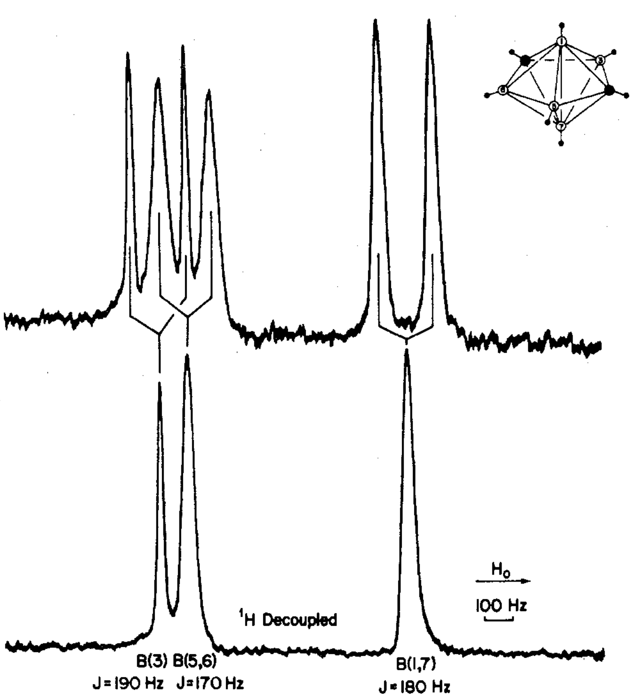

Figure 9. ^{11}B NMR of $C_2B_5H_7$.

presence of the reciprocal effect is ambiguous in the fluorinated carboranes. It seems that the general trend of substituent effects for ^{11}B NMR resonances is followed when fluorine is substituted on the cage.

Only isomers with one and two fluorines on the cage were isolated and identified. (There were other peaks in the gas chromatogram of the crude mixture which probably were the other isomers of $F_2C_2B_5H_5$, but they were not abundant enough to collect and characterize). However, mass spectral evidence indicated that in the mixture species with three or four fluorines on the cage were present. If large quantities of material were fluorinated, it would probably be possible to isolate some of the other isomers. The fact that each reaction yielded some $C_2B_5H_7$ as well as BF_3 and $BF_2CH_2BF_2$ might indicate that the fluorination proceeded to a certain extent and then decomposition of the fluorinated product occurred. Whether the last stable fluorinated carborane was $C_2B_5H_3F_4$ and adding one more fluorine destabilized the cage so much that it decomposed or whether something in the fluorination technique itself caused the decomposition of the cage is not clear.

The isomers with one, two, three, and four fluorines present were not pyrophoric as was $BF_2CH_2BF_2$, but they were definitely moisture sensitive and possibly thermally unstable. Even at 0° in an evacuated, flame-dried tube, substantial decomposition occurred. Spectroscopic studies of organometallic compounds prepared from these partially fluorinated lower carboranes may be a valuable source of structural information.

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Registry No. I, 55124-14-6; II, 55124-15-7; III, 55124-16-8; IV, 55124-17-9; V, 55124-18-0; VI, 55145-42-1; VII, 55145-41-0; $C_2B_5H_7$, 20693-69-0.

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Gas-Phase Molecular Structure of Trifluoromethyliminosulfur Difluoride [F_3CNSF_2]

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Structural and dynamic parameters for trifluoromethyliminosulfur difluoride [F_3CNSF_2] were found by least-squares fitting of the calculated to the experimental molecular–electron scattering function, over the range q = 10–125 Å^{-1}. The r_g parameters are C—F = 1.332 ± 0.005 Å, [S=N] = 1.447 ± 0.006 Å, N—C = 1.469 ± 0.010 Å, S—F = 1.583 ± 0.004 Å, ∠CNS = 130.4 ± 0.7°, ∠NSF = 112.6 ± 0.5°, ∠FSF = 81.1 ± 1.6°, and ∠NCF = 110.3 ± 0.4°. A wide range of models were tested, covering many positional isomers about the S=N and N—C bonds. The bisector of the SF_2 angle is essentially cis to the N—C bond; the thermal average position of the CF_3 group is approximately gauche with respect to the N—S bond.

