for the best model.

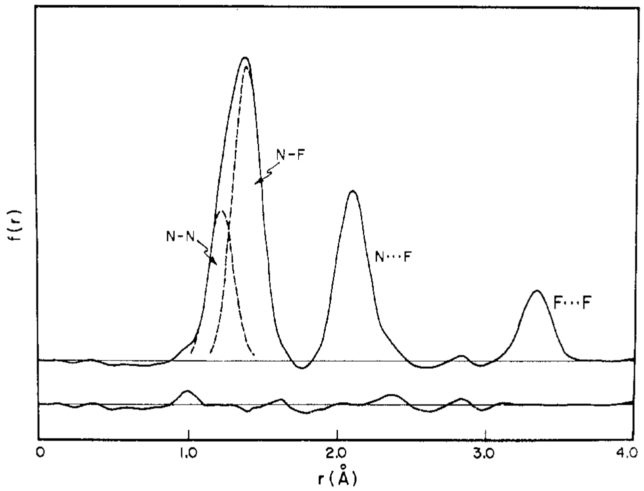

Figure 2.—The experimental radial distribution curve for *trans*-N_2F_2. The dotted lines show the resolved peaks for individual atom pairs. The lower curve gives the difference between the experimental curve and the curve calculated from the best model.

cis-$\mathbf{N_2F_2}$.—The reduced experimental intensity, $M_{0,\text{exptl}}(q)$, corrected for 9% *trans*-N_2F_2 impurity, 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 using a damping factor $\gamma = 0.00022$. The peak at 1.40 A was resolved into two Gaussians. The first corresponds to the bonded N═N distance of 1.214 A with a mean amplitude of 0.06 A; the second corresponds to the two bonded N—F pairs at a distance of 1.410 A with a mean amplitude of 0.063 A. The peak at 2.2 A was also resolved into two Gaussians. The first was assigned to the two nonbonded N···F pairs at a distance of 2.209 A with a mean amplitude of about 0.06 A, while the second was

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TABLE I

STRUCTURAL PARAMETERS FOR *trans*-N_2F_2

		Estd error	Std dev	l_{ij}	Estd error	Std dev
N=N, A	1.2305	±0.010	0.0026	0.0369	±0.009	0.0030
N—F, A	1.3962	±0.008	0.0015	0.0565	±0.005	0.0018
N···F, A	2.0933	±0.012	0.0021	0.0703	±0.007	0.0022
F···F, A	3.3389			0.0709	±0.014	0.0048
∠NNF, deg	105.50	±0.7	0.23			

TABLE II

STRUCTURAL PARAMETERS FOR *cis*-N_2F_2

	This work						
		Estd error	Std dev	l_{ij}	Estd error	Std dev	Microwave results[a]
N=N, A	1.2139	±0.012	0.0034	0.0604	±0.011	0.0035	1.214 ± 0.005
N—F, A	1.4101	±0.009	0.0016	0.0633	±0.007	0.0023	1.384 ± 0.010
N···F, A	2.2087	±0.013	0.0024	0.0557	±0.009	0.0030	
F···F, A	2.3810			0.0961	±0.023	0.0076	
∠NNF, deg	114.44	±1.0	0.32				114.5 ± 0.5

[a] Reference 10.

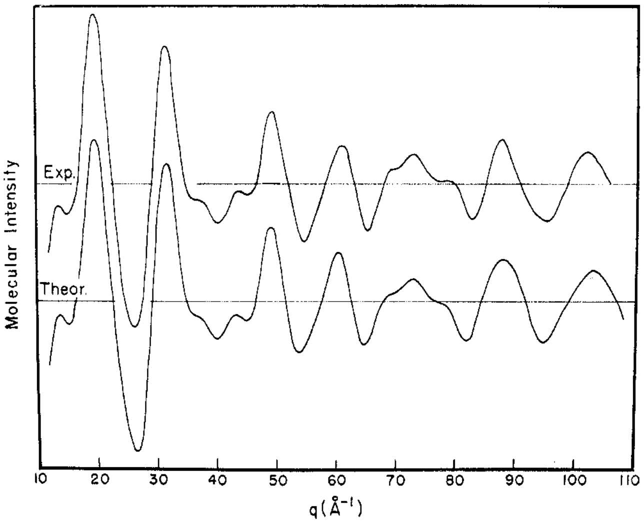

Figure 3.—The experimental $M_0(q)$ curve for *cis*-N_2F_2 compared with the calculated $M_0(q)$ curve for the best model.

