Structures of Azomethane, 1,1,1-Trifluoroazomethane, and Hexafluoroazomethane, Determined by Electron Diffraction

C. H. Chang, R. F. Porter, and S. H. Bauer

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received February 13, 1970

Abstract: Analysis of electron diffraction patterns has shown that the samples of azomethane and 1,1,1-trifluoroazomethane which were investigated were in the *trans* configurations about the N═N bond, but that the sample of hexafluoroazomethane was in the *cis* configuration. The geometric parameters are for $CH_3N{=}NCH_3$, N═N = 1.254 ± 0.003, C—N = 1.474 ± 0.003, C—H = 1.107 ± 0.006 Å, ∠NNC = 111.9 ± 0.5°, ∠NCH = 109.4 ± 1.5°; for $CH_3N{=}NCF_3$, N═N = 1.219 ± 0.008, C—N(H) = 1.440 ± 0.012, C—N(F) = 1.476 ± 0.012, C—H = 1.107 (assumed), C—F = 1.322 ± 0.003 Å, ∠NNC(H) = 110.5 ± 4°, ∠NNC(F) = 126.2 ± 2°, ∠NCH = 109.4° (assumed), ∠NCF = 109.3 ± 0.6°; and for $CF_3N{—}NCF_3$, N═N = 1.236 ± 0.015, C—N = 1.490 ± 0.006, C—F = 1.326 ± 0.002 Å, ∠NNC = 133.0 ± 1°, and ∠NCF = 109.3 ± 0.3°. The estimated errors are three times the standard deviations obtained from least-squares fitting of the intensity data. A summary of N═N bond lengths is presented; the reported values cover the ranges 1.21–1.29 Å.

Whether hexafluoroazomethane, $CF_3N{=}NCF_3$, as initially prepared,[1] was in the *cis* or *trans* configuration has not been satisfactorily resolved. An early electron diffraction study of azomethane,[2] $CH_3N{=}NCH_3$, indicated a *trans* configuration about the N═N bond. The proposed *trans* configuration for the perfluoro compound was based on apparent similarities between $(CF_3)_2N_2$ and $(CH_3)_2N_2$ of their chemical properties, of their uv absorption spectra,[3] and of product analysis following thermal decomposition.[4] Although Ramaswamy[5] did find a dipole moment of 0.46 D for $(CF_3)_2N_2$, this was given no weight in view of the possibility that his sample contained impurities.[3] Low-temperature infrared spectra of the perfluoro compound reported by Freitag[6] showed no absorption in the 1450–1650-cm^{-1} region, assigned in most azo compounds to the N═N stretching frequency. However, Pritchard, *et al.*,[7] and Dubov, *et al.*,[8] did observe bands at 1581, 1562, and 1532 cm^{-1}.

Preparation of the partially fluorinated compound, 1,1,1-trifluoroazomethane, $CH_3N{=}NCF_3$, has been reported recently.[9] Azomethane and its partially and totally fluorinated derivates provide an interesting series of compounds for observation of structural changes as affected by substitution of CF_3 for CH_3 groups. This report covers the results of an electron diffraction study of these three compounds.

Experimental Section

Azomethane. Azomethane was prepared from 1,2-dimethylhydrazine hydrochloride and cupric chloride by the procedure of Jahn.[10] The 60-MHz nmr spectrum of the purified sample in TMS solution indicated a single proton resonance with a chemical shift (δ) of 3.73 ppm downfield from the reference. The sample was stored in a 500-ml bulb at a pressure of 20 cm. To prevent photochemical deterioration of the sample, the bulb was covered with black tape and left in the dark until used. This amount is adequate for obtaining a complete set of electron diffraction photographs.

Hexafluoroazomethane. Hexafluoroazomethane was obtained from Merck Sharp and Dohme of Canada. The ^{19}F nmr spectrum of the compound in CCl_4 solution indicated a single narrow resonance. The chemical shift at a frequency of 94.6 MHz was 74.0 ppm upfield from the $CFCl_3$ reference. This shift is somewhat less than the value of 79.7 ppm given by Mitsch and Ogden,[11,12] but is close to the values for CF_3 groups in $CF_3{—}N{=}N{—}CF_2Cl$ (74.7 ppm) and $CF_3{—}N{=}N{—}CF_2Br$ (74.5 ppm). The infrared spectrum taken with this sample showed the same triplet as was previously reported.[7,9]

