spectrum of $Pt_2(pop)_4Cl_2^{4-}$, which could mean that some of the intensity in the low-energy region is attributable to $d\pi^*(\delta^*) \rightarrow d\sigma^*$ triplet absorptions.

When the energy of the σ donor orbital of the axial ligand is comparable to that of $5d_{z^2}(Pt)$, a more complex $\sigma \rightarrow d\sigma^*$ spectrum is expected. In this case, two occupied σ levels (one derived from $d\sigma(Pt_2)$, the other from $\sigma(X \cdots X)$) can participate in relatively low-energy $\sigma \rightarrow d\sigma^*$ transitions. The electronic spectrum of $Pt_2(pop)_4I_2^{4-}$ exhibits intense bands at 338 and 435 nm that are attributable to delocalized $\sigma(Pt,I) \rightarrow d\sigma^*$ transitions (Figure 3). A similar pattern of $\sigma \rightarrow d\sigma^*$ transitions also has been observed in the spectra of binuclear rhodium(II) isocyanide complexes with I^- axial ligands.[19]

X-ray Photoelectron Spectra (XPS). Previous studies have established that the platinum $4f_{7/2}$ binding energy increases about 1.1 eV/unit increase in the formal oxidation state of platinum (ligand effects are sometimes as large, ca. 0.8 eV).[22,23] XPS results for several of the platinum diphosphite complexes are given in Table II. In accord with expectation, there is roughly a 1-eV increase in platinum $4f_{7/2}$ binding energy in going from Pt^{II} to Pt^{III}. The order of $Pt(4f_{7/2})$ energies does not parallel $E(d\sigma \rightarrow d\sigma^*)$, because it reflects a balance of σ and π electronic effects at each Pt center. The $Pt(4f_{7/2})$ energies of complexes containing axial ligands (SCN^-, NO_2^-) that can participate in π back-bonding are higher than would be expected if only σ-donor bonding occurred. Again, the results for $Pt_2(pop)_4I_2^{4-}$ indicate strong mixing of $d\sigma(Pt_2)$ and $\sigma(I \cdots I)$ orbitals; here the electron density at each "Pt^{III}" center must be unusually large.

Acknowledgment. We thank Miriam Heinrichs, Vince Miskowski, Max Roundhill, Bill Schaefer, and Al Stiegman for helpful discussions. This research was supported by National Science Foundation Grant CHE84-19828. NMR experiments were performed at the Southern California Regional NMR Facility supported by National Science Foundation Grant CHE84-40137.

---

[22] Barton, J. K.; Best, S. A.; Lippard, S. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 3785–3788.

[23] Nefedov, V. L.; Salyn, Ya, V. *Inorg. Chim. Acta* **1978**, *28*, L135–L136.

Contribution from the Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, D-1000 Berlin 33, West Germany, and Institut für Physikalische und Theoretische Chemie, Universität Tübingen, D-7400 Tübingen 1, West Germany

Preparation, ^{19}F NMR Spectroscopy, and Electron Diffraction Study of *N*-(Trifluoromethyl)methanimines

Dieter Lentz*[1a] and Heinz Oberhammer[1b]

Received November 27, 1984

Hydrogen halide addition to trifluoromethyl isocyanide results in the formation of both isomers of the compounds $CF_3N{=}CHF$, $CF_3N{=}CHCl$, and $CF_3N{=}CHBr$. The ratios of the isomers as determined by NMR spectroscopy are 15.4:1 ($CF_3N{=}CHF$), 6.7:1 ($CF_3N{=}CHCl$), and 3.8:1 ($CF_3N{=}CHBr$) ($\Delta G = 6.8 \pm 0.5$, 4.7 ± 0.5, and 3.3 ± 0.5 kJ/mol, respectively). The free enthalpies of activation of isomerization were determined by variable-temperature NMR studies. Electron diffraction studies of $CF_3N{=}CHF$ and $CF_3N{=}CHCl$ show that the *E* isomers predominate. All of these methanimines dimerize slowly, forming the corresponding aminomethanimines $CF_3N{=}C(H)N(CF_3)(CF_2H)$, $CF_3N{=}C(H)N(CF_3)(CCl_2H)$, and $CF_3N{=}C(H)(CF_3)(CBr_2H)$. Addition of pentafluorosulfur bromide to trifluoromethyl isocyanide yields the pentafluorothio-substituted methanimine $CF_3N{=}C(Br)SF_5$.

Introduction

Methanimine, $HN{=}CH_2$, is an exceedingly unstable compound.[2] Derivatives with electronegative substituents, such as fluorine,[3] chlorine,[4] or CF_3 groups[5] however, are much more stable. In our studies on the reactivity of trifluoromethyl isocyanide,[6] we were interested in the α-addition reactions of this compound. In 1892 Nef reported that the α-additions of hydrogen halides to isocyanides at −15 °C yield the salts of the halomethanimines.[7] Due to the lower basicity of trifluoromethyl-substituted nitrogen compounds there seemed a chance that hydrogen halide addition would stop at the halomethanimine. The present paper describes our work on the reactions of the hydrogen halides HF, HCl, and HBr with CF_3NC, which give rise to $CF_3N{=}CHF$, $CF_3N{=}CHCl$, and $CF_3N{=}CHBr$. All of these methanimines may exist in the isomeric forms shown in Figure 1. Two of these methanimines, $CF_3N{=}CHF$ and $CF_3N{=}CHCl$, have been described previously in a German patent,[8] but no information about their isomeric forms has been given.

Table I. Correlation Coefficients with Values Larger than 0.6

	HCl[a]	HF[b]		HCl	HF
CF/N—C		−0.68	CX/FCF		−0.67
CF/N═C	−0.81		FCF/NCX	0.61	0.70
CF/CX		−0.84	FCF/*l*(F··F)		−0.72
CF/FCF	0.86	0.80	CNC/NCX		−0.66
CF/NCX	0.73		CNC/tilt	−0.71	−0.82
CF/*l*(CF)	−0.70		CNC/*l*(F··F)		0.71
N═C/FCF	−0.70		NCX/tilt		0.81
N═C/NCX	−0.87		NCX/*l*(CF)	−0.81	
N═C/*l*(CF)	0.84				

[a] For $CF_3N{=}CHCl$. [b] For $CF_3N{=}CHF$.

Experimental Section

Materials. HCl (Merck) was dried over Sicapent (P_2O_5/SiO_2 Merck). The compounds HBr,[9] CF_3NCF_2,[5] $(CF_3)_2NH$,[10] CF_3NC,[6] SF_5Br,[11] and

---

[1] (a) Freie Universität Berlin. (b) Universität Tübingen.

[2] Pearson, R.; Lovas, F. J. *J. Chem. Phys.* **1977**, *66*, 4149.

[3] Cuculo, J. A.; Bigelow, L. A. *J. Am. Chem. Soc.* **1952**, *74*, 710. Sekiya, A.; DesMarteau, D. D. *J. Org. Chem.* **1981**, *46*, 1277. Christen, D.; Oberhammer, H.; Hammaker, R. M.; Chang, S. Ch.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1982**, *104*, 6186.

[4] Hirschmann, K. P.; Simon, H. L.; Young, D. E. *Spectrochim. Acta, Part A* **1971**, *27A*, 421.

[5] "Gmelins Handbuch der Anorganischen Chemie", 8th ed.; Springer Verlag: West Berlin, 1981; Perfluorohalogenorgano Compounds Part 9, pp 125 ff. Klauke, E.; Holtschmidt, H.; Findeisen, K. Ger. Offen. 2 101 107, 1971–1972; *Chem. Abstr.* **1972**, *77*, 125 952.