Introduction

Investigation of the physical and chemical properties of sulfur tetrafluoride led to a new class of compounds, the iminosulfur difluorides. Glemser and Schröder[1] reported the synthesis of a compound with the empirical formula NSF_3; it was assigned the structural formula $FN{=}SF_2$. Reactions of alkyl isocyanates with SF_4 generate compounds of the type $RN{=}SF_2$.[2] Of these, F_3CNSF_2 is of special interest, since its structure is representative of a uniquely bonded collection of atoms which heretofore had not been quantitatively investigated. One presumes that the nonbonding electron pair associated with the nitrogen atom induces a nonlinear configuration to CNS. Furthermore, the double-bonded N=S, plus the nonbonding electron pair on the sulfur atom, places the terminal fluorine atoms in a unique charge distribution. To resolve the question of the cis–trans conformation about

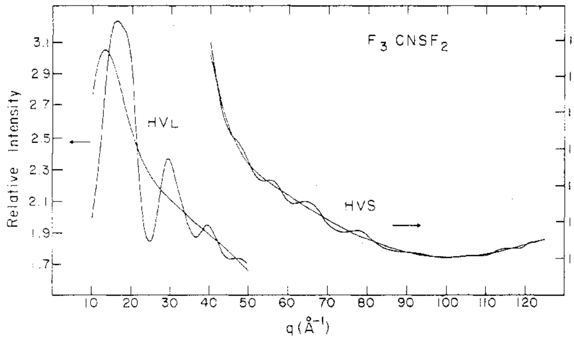

Figure 1. Relative intensity functions and refined backgrounds for F_3CNSF_2.

Table I. Geometric Parameters for F_3CNSF_2[a]

	CF_3NSF_2 (r_g)	$ClNSF_2$[c] (r_g)	$Hg(NSF_2)_2$[d] (xtal)
C–F	1.332 (0.005)[b]		
S=N	1.447 (0.006)	1.476 (0.003)	1.439 (0.014)
N–C	1.469 (0.010)		
S–F	1.583 (0.004)	1.596 (0.002)	
∠CNS	130.4 (0.7)	120.0 (0.2)	
∠NSF	112.6 (0.5)	111.2 (0.1)	
∠FSF	81.1 (1.6)	89.8 (0.2)	
∠NCF	110.3 (0.4)		
τ(CNSα)	7.9 (1.5)[e]		
τ(SNCF$_1$)	26.9 (2.2)[f]		

[a] All distances and l_{ij}'s in angstroms; all angles in degrees. [b] Estimated errors are given as 3 times the calculated standard deviation, plus a minor correction for the scale factor. [c] Reference 11. [d] Reference 12. [e] The angle between the bisector (α) and the SNC plane. [f] The angle between CF_1 and the SNC plane.

N=S and to establish the local symmetry for the SF_2 group, a gas-phase electron diffraction investigation of F_3CNSF_2 was undertaken.

Experimental Section

The sample of trifluoromethyliminosulfur difluoride was distilled prior to use. It was frozen and degassed before each photograph was taken. During the exposures the reservoir was raised to −78.6° to supply a pressure of ~10 Torr. The lead tube and the nozzle were kept at room temperature. The diffraction patterns were recorded on Kodak process plates, using a sector which was cut to flatten the scattering from benzene. MgO powder was mounted on a screen directly above the nozzle tip, and it was slid into position for recording calibration photographs before and after each set of gas photographs.

Six ring diameters of each MgO pattern were measured and used to determine the wavelength and sample-to-plate distances[3,4] at two positions: 124.1 mm (HVS), and 256.6 mm (HVL). The accelerating voltage was 61.86 kV. Two ranges of scattering angles were thus recorded: q = 10–50 Å^{-1} and q = 40–125 Å^{-1} [$q \equiv (40/\lambda)\sin(\theta/2)$].

Data Reduction and Results

The diffraction photographs were scanned with a modified Jarrel-Ash microdensitometer[5] at 100-μm intervals for HVS and at 200-μm intervals for the HVL plates. The optical densities were converted to relative intensities, using the two-plate procedure described by Hencher and Bauer;[6] the radial distances were corrected for flatness of the photographic plate. A seven-point interpolation procedure was used to convert the digitized microdensitometer values to total scattered intensities at integral q (Å^{-1}) values. Three tracings of each plate were averaged.[5] The interpolation procedure introduces no significant correlations between adjacent q values, since generally six points are recorded between integral q's. The total scattered intensity functions and the final "refined" background functions are plotted in Figure 1 and listed in Appendix A (supplementary material).