1,1,1-Trifluoroazomethane. Trifluoroazomethane was prepared from trifluoronitrosomethane (CF_3NO) and methylamine by a procedure similar to that used by Dinwoodie and Haszeldine.[9] The CF_3NO gas was first transferred *in vacuo* into a 500-ml bulb at a pressure of 10 cm. The reagent was then frozen with liquid nitrogen and an equivalent amount of CH_3NH_2 was condensed in the bulb. The mixture was then allowed to warm slowly. After repeated condensation and rewarming the reaction mixture was transferred into a −80° trap which was pumped for a few minutes to remove unreacted CF_3NO and volatile impurities. The material recovered from the −80° trap was $CF_3{—}N{=}N{—}CH_3$. The hydrogen nmr spectrum of the compound in CCl_4 solution indicated a narrowly spaced 1:3:3:1 quartet, centered slightly downfield from azomethane, and a chemical shift (δ) relative to TMS of 4.07 ppm. The quartet structure, which is presumed to be due to the long-range coupling of the H and F atoms, gave a coupling constant of 1.8 cps. The ^{19}F nmr spectrum of the compound indicates a line without resolved structure slightly upfield from $CF_3N{=}NCF_3$. The chemical shift relative to $CFCl_3$ is 74.7 ppm.

Electron Diffraction Photographs. Sectored electron diffraction photographs of these three compounds were taken with the samples at room temperature, using the apparatus previously described.[13] Optical densities as dependent on radial position were obtained with a digital microphotometer. The data reduction procedure followed in this laboratory has been published.[14,15]

Structural Analyses

$CH_3N{=}NCH_3$. The experimental intensity and background curves are shown in Figure 1 for two sets of data covering q = 8–127 $Å^{-1}$. Numerical values for the intensities have been deposited with ASIS–NAPS.[16]

---

(1) O. Ruff and M. Ciese, *Chem. Ber.*, **69**, 598 (1936).

(2) H. Boersch, *Montash.*, **65**, 311 (1935).

(3) O. Ruff and W. Willenberg, *Chem. Ber.*, **73**, 724 (1940).

(4) D. Clark and H. O. Pritchard, *J. Chem. Soc.*, 2136 (1956).

(5) K. L. Ramaswamy, *Proc. Indian Acad. Sci., Sect. A*, **2**, 364 (1935).

(6) W. O. Freitag, Ph.D. Thesis, University of Pennsylvania, 1955.

(7) G. O. Pritchard, H. O. Pritchard, H. I. Schiff, and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **52**, 849 (1956).

(8) S. S. Dubov, *et al.*, *Zh. Vses. Khim. Obsh.*, **6**, 596 (1961).

(9) A. H. Dinwoodie and R. N. Haszeldine, *J. Chem. Soc.*, 2266 (1965).

(10) F. P. Jahn, *J. Amer. Chem. Soc.*, **59**, 1761 (1937).

(11) W. J. Chambers, C. W. Tullock, and D. D. Coffman, *ibid.*, **84**, 2337 (1962).

(12) R. A. Mitsch and P. H. Ogden, *J. Org. Chem.*, **31**, 3833 (1966).

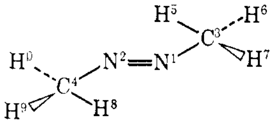
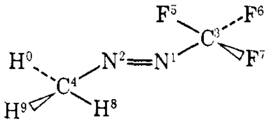
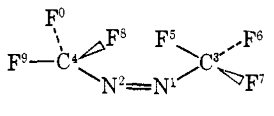
(13) S. H. Bauer and K. Kimura, *J. Phys. Soc. Jap.*, **17**, 300 (1962).

(14) J. L. Hencher and S. H. Bauer, *J. Amer. Chem. Soc.*, **89**, 5527 (1967).

(15) W. Harshbarger, G. Lee, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, **8**, 1683 (1969).

(16) Material supplementary to this article has been deposited as

Table I. Structural Parameters[a] for CH$_3$N=NCH$_3$, CH$_3$N=NCF$_3$, and CF$_3$N=NCF$_3$