[6] Lentz, D. *J. Fluorine Chem.* **1984**, *24*, 523. Lentz, D. *Chem. Ber.* **1984**, *117*, 415.

[7] Nef, J. N. *Justus Liebigs Ann. Chem.* **1892**, *270*, 267.

[8] Klauke, E.; Holtschmidt, H. Ger. Offen. 2 137 267, 1973; *Chem. Abstr.* **1973**, *78*, 110 627*c*.

0020-1669/85/1324-4665$01.50/0

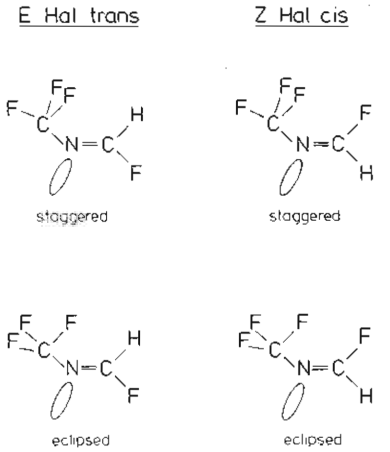


Figure 1. Possible isomers and conformations of $CF_3N{=}CHF$.

Table II. Geometric Parameters of the *E* Isomers of $CF_3N{=}CHCl$ and $CF_3N{=}CHF^e$

	$CF_3N{=}CHCl$	$CF_3N{=}CHF$
C—F	1.332 (4)	1.332 (4)
N—C	1.427 (6)	1.414 (7)
N=C	1.277 (11)	1.277 (7)
C—X	1.707 (5)	1.312 (10)
C—H	1.09^a	1.09^a
∠FCF	107.8 (3)	1.708 (4)
∠CNC	116.3 (8)	117.3 (9)
∠NCX	119.5 (9)	117.7 (14)
∠NCH	125^a	125^a
tilt[b]	4.6 (5)	4.8 (7)
% cis	18 (6)	13 (9)
ΔG,[c] kJ/mol	4.7 (5)	6.8 (5)
$R_{50}{}^d$	4.2	2.7
$R_{25}{}^d$	9.6	8.8

[a] Not refined. [b] Tilt angle of CF_3 group toward the nitrogen lone pair. [c] From NMR data. [d] Agreement factor for 50- and 25-cm camera distance. [e] For error limits, see text; r_a values in Å, angles in deg.

ClF[12] were prepared by using the literature methods.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass or metal vacuum apparatus. Volatile starting materials were measured quantitatively by PVT techniques or by weight. Infrared spectra were recorded on a Beckman Acculab 10 or IR 12 spectrometer with a 10-cm gas cell fitted with KCl windows. Raman spectra were obtained with a Cary 82 instrument equipped with a Spectraphysics krypton laser using the 647-nm exciting line. The ^{19}F NMR and ^1H NMR spectra were recorded on Varian 360 L or JEOL FX 90Q instruments with $CFCl_3$ and Me_4Si as external reference standards. The NMR data of all of the compounds described below are listed in Table V. Mass spectra were obtained on Varian MAT CH 5 DF or MAT 711 instruments at 70 or 80 eV. Elemental analyses were carried out by Beller, Göttingen, West Germany.

Preparation of *N*-(Trifluoromethyl)fluoromethanimine, $CF_3N{=}CHF$. Anhydrous HF (15 mmol) and CF_3NC (14 mmol) were condensed into a 100-mL Kel-F reactor equipped with a stainless-steel valve. After 12 h of shaking at room temperature, the reactor was cooled with liquid nitrogen. The compounds were isolated by fractional condensation through traps at −78, −130, and −196 °C. The trap at −130 °C contained 1.0 g of a mixture of $CF_3N{=}CHF$, $(CF_3)(CF_2H)NH$, and traces of CF_3NC as determined by infrared spectroscopy. The trap at −196 °C contained unreacted CF_3NC. The crude product was condensed onto KF and stirred for 2 h at ambient temperature. A second fractional condensation yielded $CF_3N{=}CHF$ (0.9 g; 55%) in the trap at −130 °C. The colorless gas $CF_3N{=}CHF$ has a boiling point of 5 °C. Its IR spectrum (gas, 5 mbar) has absorption bands at 1730 (s), 1370 (w), 1285 (m), 1232 (s), 1210 (vs), 1172 (vs), 920 (w), and 741 (w) cm^{-1}. Bands in the Raman spectrum (liquid) appear at 3100 (m, p), 3025 (s, p), 1810 (w, p), 1710 (s, p), 1371 (m, p), 1276 (w, p), 1187 (w, br, dp), 1143 (w, p), 998 (w, dp), 908 (s, p), 842 (w, p), 713 (vs, p), 650 (w, p), 610 (w, dp), 585 (vw), 454 (m, p), 415 (m, p), 363 (vw), 302 (vw, dp), and 220 (w, p) cm^{-1}. The mass spectrum (80 eV) exhibits *m/e* peaks that correspond to the following ions: M^+, 30; CF_3NCH^+, 15; CF_3NC^+, 12; CF_2NC^+, 10; CF_3^+, 100; C_2FH^+, 85. A high-resolution spectrum of the molecular ion gave *m/e* 115.0049 (calcd 115.0045).

Table III. Vibrational Amplitudes (Å) for *E* Isomers of $CF_3N{=}CHCl$ and $CF_3N{=}CHF$ without Distances Involving Hydrogen

	$CF_3N{=}CHCl$	$CF_3N{=}CHF$
C–F	0.048 (6)	0.048^a
N–C	0.050^a	0.050^a
N=C	0.040^a	0.040^a
C–X	0.048 (5)	0.048^a
F··F	0.055 (5)	0.057 (6)
N··F		
C··C		
N··X	0.060 (8)	
C··F_1	0.080^a	0.074 (12)
C··F_2	0.170 (23)	0.106 (13)
X··F_1	0.098 (13)	0.072 (15)
X··F_2	0.153 (13)	0.124 (14)

[a] Not refined. [b] Error limits are 3σ values.

Preparation of (Difluoromethyl)(trifluoromethyl)amine, $(CF_3)(CF_2H)NH$. (Difluoromethyl)(trifluoromethyl)amine, $(CF_3)(CF_2H)NH$, was obtained as a byproduct of the HF addition to CF_3NC. During one of several reactions described above, $(CF_3)(CF_2H)NH$ was formed as a major product and collected in the trap at −130 °C. It is a colorless liquid, bp 23 °C (extrapolated from vapor pressure measurements, nine data points between −64 and −27 °C). Its IR spectrum (gas, 5 mbar) exhibits absorption bands at 3462 (m, NH), 3062 (w, CH), 1520 (s), 1405 (m), 1330 (ns), 1260 (vs), 1190 (vs), 1120 (s), 1080 (s), 935 (m), 730 (w), and 620 (w) cm^{-1}. Its mass spectrum (80 eV) exhibited *m/e* peaks consistent with the presence of the following ions: M^+, 9; $(M - H^+)$, 19; $(M - F)^+$, 20; $C_2HF_4N^+$, 8; $C_2HF_3N^+$, 14; smaller fragment ions. It decomposes slowly at room temperature, forming a yellow oil of low volatility, which has not been characterized.