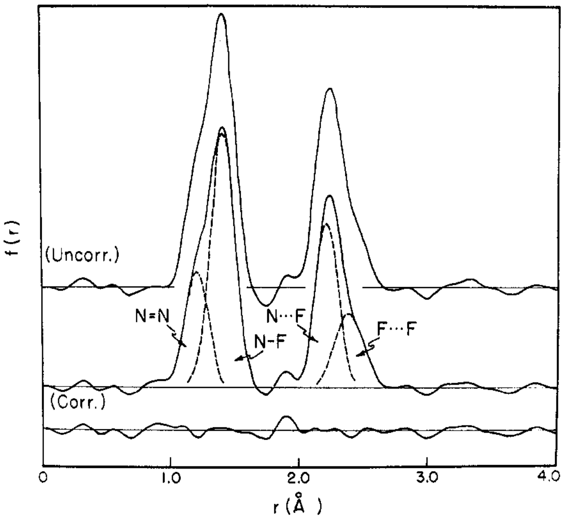

Figure 4.—The experimental radial distribution curve for *cis*-N_2F_2. The dotted lines show the resolved peaks for individual atom pairs. The lower curve shows the difference between the experimental curve and the curve calculated from the best model.

ascribed to the F···F pair at a distance of 2.381 A with a mean amplitude of 0.10 A. The lower curve in Figure 4 shows the difference between the experimental radial distribution function and the theoretical function calculated for the distances and amplitudes given above. The ratios of the observed area to that calculated are 265:260 for the first peak and 178:183 for the second. The least-squares analysis of the molecular intensity curve of *cis*-N_2F_2 was performed as described above for *trans*-N_2F_2. The refined structural parameters are summarized in Table II.

Discussion

trans- and *cis*-N_2F_2 are planar with C_{2h} and C_{2v} symmetry, respectively. The N=N and N—F distances in the two isomers are similar and within the range of such distances reported for other molecules with N=N (Table III) and N—F (Table IV, ref 11) bonds. However, several surprising features are present. In the *trans* isomer, ∠NNF = 105.5 ± 1.0° is the smallest value reported for X—N=Y angles. Kuczkowski and Wilson's[10] summary shows a range from 108.6° in HNO[12] to 142° in H_3CNCS.[13] For the *cis* compound the microwave and electron diffraction values agree for the N=N distance and the NNF bond angle but disagree for the N—F distance. The r_g average from diffraction data should be larger than the r_0 average derived from rotational constants, but the magnitude of the difference (0.026 A) is too large to be thus accounted for. We doubt that the difference arises from shrinkage effects.

One can readily imagine an asymmetrical pyramidal 1,1-difluorodiazine structure (symmetry C) which has the distances given in Table II. Such a structure has recently been reported for one of the isomers of S_2F_2.[14] However, the symmetry and the moments of inertia for such a configuration are completely incompatible with the microwave data. It is interesting to note that Kuczkowski and Wilson[10] observed rotational transi-

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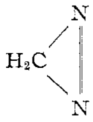
Table III

Summary of Observed N—N Bond Lengths

Molecule	N=N bond length, A	Ref
FN=NF (*cis*)	1.214 ± 0.012	This work
	1.214 ± 0.005	*a*
FN=NF (*trans*)	1.230 ± 0.010	This work
	1.228 ± 0.003	*b*
$CH_3N{=}NCH_3$ (*trans*)	1.24 ± 0.05	*c*
$CH_3N{=}NN$	1.24 ± 0.02	*d*
HN=NN	1.240 ± 0.003	*e*
$C_6H_5N{=}NC_6H_5$ (*cis* and *trans*)	1.25 ± 0.04	*f*