	 CH$_3$N=NCH$_3$	 CH$_3$N=NCF$_3$	 CF$_3$N=NCF$_3$
N=N	1.253$_7$ ± 0.0008[b]	1.218$_8$ ± 0.0028	1.236$_0$ ± 0.0050
N—CH	1.474$_2$ ± 0.0008	1.440$_2$ ± 0.0062	
N—CF		1.475$_8$ ± 0.0053	1.489$_6$ ± 0.0020
C—H	1.106$_8$ ± 0.0019	1.1068	
C—F		1.332$_0$ ± 0.0010	1.325$_7$ ± 0.0007
∠NNCH	111.88$_9$ ± 0.159	110.46$_0$ ± 1.291	
∠NNCF		126.23$_6$ ± 0.610	133.00$_0$ ± 0.279
∠NCH	109.40$_7$ ± 0.471	109.40$_7$	
∠NCF		109.25$_2$ ± 0.216	109.33$_1$ ± 0.102
τNCX$_5$	8.26$_2$ ± 0.245	0.0	1.07$_8$ ± 0.049
τNCX$_8$	8.26$_2$ ± 0.245	0.0	49.55$_8$ ± 1.027
τCNNC	180.0	180.0	0.0
$l_{N=N}$	0.045$_9$ ± 0.0008	0.0492	0.049$_2$ ± 0.0055
l_{C-N}	0.062$_1$ ± 0.0007	0.0559	0.048$_5$ ± 0.0020
l_{C-H}	0.081$_2$ ± 0.0017	0.0870	
l_{C-F}		0.051$_2$ ± 0.0009	0.055$_6$ ± 0.0012
$l_{C\cdots N}$	0.068$_8$ ± 0.0013	0.0720	0.118$_3$ ± 0.0184
$l_{C\cdots C}$	0.095$_5$ ± 0.0068	0.0950	0.097$_5$ ± 0.0122
$l_{N_1\cdots X_5}$	0.113$_2$ ± 0.0057	0.078$_2$ ± 0.0036	0.088$_3$ ± 0.0031
$l_{N_2\cdots H_5}$	0.097$_0$ ± 0.0142		
$l_{N_2\cdots H_6}$	0.161$_4$ ± 0.0348		
$l_{N_2\cdots H_7}$	0.27$_8$ ± 0.0701		

[a] Bond distances in ångström units, angles in degrees. [b] Calculated standard deviations; the estimated error limits are given in the Abstract at three times the standard deviation.

The top curve of Figure 2 is the final experimental radial distribution curve computed with a damping factor of γ = 0.001446. There are three bonded distances: C—H = 1.107 and N=N = 1.254 Å contribute to the first peak, and C—N = 1.474 Å is the second peak. The third peak is readily resolved into four nonbonded distances: H···H = 1.811, N···H = 2.119, C···N = 2.264, and N···H = 2.318 Å. Other nonbonded distances are indicated in the figure. It is assumed that the CH$_3$ group has threefold symmetry and that its axis of symmetry coincides with the C–N bond. Seven geometrical parameters and nine root-mean-square amplitudes were refined independently in the least-squares analyses of the reduced molecular intensity function. They are: N=N, C—N, C—H, ∠NNC, ∠NCH, τ(CNNC), τ(HCNN) (torsional angles τ(NNCH$_5$) = τ(NNCH$_8$),

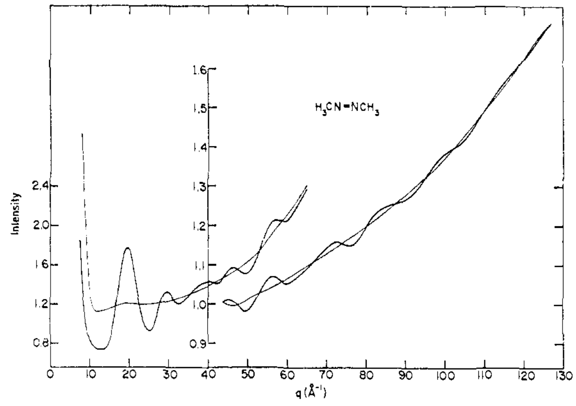


Figure 1. The experimental intensity and background curves for CH$_3$N=NCH$_3$.

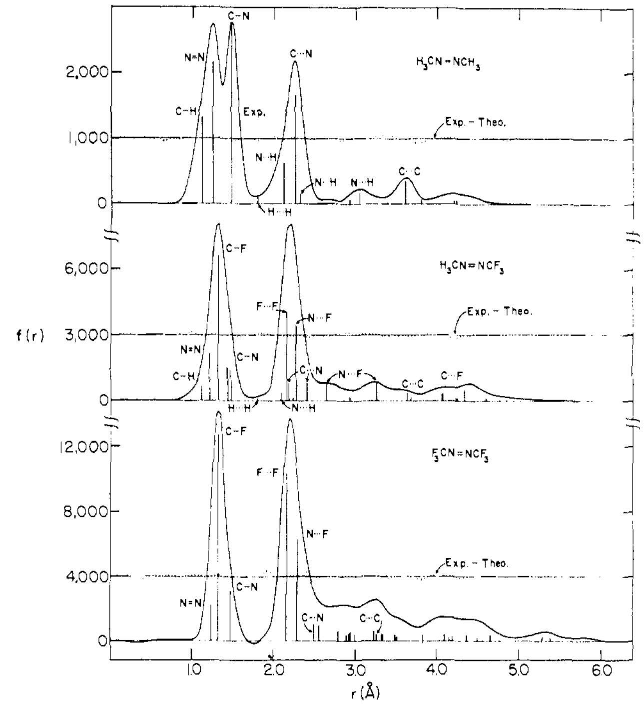


Figure 2. The refined experimental radial distribution curves and difference curves between experimental and theoretical values for CH$_3$N=NCH$_3$, CH$_3$N=NCF$_3$, and CF$_3$N=NCF$_3$.