Preparation of *N*-(Trifluoromethyl)((difluoromethyl)(trifluoromethyl)amino)methanimine, $CF_3N{=}C(H)N(CF_3)(CF_2H)$. $CF_3N{=}CHF$ (4 mmol) was condensed into an NMR tube and sealed under vacuum. The tube was heated to 100 °C, and the reaction was monitored by ^{19}F NMR spectroscopy. After 16 h the signals of the starting material disappeared, and the colorless liquid $CF_3N{=}C(H)N(CF_3)(CF_2H)$ was obtained with less than 10% impurities. The IR spectrum (gas, 5 mbar) exhibits absorption bands at 1693 (s), 1449 (m), 1402 (m), 1355 (s), 1303 (s), 1265 (vs), 1219 (sh), 1191 (vs), 1132 (s), 1118 (s), 1030 (w), 998 (w), 955 (vw), 910 (m), 890 (vw), 865 (vw), 830 (w), 770 (m), 701 (m), 640 (w), and 603 (w) cm^{-1}. Bands in the Raman spectrum (liquid) appear at 3052 (m, p), 3015 (m, p), 1689 (vs, p), 1669 (sh), 1448 (w, p), 1400 (m, p), 1320 (w, p), 1181 (br, w, p), 1105 (br, w, p), 905 (vs, p), 862 (w, p), 824 (s, p), 763 (m, p), 750 (w, p), 707 (w, p), 699 (w, p), 637 (w, p), 582 (vw, p), 519 (vw, p), 494 (vw, p), 349 (w, p), 299 (m, p), 271 (w, p), 243 (w, p), 184 (w, p), and 126 (m, p) cm^{-1}. The mass spectrum (80 eV) exhibits *m/e* peaks consistent with the presence of the following ions: M^+, 5; $(M - F)^+$, 13; $C_3H_3F_5N_2{}^+$, 2; $C_3H_2F_5N_2{}^+$, 37; $C_3HF_4N_2{}^+$, 2; $C_2HF_5N^+$, 17; $C_2H_2F_4N^+$, 13; $C_2HF_4N^+$, 1; $C_2F_4N^+$, 7; $C_2H_2F_3N^+$, 9; $C_2HF_3N^+$, 73; $CH_2F_3N^+$, 18; $C_2H_2F_2N^+$, 1; $C_2HF_2N^+$, 6; $C_2F_2N^+$, 1; CF_3^+, 100; CHF_2N^+, 11; CHF_2^+, 43. A high-resolution spectrum of the molecular ion gave *m/e* 230.0093 (calcd 230.0090).

Preparation of *N*-(Trifluoromethyl)chloromethanimine, $CF_3N{=}CHCl$. Equimolar amounts of CF_3NC (13.7 mmol) and HCl were condensed into a 250-mL glass vessel equipped with a PTFE valve and a magnetic stirring bar. The reaction vessel was placed into a cooling bath (−140 °C) and warmed within 5 h to room temperature with stirring. Fractional condensation of the products through a system of traps at −78, −150, and −196 °C in a dynamic vacuum of 10^{-2} mbar yielded pure $CF_3N{=}CHCl$ (1.4 g, 78%). It is a colorless liquid, bp 27 °C (extrapolated from 17 data points between −65 and 7 °C). The IR spectrum (gas, 5 mbar) exhibits absorptions at 1790 (w), 1725 (w), 1660 (s), 1335 (w), 1248 (vs), 1210 (s), 1192 (s), 953 (w), 905 (m), 872 (m), 795 (w), and 669 (m) cm^{-1}. Bands in the Raman spectrum (liquid) appear at 3270 (vw, p), 3070 (w, p), 3033 (s, p), 2952 (m, p), 1891 (vw), 1795 (vw, p), 1710 (vw, p), 1668 (sh), 1642 (s, p), 1331 (s, p), 1235 (vbr), 1188 (vbr),

---

(9) Brauer, G., Ed. "Handbuch der Präparativen Anorganischen Chemie"; F. Enke Verlag: Stuttgart, West Germany 1975; Vol. 1, p 296.

(10) Young, J. A.; Tsonkalas, S. N.; Dresdner, R. *J. Am. Chem. Soc.* **1958**, *80*, 3604.

(11) Christe, K. O.; Curtis, E. C.; Schack, C. J.; Roland, A. *Spectrochim. Acta, Part A* **1977**, *33A*, 69. Wessel, J.; Kleemann, G.; Seppelt, K. *Chem. Ber.* **1983**, *116*, 2399.

(12) Brauer, G., Ed. "Handbuch der Präparativen Anorganischen Chemie"; F. Enke Verlag: Stuttgart, West Germany, 1975; Vol. 1, p 166.

Table IV. Principal Geometric Parameters for $XN=C(Y)Z$ (X = H, F, Cl, or CF_3; Y, Z = H, F, or Cl)

	N=C, Å	N—X, Å	C—Y, Å	C—Z, Å	∠XNC, deg	∠NCY, deg	∠NCZ, deg
$HN=CH_2$[a]	1.273 (4)	1.021 (20)	1.092 (20)	1.092 (20)	110.4 (15)	125.1 (20)	117.9 (20)
$FN=CF_2$[b]	1.274 (6)	1.389 (2)	1.300 (3)	1.300 (3)	107.9 (2)	127.2 (2)	119.8 (2)
$ClN=CCl_2$[c]	1.266 (5)	1.683 (10)	1.718 (6)	1.718 (6)	117.1 (4)	127.5 (4)	118.7 (5)
$CF_3N=CHCl$[d]	1.277 (11)	1.427 (6)	1.09	1.707 (5)	116.3 (8)	125	119.5 (9)
$CF_3N=CHF$[d]	1.277 (7)	1.414 (7)	1.09	1.312 (10)	117.3 (9)	125	117.7 (14)

[a] r_s/r_0 values from ref 2. [b] $r_\alpha{}^0$ values from ref 3. [c] $r_\alpha{}^0$ values from ref 17. [d] r_a values from this study.

Table V. NMR Data for *N*-(Trifluoromethyl)methanimines[a]