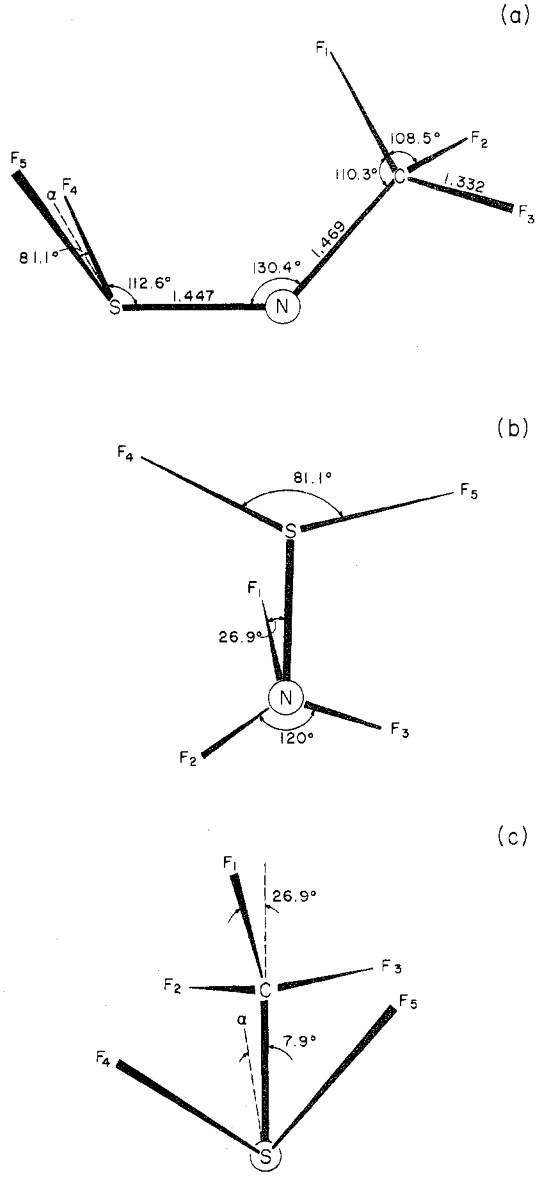

Figure 2. Projected structures for F_3CNSF_2: (a) side view; (b) projected view along the CN bond; (c) projected view along the SN bond.

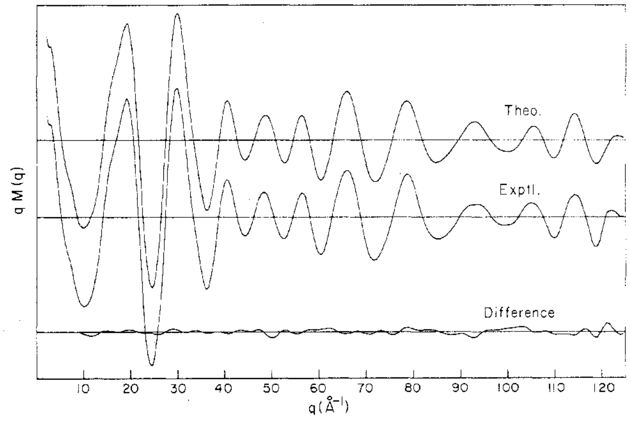

Figure 3. Theoretical and experimental functions for the molecular scattered intensity.

These data were reduced following our previously described procedures.[7,8] Hilderbrandt's algorithm[9] was used to generate the molecular coordinates from the atomic parameters. Most of the calculations were performed with an augmented DEC PDP-9 computer and a CRT visual display for interactive data reduction.[8] The final interatomic distances and bond angles

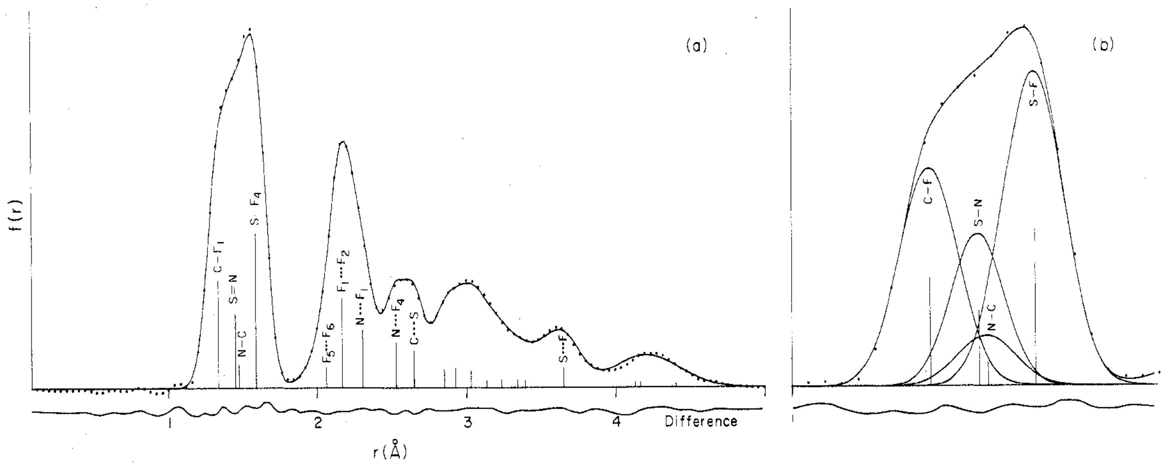

Figure 4. Comparison of the calculated with the experimental (dots) radial distribution curves: (a) entire range; (b) expanded portion showing resolution of the region between 1 and 2 A.