Document No. NAPS-400-T056 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

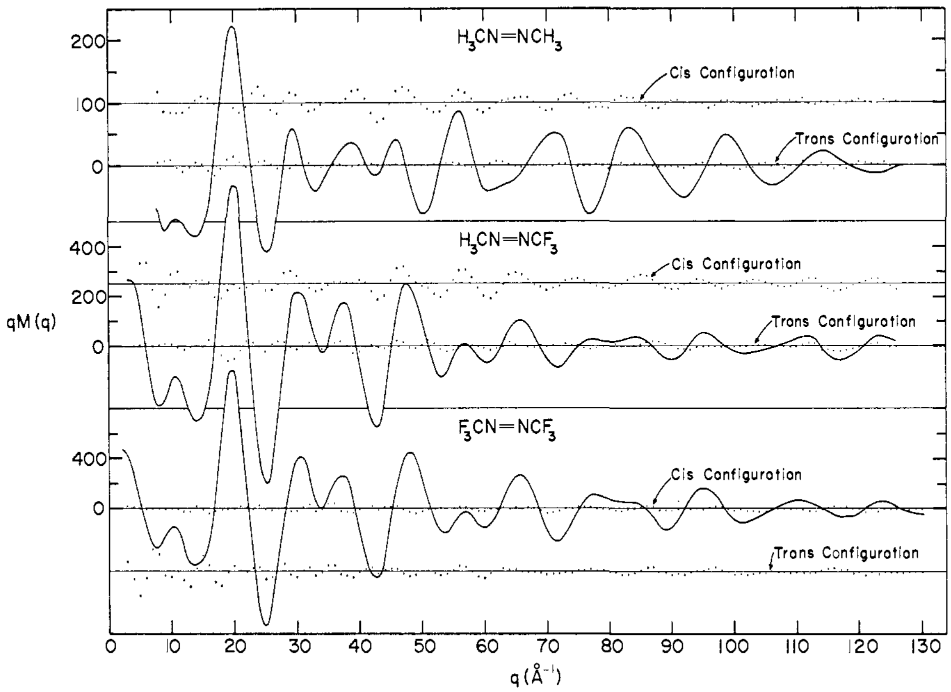


Figure 3. The reduced experimental molecular scattering curves and the difference curves between experimental and theoretical values for different models of $CH_3N{=}NCH_3$, $CH_3N{=}NCF_3$, and $CF_3N{=}NCF_3$.

see Table I), $l_{N=N}$, l_{C-N}, l_{C-H}, $l_{C\cdots N}$; $l_{C\cdots C}$, and four different nonbonded $l_{N\cdots H}$. The root-mean-square amplitudes of long nonbonded H···H distances were constrained to a set of reasonable values. In the refinements, both *cis* and *trans* configurations were tested by constraining τ(CNNC) to 0 and 180°, respectively. Two difference curves which show the agreement between the calculated $qM(q)$ curves for the *best* models of *cis* and *trans* configurations and the experimental curve are shown in Figure 3. The *trans* model is clearly superior. The final structural parameters are tabulated in Table I. Inspection of the correlation matrix shows that for the chosen parameters, correlations are very small. The error matrix is shown in Table II.

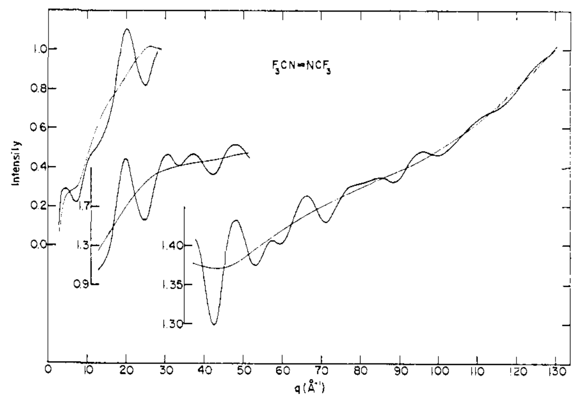


Figure 4. The experimental intensity and background curves for $CF_3N{=}NCF_3$.