compd	^1H NMR	^{19}F NMR
E-$CF_3N=CHF$	$\delta = 7.8$ $^2J_{HF} = 115$ $^4J_{HF} = 1.1$	$\phi = -46.2$ (CF) $^2J_{HF} = 115$ $\phi = -62.2$ (CF_3) $^4J_{FF} = 5.0$ (−65 °C)
Z-$CF_3N=CHF$	$\delta = 6.5$ (br, 32 °C) $^2J_{HF} = 114$ $^4J_{HF} = 1.4$ (−65 °C)	$\phi = -16.2$ (CF) $^2J_{HF} = 114$ $\phi = -59.2$ (CF_3) $^4J_{FF} = 10.5$ (−65 °C)
E-$CF_3N=CHCl$	$\delta = 8.7$ $^4J_{HF} = 1.3$	$\phi = -63.0$ $^4J_{HF} = 1.1$
Z-$CF_3N=CHCl$	$\delta = 8.0$ (br, 32 °C) $^4J_{HF} = 1.0$ (−65 °C)	$\phi = -60.7$ $^4J_{HF} = 1.0$ (−65 °C)
E-$CF_3N=CHBr$	$\delta = 9.4$ $^4J_{HF} = 1.2$	$\phi = -63.5$
Z-$CF_3N=CHBr$	$\delta = 8.8$	$\phi = -61.7$
E-$CF_3N=C(Cl)F$		$\phi = 1.7$ (CF) $\phi = -58.7$ (CF_3)
Z-$CF_3N=C(Cl)F$		$\phi = -49.3$ (CF) $\phi = -61.7$ (CF_3)
$CF_3N=C(H)N(CF_3)(CF_2H)$[b]	$\delta = 8.10$ $\delta = 7.15$ (CF_2H) $^2J_{HF} = 58$	$\phi = -58.9$ (CF_3) $^4J_{FF} = 9.2$ $^4J_{HF} = 1.4$ $\phi = -62.9$ (CF_3) $\phi = -106.5$ (CF_2H) $^2J_{HF} = 58$ $^4J_{FF} = 9.2$ $^4J_{HF} = 2.5$
$CF_3N=C(H)N(CF_3)(CCl_2H)$[b]	$\delta = 7.97$ $\delta = 8.19$	$\phi = -56.2$ (CF_3) $\phi = -61.2$ (CF_3)
$CF_3N=C(H)N(CF_3)(CBr_2H)$[b]	$\delta = 8.1$ $\delta = 8.2$	$\phi = -55.7$ (CF_3) $\phi = -60.2$ (CF_3)
$CF_3N=C(Br)SF_5$		$\phi = -61.5$ (CF_3) AB_4 pattern $\phi_A = 64.8$ (SF_5) $\phi_B = 45.8$ (SF_5)
$F_3CN=CF_2$ (at −85 °C)		$\phi = -57.9$ (CF_3) $\phi = -30.5$ (CF_{trans}) $\phi = -50.1$ (CF_{cis}) $^2J_{FF} = 85.4$ $^4J_{FF\text{-}trans} = 8.5$ $^4J_{FF\text{-}cis} = 11.6$
$(CF_3)(CF_2H)NH$	$\delta = 6.02$ (CHF_2) $^2J_{HF} = 60.5$ $^3J_{HH} = 9$ $\delta = 4.3$ (br, NH)	$\phi = -58.9$ (CF_3) $^4J_{FF} = 4$ $^3J_{HF} = 5$ $\phi = -93.1$ $^2J_{HF} = 60.5$ $^4J_{FF} = 4$ $^3J_{HF} = 5$

[a] *J* in Hz. [b] Probably the *E* isomer.

950 (vw, dp), 879 (s, p), 860 (m, p), 844 (sh, p), 783 (m, p), 767 (w, p), 688 (w, p), 671 (m, p), 658 (w, p), 598 (w, p), 577 (w, p), 508 (w, p), 445 (w, dp), 423 (w, p), 330 (vs, p), 287 (vw, dp), and 183 (m, p) cm^{-1}. The mass spectrum (80 eV) exhibits peaks consistent with the presence of the following ions: M^+, 3; $(M - H)^+$, 2; $C_2HClF_2N^+$, 23; $C_2HF_3N^+$, 100; CF_2Cl^+, 53; $C_2HF_2N^+$, 6; $C_2F_2N^+$, 6; $CF_3{}^+$, 70; $CF_2{}^+$, 28. A high-resolution spectrum of the molecular ion gave *m/e* 130.9754 (calcd 130.9750).

Preparation of *N*-(Trifluoromethyl)((dichloromethyl)(trifluoromethyl)amino)methanimine, $CF_3N=C(H)N(CCl_2H)(CF_3)$. A sample of $CF_3N=CHCl$ (19 mmol) was stored in a 75-mL stainless-steel cylinder at −20 °C for 2 weeks. After this time the sample had a much lower vapor pressure than $CF_3N=CHCl$, and the IR spectrum showed additional absorption bands that could not be assigned to $CF_3N=CHCl$. Fractional condensation under a vacuum of 10^{-2} mbar through a series of traps at −30, −78, and −196 °C yielded a colorless liquid (1.9 g) in the trap at −30 °C. Redistillation at normal pressure yielded $CF_3N=C(H)N(CCl_2H)(CF_3)$ (1.6 g), bp 98 °C. Anal. Calcd for $C_4H_2Cl_2F_6N_2$: C, 18.26; H, 0.76; Cl, 26.96; F, 43.36. Found: C, 19.27; H, 0.69; Cl, 25.04; F, 43.7. The IR spectrum (gas, 5 mbar) exhibits absorption bands at 3030 (w), 1760 (w), 1688 (s), 1465 (w), 1435 (w), 1379 (s), 1348 (s), 1280 (s), 1255 (s), 1220 (s), 1188 (vs), 1170 (vs), 1096 (m), 995 (w), 928 (m), 890 (vw), 860 (w), 788 (m), 740 (w), 660 (w), and 590 (w) cm^{-1}. The mass spectrum (80 eV) gave *m/e* peaks consistent with presence of the following ions: M^+, 3; $(M - F)^+$, 1; $(M - Cl)^+$, 10; $C_3H_2Cl_2F_3N^+$, 74; $C_2HCl_2F_3N^+$, 4; $C_2HCl_2F_2N^+$, 6; $C_2H_2ClF_3N^+$, 92; $C_2HF_3N^+$, 88; $CHCl_2{}^+$, 29; $CF_3{}^+$, 100.

Preparation of *N*-(Trifluoromethyl)bromomethanimine, $CF_3N=CHBr$. Equimolar amounts of CF_3NC (7.2 mmol) and HBr were condensed into a 250-mL glass vessel equipped with a PTFE valve and a magnetic stirring bar. The vessel was placed into a cooling bath (−150 °C) and warmed slowly to room temperature. Vacuum distillation of the volatile products through two traps at −60 and −120 °C yielded $CF_3N=CHBr$ (0.5 g; 40%) in the trap at −120 °C. It is a colorless liquid. The IR spectrum (gas, 5 mbar) exhibits absorption bands at 1670 (m), 1634 (m), 1310 (w), 1235 (vs), 1200 (s), 810 (w), and 655 cm^{-1}. The Raman spectrum (liquid) gave bands at 3052 (m, p), 3015 (s, p), 2925 (vw, p), 1675 (w, dp), 1633 (w, p), 1425 (vw, p), 1365 (vw, p), 1330 (vw, dp), 1303 (vw, p), 1087 (vw, p), 1055 (vvw, p), 894 (w, p), 865 (s, p), 840 (w, p), 798 (vw, dp), 758 (m, p), 735 (w, p), 700 (vw, dp), 680 (vw, p), 668 (vw, p), 642 (m, p), 622 (w, p), 591 (w, p), 561 (m, p), 483 (w, p), 440 (vw, p), 417 (vw, p), 322 (vw, dp), 289 (m, p), 275 (vw, dp), 246 (vs, p), 218 (m, p), 200 (vw, dp), 168 (w, p), 151 (w, dp), and 132 (w, p) cm^{-1}. The mass spectrum (80 eV) exhibits *m/e* peaks consistent with the presence of the following ions: $(M - H)^+$, 6; $(M - F)^+$, 20; CF_2Br^+, 48; $C_2HF_3N^+$, 100; smaller fragment ions. A high-resolution spectrum for $(M - H)^+$ gave for $C_2{}^{79}BrF_3N$ *m/e* 173.4188 (calcd 173.4166).

Preparation of *N*-(Trifluoromethyl)((dibromomethyl)(trifluoromethyl)amino)methanimine, $CF_3N=C(H)N(CBr_2H)(CF_3)$. A sample of $CF_3N=CHBr$ (3 mmol) was condensed into an NMR tube and sealed under vacuum. The sample was heated to 100 °C for 12 h. After this time the NMR signals of the starting material had disappeared, and two new signals were found. The sample contained less than 10% impurities. It is a colorless liquid. The infrared spectrum (gas, 5 mbar) exhibits absorption bands at 1690 (m), 1375 (w), 1345 (m), 1285 (m), 1238 (vs), 1192 (s), 1165 (sh), 1100 (w), 930 (w), 810 (w), and 660 (w) cm^{-1}. The mass spectrum (80 eV) exhibits *m/e* peaks consistent with the presence of the following ions: $(M - CF_3)^+$, 8; $(M - Br)^+$, 18; $C_2H_2BrF_3N^+$, 100; $CHBr_2{}^+$, 18; $C_2HF_3N^+$, 44; $CH_2F_3N^+$, 18; $CF_3{}^+$, 78; smaller fragment ions.