Table II. Root-Mean-Square Amplitudes

Atom pair	Distance, A	l_{ij}, A
C–F	1.332	0.043 (0.003)
S=N	1.447	0.034 (0.013)
N–C	1.469	0.045 (0.017)
S–F	1.583	0.049 (0.004)
$F_5 \cdots F_6$	2.06	0.090 (0.028)
$F_1 \cdots F_2$	2.16	0.056 (0.011)
$N \cdots F_1$	2.30	0.068 (0.017)
$N \cdots F_4$	2.52	0.059 (0.030)
$C \cdots S$	2.64	0.057 (0.027)
$F_1 \cdots F_4$	3.84	0.11 (0.021)

are listed in Table I, and the dynamic parameters, in Table II. These were obtained by an iterative least-squares procedure for fitting the molecular scattering function calculated for the best model to that observed. The final model is illustrated in Figure 2a. The estimated uncertainties were set equal to 3 times the calculated standard deviations plus an estimated error due to the scale factor, which is relatively trivial. Figure 2b illustrates the orientation of the F_3C group as viewed along the C—N bond; the projected image of the model as seen along the S═N bond (Figure 2c) reveals the orientation of the S—F bonds relative to the CNS plane. Thus, the minimum energy conformation is essentially cis.

The computed and calculated scattering functions are compared in Figure 3; Figure 4a shows the experimental radial distribution function (dots), the computed curve for the final model, and the corresponding difference curve. The r_{ij} positions are indicated by bars whose height is proportional to nZ_iZ_j/r_{ij}. Figure 4b is a resolved first peak on an expanded scale.

A number of models were tested and rejected because they did not fit the experimental scattered intensity function. These are best described by imposing C_{2v} symmetry on the $N{=}SF_2$ group and testing a sequence of angles for orientation of a line which originates at the sulfur atom and bisects the SF_2 angle (designated Sα) about the CNS plane for a wide range of FSF angles from 90 to 180°. The only model which is consistent with our data has $\angle FSF = 81.1°$, $\angle FSN = 112.6°$, and the Sα line rotated 7.9° from the symmetric position about the SNC plane. Of course, this should be considered as the *thermal average* value, for which the minimum energy position *may* actually be in the CNS plane.

Once the correct model was found, all of the geometric parameters were varied simultaneously. The corresponding correlation matrix is listed in Appendix B (supplementary material). Since there were 20 different l_{ij}'s, 15 distinct values were selected for variation in a cyclic least-squares fitting procedure. These were divided into two groups, the bonded plus adjacent atom pairs and all of the others. Convergence was obtained for all the combinations tested (Table II). The radial distribution curve for the best model which fitted the experimental function has an R factor of 0.0251: the calculated molecular scattering function fits the experimental curve with $\sigma = 0.0147$ and an R factor of 0.0611.

Discussion

The bond distances and angles found in F_3CNSF_2 are quite close to comparable internuclear separations reported for the few analogous compounds which have been investigated. The dimensions of CF_3 agree well with those found in many X–CF_3 species.[10] The iminosulfur difluoride parameters are comparable to but somewhat smaller than those in chloroiminosulfur difluoride:[11] S═N = 1.476 Å, S—F = 1.596 Å, $\angle ClNS = 120°$, $\angle NSF = 111.2°$, and $\angle FSF = 89.8°$ (see Table I). The larger S═N bond distance in $ClNSF_2$ (by 0.029 Å) may be due to the electronegativity of the Cl atom. The $\angle CNS$ is 10° larger and $\angle FSF$ is 8.8° smaller in F_3CNSF_2 than in the chloro derivative. There is clearly considerable p–π interaction in the latter compound which is not present in the former. The $\angle NSF$ angles are almost identical in the two compounds, while the S—F distances are nearly equal, to within the sum of the stated error limits.

Registry No. F_3CNSF_2, 1512-14-7.

Supplementary Material Available. Appendices A and B, showing total scattered intensity functions, final refined background functions, and the parameter correlation matrix for CF_3NSF_2, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50052R.

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