$CF_3N{=}NCF_3$. Three sets of data ranging from q = 3 to 130 Å^{-1} were taken as shown in Figure 4. The background oscillations in the region of small q are independent of molecules studied. The same features appear in all these traces. Numerical values for the intensities are deposited with ASIS-NAPS.[16] The bottom curve in Figure 2 is the final experimental radial distribution curve, computed with a damping factor of 0.001380. The first peak is resolved into three bonded distances: N=N = 1.236, C—F = 1.326, and C—N = 1.490 Å. The second peak is due mainly to two nonbonded distances, F···F = 2.167 and N···F = 2.299 Å. This is followed by a spectrum of longer nonbonded separations. In constructing the theoretical model, we assumed that the CF_3 group has a threefold symmetry axis which coincides with C-N bond direction. The set of geometrical parameters which corresponds to that introduced for $(CH_3)_2N_2$ were refined in a least-squares analysis of the reduced molecular intensity curve. Only six l_{ij}'s were varied and a reasonable set of values was assigned to other long nonbonded atomic pairs, since these proved less sensitive to the refinement. The curve for the best *trans* model fits reasonably well with the experimental diffraction pattern (see lower part of Figure 3) except in the low-angle region. The possibility that the sample consisted of a mixture of the *cis* and *trans* configurations was ruled out, since the ^{19}F nmr spectrum showed only a narrow singlet. However, a much better fit was obtained by refining seven geometrical parameters and six root-mean-square amplitudes when the torsional angle τ(CNNC) was constrained to 0° (refer to Figure 3); the results are summarized in Table I. The correlation matrix does indicate larger couplings between parameters than were found for $(CH_3)_2N_2$, the largest being 0.81 between r(N=N) and l(C—F), and 0.70 between r(C—F) and l(N=N), as expected from the radial distribution curve. The differences between the experimental radial distribution function and a theoretical one computed for the best model (*cis* configuration) is the dotted curve shown in Figure 2. The error matrix is shown as Table III.

Table II. Error Matrix for $CH_3{=}NNCH_3$

	N=N	N–CH	C–H	∠NNCH	∠NCH	τNCH$_2$	$l_{N=N}$	l_{C-N}	l_{C-H}	$l_{C\cdots N}$	$l_{C\cdots C}$	$l_{N_1\cdots H_5}$	$l_{N_2\cdots H_5}$	$l_{N_2\cdots H_6}$	$l_{N_2\cdots H_7}$
N=N	0.0008														
N–CH	0.0003	0.0008													
C–H	0.0007	0.0004	0.0019												
∠NNCH	−0.0062	−0.0066	−0.0050	0.1586											
∠NCH	−0.0040	−0.0077	−0.0080	0.1342	0.4713										
τNCH$_5$	0.0008	0.0012	−0.0009	−0.0238	−0.0613	0.2452									
$l_{N=N}$	−0.0001	0.0003	0.0004	−0.0023	−0.0030	−0.0001	0.0008								
l_{C-N}	−0.0003	−0.0002	−0.0003	0.0026	−0.0017	0.0004	−0.0003	0.0007							
$_{C-H}$	−0.0005	0.0004	−0.0004	0.0016	−0.0030	0.0005	0.0008	−0.0004	0.0017						
$l_{C\cdots N}$	0.0001	0.0001	0.0003	−0.0082	0.0066	−0.0004	−0.0001	−0.0000	−0.0001	0.0013					
$l_{C\cdots C}$	0.0001	0.0001	0.0000	0.0052	−0.0118	0.0016	0.0000	−0.0000	−0.0001	−0.0001	0.0068				
$l_{N_1\cdots H_5}$	0.0002	0.0003	0.0003	−0.0224	0.0101	−0.0015	0.0001	−0.0002	−0.0001	0.0018	0.0006	0.0057			
$l_{N_2\cdots H_5}$	0.0003	0.0002	0.0005	−0.0061	−0.0139	0.0039	−0.0000	0.0000	−0.0001	0.0007	−0.0014	−0.0005	0.0142		
$l_{N_2\cdots H_6}$	0.0007	−0.0010	0.0023	0.0404	0.1096	−0.1064	0.0005	−0.0008	−0.0006	−0.0027	−0.0027	0.0031	−0.0065	0.0348	
$l_{N_2\cdots H_7}$	−0.0017	−0.0016	−0.0022	0.0322	0.0714	−0.0233	−0.0002	−0.0000	0.0005	−0.0024	0.0019	0.0012	−0.0158	0.0263	0.0701