Attempted Preparation of *N*-(Trifluoromethyl)chlorofluoromethanimine, $CF_3N=CClF$. Equimolar amounts of CF_3NC (7 mmol) and ClF were condensed into a 100-mL pressure vessel. The reaction mixture was warmed slowly to room temperature within 12 h. Fractional condensation through two traps at −130 and −196 °C yielded 1 g of material in the trap at −130 °C. The infrared spectrum, the ^{19}F NMR spectrum, and GLC analysis (10% Kel-F oil No. 3; Chromosorb PAW 80–100 mesh; −10 °C isothermic) show the presence of $CF_3N=CF_2$, $CF_3N=CCl_2$, $CF_3N=CClF$[13] (ratio 40:30:30) and traces of CF_3NCO.

Preparation of Bromo(pentafluorothio)-*N*-(trifluoromethyl)methanimine, $CF_3N=C(Br)SF_5$. Equimolar amounts of CF_3NC (27 mmol) and SF_5Br and $CFCl_3$ (31 g) were condensed into a 250-mL glass vessel equiped with a PTFE valve and a magnetic stirring bar. The reaction vessel was placed into a cooling bath (−150 °C) and warmed to room temperature over 48 h. Fractional condensation in a dynamic vacuum of 10^{-2} mbar through traps at −78 and −196 °C yielded $CF_3N=C(Br)SF_5$ (5.1 g; 62%), which is a colorless liquid, bp 81 °C. Anal. Calcd for C_2BrF_8NS: C, 7.95; Br, 26.46; F, 50.33; N, 4.64; S, 10.62. Found: C, 9.05; Br, 25.49; F, 50.4; N, 5.07; S, 10.21. The IR spectrum (gas, 5

---

(13) Barr, D. A.; Haszeldine, R. N.; Willis, C. J. *J. Chem. Soc.* **1964**, 1351.

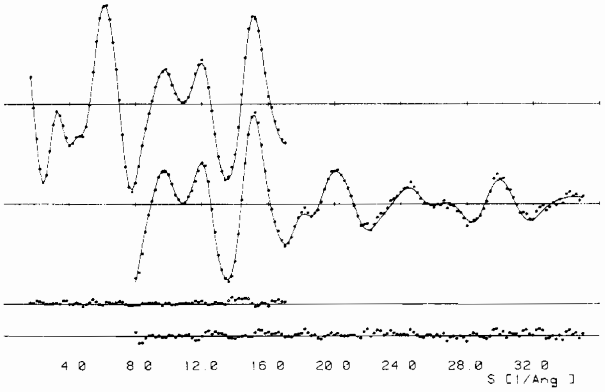


Figure 2. Experimental (···) and calculated (—) molecular electron diffraction intensities for $CF_3N{=}CHCl$ and differences.

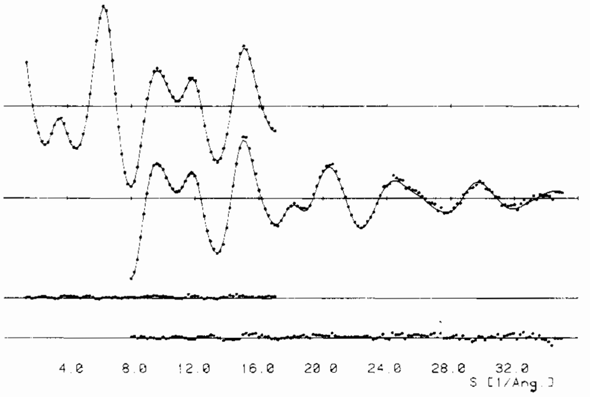


Figure 3. Experimental (···) and calculated (—) molecular electron diffraction intensities for $CF_3N{=}CHF$ and differences.

mbar) exhibits absorption bands at 1738 (vw), 1700 (m), 1260 (s), 1222 (vs), 1105 (vw), 959 (m), 910 (vs), 890 (m), 868 (vw), 813 (m), 745 (vw), 699 (w), 670 (vw), 650 (vw), and 610 (w) cm^{-1}. Bands in the Raman spectrum (liquid) appear at 1733 (w, p), 1690 (w, p), 1201 (vw, p), 943 (vw, dp), 898 (sh), 873 (w, p), 856 (sh), 842 (sh), 793 (w, dp), 738 (vw, p), 684 (vs, p), 665 (w, p), 640 (w, p), 620 (w, dp), 547 (vw), 538 (vw, p), 508 (w, p), 495 (sh), 420 (w, p), 390 (vw, dp), 353 (vw, p), 315 (s, p), 232 (m, p), 218 (vs, p), 159 (w, dp), and 112 (m, p) cm^{-1}. The mass spectrum exhibits *m/e* peaks consistent with the presence of the following ions: $(M - Br)^+$, 19; $(M - SF_5)^+$, 57; SF_5^+, 42; SF_4^+, 6; SF_3^+, 41; Br^+, 12; CF_2NC^+, 16; SF_2^+, 14; CF_3^+, 100.

Attempted Preparation of *N*-(Trifluoromethyl)(bis(trifluoromethyl)amino)methanimine, $CF_3N{=}C(H)N(CF_3)_2$. Equimolar amounts of CF_3NC (7 mmol) and $(CF_3)_2NH$ were condensed into a 250-mL glass vessel equipped with a PTFE valve and a magnetic stirring bar. The reaction vessel was placed into a cold bath (−125 °C) and warmed slowly to room temperature and the reaction mixture then stirred for an additional 2 days at room temperature. Fractional condensation of the volatile products through traps at −78 and −196 °C yielded a mixture of unreacted CF_3NC and $(CF_3)_2NH$ in the trap at −196 °C, as detected by infrared spectroscopy. In the vessel there remained a small amount of a yellow oil of unknown composition.

Variable-Temperature NMR Spectra and the Determination of the Free Enthalpies of Activation. Variable-temperature NMR spectra were recorded on a JEOL FX 90Q instrument on the neat substances or solutions in diglyme (approximately 10–20%). ΔG values were calculated from the molar ratios of the isomers determined by integration. The molar ratio at the coalescence temperature was extrapolated from the molar ratios at several temperatures below the coalescence temperature. $\Delta G^{\ddagger}$ values were calculated from line distances at low temperature and the mole ratio at T_{co} by using literature methods.[14]

Gas Electron Diffraction. The electron diffraction intensities were recorded with a Balzers KD-G2[15] gas diffractograph at two camera distances (25 and 50 cm) and with an accelerating voltage of about 60 kV. The sample temperatures were −38 and −55 °C for the chlorine and fluorine derivatives, and the temperature of the inlet system and nozzle was 20 °C in both cases. The camera pressure never exceeded 2.7×10^{-5} mbar, and exposure times were 6–10 and 15–30 s for the long and short camera distances, respectively. The electron wavelength was determined from ZnO diffraction patterns. Two plates for each compound and camera distance were analyzed by the usual procedure.[16] The averaged molecular intensities in steps of $\Delta s = 0.2$ $Å^{-1}$ are presented in Figures 2 and 3.