[a] Reference 10. [b] V. Dobyns and L. Pierce, *J. Am. Chem. Soc.*, **84,** 2651 (1962). [c] H. Boersch, *Sitzber. Akad. Wiss. Wien*, **144,** 1 (1935). [d] L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **59,** 13 (1937). [e] E. Amble and B. P. Dailey, *J. Chem. Phys.*, **18,** 1422 (1950). [f] G. C. Hampson and J. Robertson, *J. Chem. Soc.*, 409 (1941).

tions for *cis*-N_2F_2 in a vibrationally excited state. By examining the temperature dependence of the intensities of these transitions, they deduced a vibrational frequency of 300 ± 35 cm^{-1} and proposed that it be assigned to the symmetrical N—F bending mode. The rather large 0.10 A rms amplitude of vibration which we observe for the F···F pair supports this assignment.

A major structural difference between the *cis* and *trans* isomers is the larger ∠NNF in the *cis* compound, 114.4 *vs.* 105.5°. This is expected because of the crowding of the F—F atoms, which is not present in the *trans* isomer, and was predicted by Noggle, Baldeschwieler, and Colburn[8] on the basis of their double-resonance nmr experiments. The value they determined for the indirect N···F coupling constant in *trans*-N_2F_2 was about twice that in the *cis* isomer. A second difference between the structures of the two compounds is the shorter N=N bond in the *cis* isomer, 1.214 ± 0.012 A *vs.* 1.230 ± 0.010 A in *trans*-N_2F_2. Further the N—F distance is longer in the *cis* isomer (1.410 ± 0.009 A) than in the *trans* (1.369 ± 0.008 A). Since the error includes three times the standard deviation obtained from the least-squares analysis, plus an estimated systematic error of 0.005 times the distance, the cited differences appear to be real. The peak in the radial distribution curve for *trans*-N_2F_2 (Figure 2) consisting of the NN and NF distances is slightly asymmetric, whereas the corresponding peak in the radial distribution curve for *cis*-N_2F_2 (Figure 4) shows a definite shoulder indicating a greater separation between the NN and NF bond distances in the *cis* isomer than in the *trans*.

The N_2F_2 system is the first pair of *cis–trans* isomers for which it has been demonstrated that there is a difference in bond lengths. Note that the enthalpy of *trans*-N_2F_2 is 3.0 kcal/mole higher than that of *cis*-N_2F_2.[5] This should not be surprising for in spite of the presumed repulsions between the terminal substituents there are numerous *cis–trans* pairs in which the *cis* isomer has the lower energy. In the species HFC=CHX, with X = I, Br, Cl, or F, the *cis* configuration is more stable.[15] In the 1,2-dihalogenoethylenes, the *cis* form is more stable for the difluoro[15,16] and dichloro[17] compounds; the dibromo pair[18] has approximately the same energy, but in the diiodo the *trans* form is more stable.[19] Butene-2 and 1-bromopropene are additional examples in which the *cis* configuration is more stable than the *trans*.[20] It appears indeed that the *cis* structure is generally favored unless the groups involved are excessively bulky. For the N_2F_2 pair the shorter N=N distance and longer N—F distances in the *cis* isomer correlate well with the relative "extended Hückel" overlap populations as calculated by Kaufman, *et al.*[21]

Acknowledgments.—The authors wish to thank Dr. Frederic A. Johnson of the Rohm and Haas Co., Redstone Arsenal Research Division, Huntsville, Ala., for providing the samples studied. Grateful acknowledgment is made for support of this work by the Office of Naval Research (ARPA) under Contract No. Nonr-401(41). R. K. B. wishes to thank the National Science Foundation for generous support through cooperative graduate fellowships (1960–1962).

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