Table III. Error Matrix for $CF_3N{=}NCF_3$

	N=N	N–CF	C–F	∠NNCF	∠NCF	τNCF$_5$	τNCF$_8$	$l_{N=N}$	l_{C-N}	l_{C-F}	$l_{C\cdots N}$	$l_{C\cdots C}$	$l_{N_1\cdots F_5}$
N=N	0.0050												
N–CF	0.0020	0.0020											
C–F	−0.0011	−0.0006	0.0007										
∠NNCF	−0.0240	−0.0096	0.0066	0.2785									
∠NCF	−0.0122	−0.0094	0.0068	0.0596	0.1022								
τNCF$_5$	−0.0006	−0.0003	−0.0002	−0.0065	0.0013	0.0485							
τNCF$_8$	−0.0228	−0.0133	0.0091	−0.2709	0.1287	−0.0308	1.0271						
$l_{N=N}$	0.0041	0.0021	−0.0017	−0.0217	−0.0165	−0.0004	−0.0214	0.0055					
l_{C-N}	0.0018	0.0008	−0.0008	−0.0096	−0.0073	−0.0001	−0.0088	0.0021	0.0020				
l_{C-F}	0.0022	0.0011	−0.0007	−0.0111	−0.0074	−0.0002	−0.0112	0.0024	0.0010	0.0012			
$l_{C\cdots N}$	0.0039	0.0029	0.0009	−0.0361	−0.0213	−0.0018	−0.0666	0.0023	0.0002	0.0016	0.0184		
$l_{C\cdots C}$	−0.0024	−0.0010	0.0008	0.0258	0.0085	−0.0019	0.0408	−0.0022	−0.0010	−0.0011	−0.0043	0.0122	
$l_{N_1\cdots F_5}$	0.0005	0.0009	0.0006	−0.0036	−0.0120	−0.0006	−0.0236	−0.0011	−0.0006	−0.0003	0.0062	−0.0011	0.0031

Table IV. Error Matrix for $CH_3N{=}NCF_3$

	N=N	N–CH	N–CF	C–F	∠NNCH	∠NNCF	∠NCF	l_{C-F}	$l_{N_1\cdots F_5}$
N=N	0.0028								
N–CH	0.0011	0.0062							
N–CF	0.0011	−0.0048	0.0053						
C–F	0.0011	0.0015	−0.0007	0.0010					
∠NNCH	−0.0344	−0.0068	−0.0544	−0.0241	1.2913				
∠NNCF	−0.0192	0.0193	−0.0265	−0.0088	0.4736	0.6097			
∠NCF	0.0050	0.0264	−0.0285	0.0062	0.3736	0.1324	0.2167		
l_{C-F}	0.0010	−0.0015	0.0015	0.0001	−0.0158	−0.0093	−0.0074	0.0009	
$l_{N_1\cdots F_5}$	−0.0011	0.0025	−0.0027	0.0003	0.0351	0.0104	−0.0088	−0.0008	0.0036

$CH_3N{=}NCF_3$. Three sets of data covering diffraction angles from $q = 3$ to 126 Å^{-1} are plotted in Figure 5. Corresponding numerical data are deposited with ASIS-NAPS.[16] The reduced molecular scattering curve and the final experimental radial distribution curve computed with a damping factor of 0.001470 are shown in Figures 2 and 3. In the former, the first peak is considerably wider compared to that of $F_3CN{=}NCF_3$. It consists of five bonded distances: C—H = 1.107, N=N = 1.219, C—F = 1.322, C—N(H) = 1.440, and C—N(F) = 1.476 Å. In this case the same assumptions were used in constructing the theoretical models as were introduced for $CH_3N{=}NCH_3$ and $CF_3N{=}NCF_3$. However, since the terminal groups differ, more geometrical parameters are required to specify the structure. We constrained C-H = 1.107 Å, ∠NCH = 109.41° and assumed $\tau(NCX_5) = \tau(NCX_8) = 0.0$ in the final least-squares analysis. Most l_{ij}'s were constrained to values taken either from the results for $CH_3N{=}NCH_3$ and $CF_3N{=}NCF_3$ or from the radial distribution curve. The fit for *trans* configuration is clearly much better than that for *cis*, as is evident from Figure 3. Results of the structure refinement are shown in Table I. In view of the constraints introduced in the least-squares analyses the correlation matrix shows only two values at 0.50, the others being considerably smaller. The error matrix is given in Table IV.