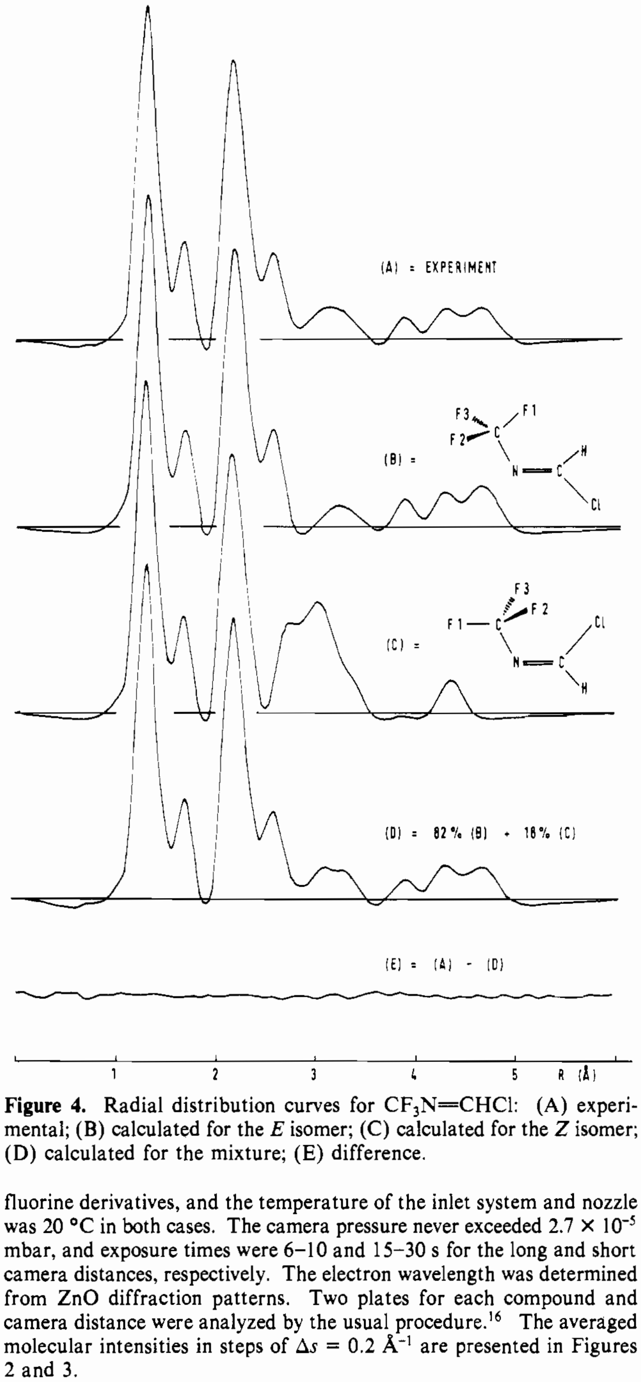


Figure 4. Radial distribution curves for $CF_3N{=}CHCl$: (A) experimental; (B) calculated for the *E* isomer; (C) calculated for the *Z* isomer; (D) calculated for the mixture; (E) difference.

Structure Analysis. $CF_3N{=}CHCl$. The experimental radial distribution function is presented in Figure 4 (curve A). Model calculations demonstrate clearly that the *E* isomer, with a CF_3 group eclipsing the N=C bond, predominates. Differences between experimental and calculated radial distribution functions (curves A and B) are largest in the range 2.8–3.3 Å. These differences can be accounted for by adding 15–20% *Z* isomer to the calculated function. Assuming equal bond lengths and FCF angles for both isomers, the CNC and NCCl angles for the *Z* isomer have to be increased as compared to the values for the *E* isomer. These values were not refined in the least-squares analysis. The $NCCl_z$ angle was set to the corresponding value for $ClN{=}CCl_2$ (127.5°),[17] and the CNC angle was increased to 120°. For the *Z* isomer the CF_3 group has to be rotated to the staggered position (see curve C in Figure 4). With the CF_3 group eclipsing the C=N bond also in the *Z* isomer, no satisfactory agreement with experiment was obtained, and the $F_1 \cdots Cl$ nonbonded distance would be impossibly short (2.40 Å) as compared to the sum of the Van der Waals radii (3.15 Å). In the least-squares refinement a diagonal weight matrix was applied to the

---

(14) Shanon-Atidi, H.; Ber-Elie, K. H. *J. Phys. Chem.* **1970**, *74*, 961. Kessler, H. *Angew. Chem.* **1970**, *82*, 237.

(15) Oberhammer, H. "Molecular Structures by Diffraction Methods"; The Chemical Society: London, 1976; Vol. 4, p 24.

(16) Oberhammer, H.; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, *70*, 273.

(17) Christen, D.; Kalcher, K. *J. Mol. Struct.* **1983**, *97*, 143.

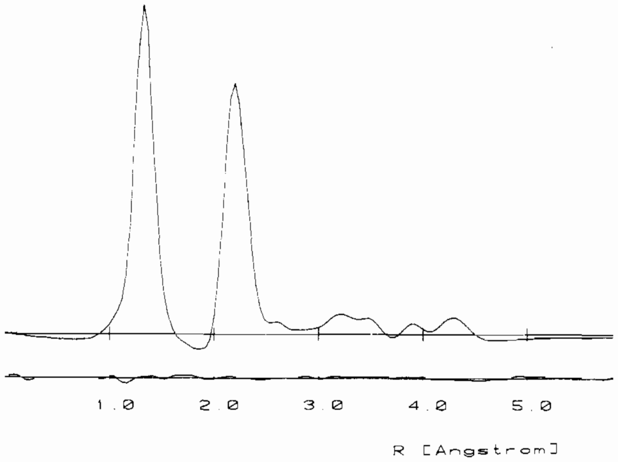


Figure 5. Experimental radial distribution curve for $CF_3N{=}CHF$ and difference curve for a mixture (87% *E* and 13% *Z*).

molecular intensities, and the scattering amplitudes and phase shifts of Haase[18] were used. For the CF_3 group, C_{3v} symmetry was assumed with a possible tilt angle between the C_3 axis and the C–N bond direction. The geometric parameters for the hydrogen atom (C–H bond length and NCH angle) were transferred from $HN{=}CH_2$.[2] Assumptions for the vibrational amplitudes are evident from Table III. With the above assumptions eight geometric parameters, seven vibrational amplitudes, and the relative ratio of the two isomers were refined simultaneously. Correlation coefficients larger than 0.6 are given in Table I, and the final results of the least squares analysis are summarized in Tables II and III. Error limits for geometric parameters are based on 2σ values, and a possible scale error of 0.1% is included for the bond lengths. Systematic errors due to assumptions for the C—N and N═C vibrational amplitudes are also included. These amplitudes were varied systematically by ±0.003 Å. Error limits for vibrational amplitudes are 3σ values, and the estimated uncertainty for the *Z* contribution includes systematic errors due to the assumptions made for the geometric parameters and vibrational amplitudes of the *Z* isomer.