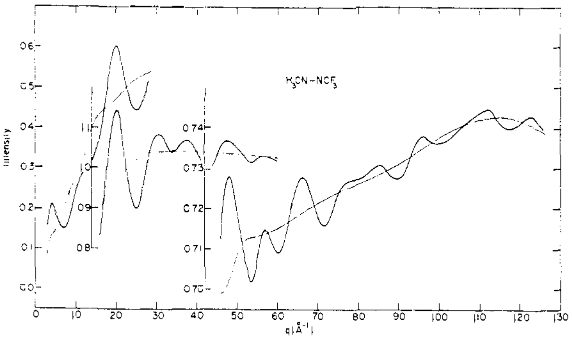
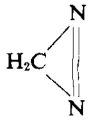
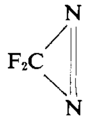


Figure 5. The experimental intensity and background curves for $CH_3N{=}NCF_3$.

Discussions

Two questions merit consideration. (i) Were the samples used in this study mixtures of the two isomers? Their nmr spectra indicated that they were pure, to the level of detection by this technique. This was confirmed by the resolution of the peaks in the radial distribution curves, but the sensitivity level for the latter is less than that of the nmr spectra. (ii) Were these compounds the lowest energy isomers? Although three different methods of preparation were used, in all cases the mechanisms appear to involve free radicals and are presumed to be nonconcerted. This suggests that the *cis vs. trans* configurations were established near the terminus of the reaction path, and that the lowest energy forms were thus prepared. It then follows that while the most stable forms for $(CH_3)_2N_2$ and $(CF_3)(CH_3)N_2$ are *trans*, that for $(CF_3)_2N_2$ is *cis;* further, that the differences in stabilities are greater than about 2 kcal. As shown in Table I, bond lengths and valence angles obtained for $CH_3N{=}NCF_3$ are in agreement with corresponding parameters in the other two compounds; *e.g.*, C-F = 1.322 ± 0.003 Å in trifluoro- and 1.326 ± 0.002 Å in hexafluoroazomethane; ∠NNC = 110.46 ± 3.9° in trifluoro- and 111.8 ± 0.5° in azomethane. The N=N distances are all within the range of values reported for other molecules, but the recorded small differences appear to be real. A summary of observed N=N bond lengths and ∠NNX valence angles is presented in Table V. The shorter N=N bond present in $CH_3N{=}NCF_3$ (by 0.035 Å) was not anticipated, nor was the difference in N—CH_3 *vs.* N—CF_3 in the latter compound. In $CF_3N{=}NCF_3$, ∠NNC = 133 ± 0.8° is the largest value reported for this angle in an azo compound. Extended Hückel[17] calculations for the energy as a function of the ∠NNC angle, holding all other parameters constant, correlate very well with these observations. Figure 6 is a plot which shows the relative energy of $CF_3N{=}NCF_3$ as a function of the angle, for both the *cis* and *trans* configurations, as calculated by the extended Hückel method. The *cis* is more stable than the *trans*, and the minimum angle occurs at ≈130°. A similar calculation for $H_3CN{=}NCF_3$ was made for the *trans* form only; the minimum appears at a smaller angle (≈128°), as observed; see Figure 7.

Table V. Summaries of N-N Bond Lengths and ∠NNC Valence Angles

Molecule	Configuration	N=N, Å	∠NNX, deg	Ref
HN=NH	*trans*	1.238 ± 0.007	109 ± 1.5	*a*
FN=NF	*trans*	1.230 ± 0.010	105.5 ± 0.7	*b*
FN=NF	*cis*	1.214 ± 0.012	114.4 ± 1.0	*b*
$CH_3N{=}NCH_3$	*trans*	1.254 ± 0.003	111.9 ± 0.5	*c*
$CH_3N{=}NCF_3$	*trans*	1.219 ± 0.008	110.5 ± 4.0 126.2 ± 1.8	*c*
$CF_3{=}NCF_3$	*cis*	1.236 ± 0.015	133.0 ± 0.8	*c*
$C_6H_5N{=}NC_6H_5$	*trans*	1.23 ± 0.05	121.5 ± 3	*d*
$C_6H_5N{=}NC_6H_5$	*cis*	1.23 ± 0.05	121 ± 3	*e*
		1.228 ± 0.003		*f*
		1.293 ± 0.009		*g*
$CH_3N{=}NN$		1.24 ± 0.02		*h*
HN=NN		1.240 ± 0.003		*i*

[a] A, Trombetti, *Can. J. Phys.*, **46**, 1005 (1968). [b] R. K. Bohn and S. H. Bauer, *Inorg. Chem.*, **6**, 309 (1967). [c] This work. [d] J. J. De Lange, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc., Ser. A*, **171**, 398 (1939). [e] G. C. Hampson and J. M. Robertson, *J. Chem. Soc.*, 409 (1941). [f] J. Dobyns and D. Pierce, *J. Amer. Chem. Soc.*, **84**, 2651 (1962). [g] J. L. Hencher and S. H. Bauer, *ibid.*, **89**, 5527 (1967). [h] L. Pauling and L. O. Brockway, *ibid.*, **59**, 13 (1937). [i] E. Amble and B. P. Dailey, *J. Chem. Phys.*, **18**, 1422 (1950).