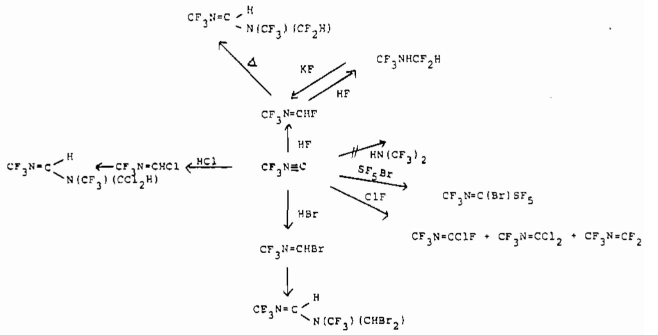
$CF_3N{=}CHF$. A preliminary analysis of the radial distribution function (Figure 5) demonstrates that the major contribution is again the *E* isomer with the CF_3 group eclipsing the C═N bond. Differences between experimental and calculated radial distribution functions can be accounted for by adding about 10% *Z* isomer. For the CNC and NCF_z angles of the *Z* isomer, the values derived in a preliminary analysis of $CF_3N{=}CF_2$[19] were transferred (CNC = 119° and NCF_z = 129°). Furthermore, the CF_3 group in the *Z* isomer was assumed to stagger the C═N bond, in analogy to the results obtained for $CF_3N{=}CF_2$. The eclipsed position would result in an F···F distance of 2.36 Å as compared to the sum of the Van der Waals radii of 2.70 Å.

In the final least-squares analysis the same constraint for the CF_3 group was applied as in the case of the chlorine compound, and slightly different assumptions were made for the vibrational amplitudes (see Table III). Correlation coefficients are included in Table I and the results are listed in Tables II and III. The estimated error limits are analogous to those for $CF_3N{=}CHCl$.

Results and Discussion

The preparation and reactions of the *N*-(trifluoromethyl)methanimines are shown in Scheme I. In contrast to common isocyanides the α-addition reaction of the hydrogen halides HCl and HBr stops at the stage of halomethanimine formation. In the case of $CF_3N{=}CHF$ further HF addition occurs, and $(CF_3)(CF_2H)NH$ is formed as a byproduct, which undergoes HF elimination on reaction with potassium fluoride. Analogous to *N*-(trifluoromethyl)difluoromethanimine,[5] the *N*-(trifluoromethyl)halomethanimines $CF_3N{=}CHF$, $CF_3N{=}CHCl$, and $CF_3N{=}CHBr$ dimerize slowly at room temperature, forming the corresponding *N*-(trifluoromethyl)aminomethanimines (Scheme I). This dimerization reaction can be accelerated by heating a neat sample to 100 °C. The spectroscopic data for these compounds are given in Table V and the Experimental Section. No mechanism for the formation of these dimers, $CF_3N{=}C(H)N(CF_3)(CX_2H)$ (X = F, Cl, Br), is given. The intermediate formation of $(CF_3)(CX_2H)NH$ and CF_3NC followed by α-addition of the amine to CF_3NC can be excluded due to the nonreactivity of CF_3NC toward $(CF_3)_2NH$. The α-addition reaction of SF_5Br to CF_3NC results in the formation of the pentafluorothio-substituted methanimine $CF_3N{=}C(Br)SF_5$.

Scheme I. Schematic Representation of the $CF_3N{=}C<$ Chemistry



All of these compounds can exist as two isomers (*E* or *Z* isomer), shown in Figure 1, with the CF_3 group in the staggered or eclipsed conformation. According to the NMR spectra (Table V) and vibrational spectroscopic data (Experimental Section) the *E* and Z isomers of $CF_3N{=}CHF$, $CF_3N{=}CHCl$, $CF_3N{=}CHBr$, and $CF_3N{=}C(Cl)F$ are present. Of the compounds $CF_3N{=}C(H)N(CF_3)(CX_2H)$ (X = F, Cl, Br) and $CF_3N{=}C(Br)SF_5$ only one isomer be can unambiguously detected by NMR spectroscopy. The $^4J_{FF}$ coupling constant of $CF_3N{=}CHF$ (10.5 Hz for the minor isomer vs. 5.0 Hz for the major isomer) gives some evidence that the predominant isomer is the *E* isomer, but this is not totally without ambiguity. Furthermore, spectroscopic data can give no evidence whether the eclipsed or staggered conformation is energetically favored. However, electron diffraction can resolve these problems. Experiments carried out to deduce this are described below.

Electron Diffraction Structural Data. For both $CF_3N{=}CHF$ and $CF_3N{=}CHCl$ the isomer with the halogen atom trans to the CF_3 group, i.e. cis to the nitrogen lone pair (*E* isomer) is favored. The relative ratios of the isomers found by NMR measurements at room temperature, i.e. *E*:*Z* = 6.7 ± 1 (13 ± 2% contribution of the *Z* isomer) for $CF_3N{=}CHCl$ and *E*:*Z* = 15.4 ± 1 (6 ± 2% contribution of the *Z* isomer) for $CF_3N{=}CHF$, agree with the electron diffraction values, which have much larger uncertainties. In the *E* isomers the CF_3 group eclipses the N═C bond, whereas in the *Z* isomer the staggered conformation is observed. A comparison of structural parameters for substituted methanimines (Table IV) allows the following observations. (1) Within experimental uncertainty the N═C bond length is not affected by various substitutions. (2) The C–F and C–Cl bonds are shorter than such bonds in analogous ethylene or carbonyl compounds (e.g. C–F = 1.315 (3), 1.351 (15), 1.316 (1), and 1.338 (5) Å in $H_2C{=}CF_2$,[20] $H_2C{=}CHF$,[21] $O{=}CF_2$,[22] and $O{=}CHF$,[23] respectively, or C–Cl = 1.728 (2), 1.730 (4), 1.742 (2), and 1.7716 (2) Å in $CH_2{=}CCl_2$,[24] $H_2C{=}CHCl$,[25] $O{=}CCl_2$,[26] and $O{=}CHCl$,[27] respectively). The XNC bond angle depends on the substituent X (117° for X = Cl or CF_3, 110° for X = H, and 108° for X = F), whereas the carbon bond angles are almost independent of the substituents Y and Z.

Vibrational Spectra. The vibrational spectra (see Experimental Section) of the compounds $CF_3N{=}CHF$, $CF_3N{=}CHCl$, and

---

(18) Haase, J. *Z. Naturforsch., A: Astrophys., Phys., Phys. Chem.* **1970**, *25A*, 936.

(19) Steger, B.; Oberhammer, H., unpublished results.

(20) Mijlhoff, F. J.; Renes, G. H.; Kohata, K.; Oyanagi, K.; Kuchitsu, K. *J. Mol. Struct.* **1977**, *39*, 241.

(21) Huisman, P. A. G.; Mijlhoff, F. C.; Renes, G. H. *J. Mol. Struct.* **1979**, *51*, 191.

(22) Nakata, M.; Kohata, K.; Fukuyama, T.; Kuchitsu, K.; Wilkins, C. J. *J. Mol. Struct.* **1980**, *68*, 271.

(23) Miller, R. F.; Curl, R. F. *J. Chem. Phys.* **1961**, *34*, 1847.

(24) Nakata, M.; Kuchitsu, K. *J. Mol. Struct.* **1982**, *95*, 205.

(25) Huismann, P. A. G.; Mijlhoff, F. C. *J. Mol. Struct.* **1979**, *54*, 145.

(26) Nakata, M.; Kohata, K.; Fukuyama, T.; Kuchitsu, K. *J. Mol. Spectrosc.* **1980**, *83*, 105.

(27) Davis, R. W.; Gerry, M. C. L. *J. Mol. Spectrosc.* **1983**, *97*, 117.

Table VI. Thermodynamic Data for *N*-(Trifluoromethyl)halomethanimines[a]

compd	T_{CO}, K	ΔG_{298}, kJ/mol	$\Delta G^{\ddagger}{}_{T_{CO}}$, kJ/mol	$\Delta G_{T_{CO}}$, kJ/mol
E-$CF_3N{=}CHF$	393	6.8 ± 0.5	81.3 ± 1.3	5.5 ± 0.5
Z-$CF_3N{=}CHF$			76.8 ± 1.3	
E-$CF_3N{=}CHCl$	438	4.7 ± 0.5	91.5 ± 1.3	4.2 ± 0.5
Z-$CF_3N{=}CHCl$			87.4 ± 1.3	
E-$CF_3N{=}CHBr$	413	3.0 ± 0.5	85.7 ± 1.3	2.4 ± 0.5
Z-$CF_3N{=}CHBr$			83.4 ± 1.3	
$CF_3N{=}CF_2$	388		69.5 ± 1.3	

[a] Key: T_{CO}, coalescence temperature; ΔG_{298}, differences between the free enthalpies of formation of the *E* and *Z* isomers at 298 K; $\Delta G^{\ddagger}{}_{T_{CO}}$, free enthalpies of activation of the isomerization between the *E* and *Z* isomers at T_{CO}; $\Delta G_{T_{CO}}$, differences between the free enthalpies of formation of the *E* and *Z* isomers at T_{CO}.

$CF_3N{=}CHBr$ show some interesting features: The C–H vibrations are very weak in the infrared spectra, so that they cannot be observed at a pressure of 5 mbar. Spectra recorded at higher pressures result in their being problems in distinguishing between fundamentals and overtones. In the Raman, however, the C–H vibrations are very intense, but their ratio does not reflect the mole ratio of the isomers. This is especially striking in the case of $CF_3N{=}CHF$ (1.7:1 peak area vs. 15.4:1 from the NMR spectrum). This may be due to very different polarizabilities of the C–H bond depending on its position cis or trans to the nitrogen lone pair. All of these methanimines exhibit absorption bands for the C=N vibrations between 1600 and 1750 cm^{-1}.

NMR Data. The NMR data of the substituted methanimines are given in Table V. With the knowledge of which is the predominant isomer of the compounds $CF_3N{=}CHF$ and $CF_3N{=}CHCl$ from electron diffraction, the NMR data of the substituted methanimines are much easier to understand. In $CF_3N{=}CHF$ the fluorine of the *Z* isomer (i.e. that cis to the CF_3 group) resonates at a much lower field than the fluorine of the *E* isomer (i.e. that trans to the CF_3 group). This fact allows the assignment of the spectrum of $CF_3N{=}C(Cl)F$ and the determination of the mole ratio of the isomers, i.e. E:Z = 3.0 ± 0.5, of this compound. In addition assignment of the chemical shift values of the two nonequivalent fluorine atoms of $CF_3N{=}CF_2$ ($\phi_{trans\text{-}CF3} = -50.1$, $\phi_{cis\text{-}CF3} = -30.5$) can be given. In the *E* isomers of $CF_3N{=}CHF$, $CF_3N{=}CHCl$ and $CF_3N{=}CHBr$ the ^1H resonance is observed at lower field than in the *Z* isomers. Furthermore, the signal of the *E* isomer is sharp at room temperature and $^4J_{HF} \approx 1$ Hz can be observed, whereas the signal of the *Z* isomer is broad at room temperature. When the sample is cooled to −65 °C, the signal of the *Z* isomer becomes sharp too and the $^4J_{HF}$ can be determined. This effect might be attributed to the influence of the nitrogen lone pair, which is in the cis position relative to the proton in the *Z* isomer. In contrast to $^4J_{FF}$, $^4J_{HF}$ is almost independent of the position of the hydrogen in relation to the CF_3 group. Although in the cases of the aminomethanimines $CF_3N{=}C(H)N(CF_3)(CX_2H)$ (X = F, Cl and Br) and $CF_3N{=}C(Br)SF_5$ electron diffraction studies have not been made, the NMR interpretations are justified as follows. The ^1H NMR spectra of the aminomethanimines give sharp signals at room temperature. This is a good evidence that the hydrogen atom is trans to the nitrogen lone pair; in other words the *E* isomers of the aminomethanimines are energetically favored and are the only isomers observable by NMR spectroscopy. In $CF_3N{=}C(Br)SF_5$ the cis position of the SF_5 group relative to the CF_3 group would result in an observable $^5J_{FF}$, because FF coupling is mainly through space and not through bonds. The resonance of the CF_3 group occurs as a sharp singlet, and no FF coupling can be observed. This makes the structure with the CF_3 group and the SF_5 group in the trans position more likely, especially because the SF_5 group is a very bulky substituent.

Variable-Temperature NMR Spectra and Thermodynamic Data. The isomerization of $CF_3N{=}CHF$, $CF_3N{=}CHCl$, $CF_3N{=}CHBr$, and $CF_3N{=}CF_2$ was studied by variable-temperature ^{19}F NMR spectroscopy. The results are summarized in Table VI. The largest difference in the free enthalpies of formation between the *E* and the *Z* isomer is shown by $CF_3N{=}CHF$. This is the case both at room temperature and at the coalescence temperature. Consequently, the *E* isomer is much more dominant in the $CF_3N{=}CHF$. It is difficult to rationalize the decrease of ΔG with increasing size of the halogen substituent. The free enthalpy of activation for the isomerization of the compounds $CF_3N{=}CXY$ (X = H, F; Y = F, Cl, Br) shows a minimum for $CF_3N{=}CF_2$ and a maximum for $CF_3N{=}CHCl$ (Table VI). This can be explained by two contrary effects. The first concerns the electronegativity of the substituents X and Y. High electronegativity of X and Y lowers the activation barrier; i.e., $CF_3N{=}CF_2$ has the smallest value (69.5 ± 1.3 kJ/mol) of all the compounds studied. The second concerns the size of the substituents X and Y. Increasing size lowers the free enthalpy of activation, explaining the decrease of the activation barrier in $CF_3N{=}CHBr$ compared to that in $CF_3N{=}CHCl$. Unfortunately the variable-temperature NMR experiments give no information about the mechanism of the isomerization, which can occur either by inversion at the nitrogen atom or by rotation around the N=C double bond. However, a rotation barrier of 368 kJ/mol has been calculated by ab initio calculations for $ClN{=}CCl_2$,[28] which makes an inversion mechanism more likely.

Registry No. CF_3, 19480-01-4; HF, 7664-39-3; HCl, 7647-01-0; HBr, 10035-10-6; ClF, 7790-89-8; SF_5Br, 15607-89-3; (*E*)-$CF_3N{=}CHF$, 99298-35-8; (*Z*)-$CF_3N{=}CHF$, 99298-36-9; CF_3NHCHF_2, 99298-37-0; (*E*)-$CF_3N{=}CHCl$, 99298-38-1; (*Z*)-$CF_3N{=}CHCl$, 99298-39-2; (*E*)-$CF_3N{=}CHBr$, 99298-40-5; (*Z*)-$CF_3N{=}CHBr$, 99298-41-6; (*E*)-$CF_3N{=}CClF$, 99298-42-7; (*Z*)-$CF_3N{=}CClF$, 99298-43-8; $CF_3N{=}CF_2$, 371-71-1; $CF_3N{=}CCl_2$, 659-92-7; $CF_3N{=}C(Br)SF_5$, 99298-44-9; $CF_3N{=}CHN(CF_3)CHF_2$, 99298-45-0; $CF_3N{=}CHN(CF_3)CHCl_2$, 99298-46-1; $CF_3N{=}CHN(CF_3)CHBr_2$, 99298-47-2; $CF_3N{=}CHN(CF_3)_2$, 99298-48-3; $(CF_3)_2NH$, 371-77-7.

---

(28) Kalcher, K.; Kosmus, W. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1981**, *36A*, 391.