One interesting feature present in this series of compounds is the lengthening of C-N bond by the fluorine substitution. There are other systems which show the same behavior. On comparing $(CH_3)_2$-

---

(17) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963).

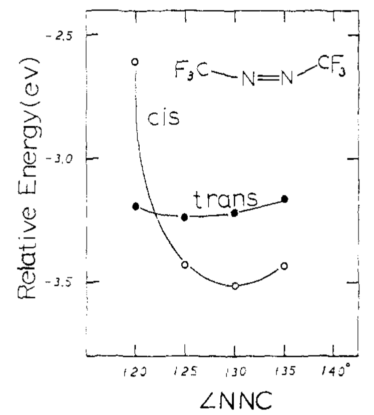


Figure 6. The relative energy as a function of <NNC for both *cis*- and *trans*-$CF_3N{=}NCF_3$, obtained by extended Hückel calculations.

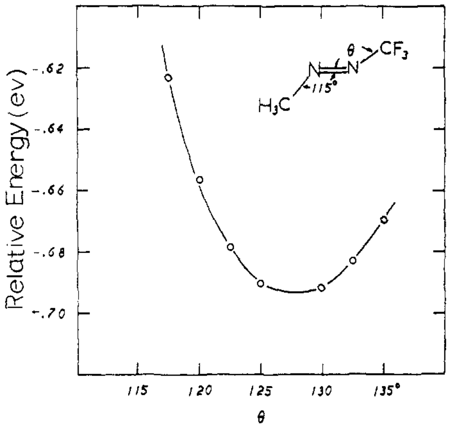
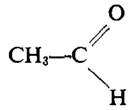
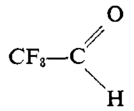


Figure 7. The relative energy as a function of <NNC(F) for *trans*-$CH_3N{=}NCF_3$, obtained by extended Hückel calculations.

$C{=}CH_2$[18a] with $(CF_3)_2C{=}CH_2$[18b] one finds that C—C is larger in the latter, 1.533 *vs.* 1.505 Å. The C—C bond length of 1.504 Å in[18c]


$CH_3{-}C({=}O)H$

contrasts with 1.540 Å in


$CF_3{-}C({=}O)H$

The bond length of C—C = 1.549 Å in hexafluoroacetone,[18b] $(CF_3)_2C{=}O$, is longer than in acetone[19] by 0.042 Å.

It is not surprising that the stable form of hexafluoroazomethane is *cis* instead of *trans*. In the HN=NH and FN=NF systems, the stable form of N_2H_2 is *trans*, while *cis* N_2F_2 has a lower enthalpy than does the *trans* isomer.[20] Also in the species HFC=CHX, with X = I, Br, Cl, and F, the *cis* isomer was found to be more stable.[21]

Azomethane reacts rapidly with boroxine, $H_3B_3O_3$, to form an adduct $(CH_3)_2N_2BH_3$.[22] Similar experiments with $(CF_3)_2N_2$ and $(CH_3)(CF_3)N_2$ failed to produce an isolable adduct. The apparent passivity of $(CF_3)_2N_2$ and $(CH_3)(CF_3)N_2$ as electron donors in this reaction may reflect shrinkage of the nonbonding orbitals in the azo groups and a corresponding shortening of the N=N bond.

Acknowledgment. We wish to thank Mr. C. C. Wan for carrying out the extended Hückel calculations, the Advanced Research Projects Agency, whose support was received through the use of the facilities of the Material Science Center, Cornell University, and the Army Research Office—Durham for additional financial support.

(18) (a) L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **32**, 824 (1960); (b) R. Hinderbrandt, A. Andreassen, and S. H. Bauer, *J. Phys. Chem.*, **74**, 1586 (1970); (c) R. Schwendeman, Thesis, University of Michigan, 1956.

(19) R. Nelson and L. Pierce, *J. Mol. Spectrosc.*, **18**, 344 (1965).

(20) C. T. Armstrong and S. Marantz, *J. Chem. Phys.*, **38**, 169 (1963).

(21) H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960).

(22) A. Kaldor, I. Pines, and R. F. Porter, *Inorg. Chem.*, **8**, 1418 (1969).