# Molecular Structure of Tris(trifluoromethylthio)amine by Gas-phase Electron Diffraction and Nuclear Magnetic Resonance Spectroscopy

By **Colin J. Marsden** and **Lawrence S. Bartell,*** Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

The structure and amplitudes of vibration of $N(SCF_3)_3$ have been investigated by electron diffraction. Principal structural parameters and uncertainties ($3\sigma$) are: $r_g$(C–F) 1.336(2), $r_g$(C–S) 1.825(6), and $r_g$(S–N) 1.705(5) Å; S–N–S 118.8(0.7), N–S–C 100.1(1.0), and F–C–F 108.3(0.3)°. The $CF_3$ groups, in or close to staggered conformations, are tilted by 4.8(0.6)°. The molecule appears not to possess $C_3$ symmetry. The NSC planes are perpendicular (within experimental uncertainties) to the $S_3$ plane. Two $CF_3$ groups lie above this plane, one below it. Fluorine-19 n.m.r. spectra show a single line at room temperature, but split into two components of relative intensity 2 : 1 below *ca.* −65 °C. From an analysis of line shapes, the barrier to internal rotation about an S–N bond has been found to be 6(1) kcal $mol^{-1}$. The near planarity of the $NS_3$ skeleton is discussed in terms of $p \longrightarrow d$ $\pi$ bonding and steric interactions. Results of semiempirical molecular-orbital calculations on a model compound are analysed.

VSEPR theory [1] is widely used for rationalising observed molecular structures, and is remarkably successful considering its simplicity. Anomalous molecules such as $N(SiH_3)_3$,[2] $O(PF_2)_2$,[3] or $O(SiH_3)_2$,[4] whose valence angles at the central atom are far larger than expected by VSEPR theory, are therefore of particular importance. The compound $N(SCF_3)_3$ has been shown to be virtually non-basic.[5] We were interested to ascertain whether it contains a planar $NS_3$ skeleton, similar to $N(SiH_3)_3$,[2] or whether it is pyramidal as is $NCl_3$.[6] Many workers have argued that $p \longrightarrow d$ $\pi$ bonding is responsible for the unusual geometries mentioned above,[7] but others have stressed that steric considerations are significant.[8] We hoped that the determination of the molecular structure of $N(SCF_3)_3$ would provide further evidence for the resolution of this question.

## EXPERIMENTAL

A sample of $N(SCF_3)_3$ was prepared from the reaction between $CF_3SNH_2$ and $CF_3SCl$ in the presence of $NMe_3$.[5] That fraction of the products passing through a trap at 0 °C but consistently retained by a trap at −45 °C was found to be tensometrically pure. Its i.r. spectrum agreed with that reported,[5] its liquid-phase Raman spectrum, which has not been published, showed no evidence of impurities, and two determinations of its gas-phase molecular weight gave 309 and 315 (calc.: 317).

Electron-diffraction patterns were recorded on 4 × 5 in Kodak Electron Image plates using the diffraction unit at the University of Michigan [9] equipped with an $r^3$ sector, at the 21-, 11-, and 7-cm distances. The energy of the incident electrons was 40 keV. Experimental conditions are given in Table 1. Absorbances were converted into exposures using expression (1) [10] in which $E$ and $A$ are respectively, the exposure and absorbance. Fuller details of the data-reduction procedures may be found elsewhere.[11]

$$E = A(1 + 0.116A + 0.0179A^2 + 0.00312A^3) \quad (1)$$

TABLE 1

Experimental conditions under which diffraction patterns of $N(SCF_3)_3$ were recorded

| | | | |
|---|---|---|---|
| Nozzle-plate distance/cm | 21.060 | 11.113 | 6.528 |
| Exposure time/s | 3—4 | 7—10 | 20—30 |
| Sample temperature/°C | 10 | 10 | 10 |
| Sample pressure/Torr | 15 | 15 | 15 |
| Nozzle temperature/°C | 24 | 24 | 24 |
| Beam current/µA | 0.59 | 0.58 | 0.58 |
| Diameter of Pt nozzle/mm | 0.25 | 0.25 | 0.25 |
| Nozzle-beam distance/mm | 0.44 | 0.45 | 0.43 |
| Number of plates used | 4 | 4 | 5 |

Molecular parameters were refined by a least-squares procedure which imposed geometrical self-consistency on the internuclear distances. Atomic elastic and inelastic

---

[1] R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, 1957, **4**, 389; R. J. Gillespie, 'Molecular Geometry,' Van Nostrand-Reinhold, New York, 1972.

[2] K. Hedberg, *J. Amer. Chem. Soc.*, 1955, **77**, 6491; B. Beagley and A. R. Conrad, *Trans. Faraday Soc.*, 1970, **66**, 2740.

[3] D. E. J. Arnold and D. W. H. Rankin, *J. Fluorine Chem.*, 1972—1973, **2**, 405; H. Y. Yow, R. W. Rudolph, and L. S. Bartell, *J. Mol. Structure*, 1975, **28**, 205.

[4] A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg, and M. Traetteberg, *Acta Chem. Scand.*, 1963, **17**, 2455.

[5] A. Haas and P. Schott, *Chem. Ber.*, 1968, **101**, 3407.

[6] H. B. Bürgi, D. Stedman, and L. S. Bartell, *J. Mol. Structure*, 1971, **10**, 31.

[7] D. W. J. Cruickshank, *J. Chem. Soc.*, 1961, 5486; E. A. V. Ebsworth in 'Organometallic Compounds of the Group IV Elements,' ed. A. G. MacDiarmid, Marcel Dekker, New York, 1968.

[8] (*a*) C. Glidewell and A. G. Robiette, *Chem. Phys. Letters*, 1974, **28**, 290; (*b*) C. Glidewell, *Inorg. Chim. Acta*, 1975, **12**, 219.

[9] L. S. Bartell in 'Physical Methods in Chemistry,' 4th edn., eds. A. Weissberger and B. W. Rossiter, Interscience, New York, 1973.

[10] W. J. Adams, personal communication.

[11] C. J. Marsden and L. S. Bartell, *Inorg. Chem.*, 1976, **15**, 2713.

scattering factors of Schäfer *et al.*[12] were used. Diagonal weight matrices were employed, with elements proportional to $s$, but the uncertainties quoted were augmented to take into account the correlation between neighbouring data points ($\gamma \approx 1$ Å).[9] Intensity data for the three camera distances were treated separately until the individual background functions had been established, leading to acceptable matching of $M(s)$ in the overlapping regions. Experimental levelled intensities and background functions are listed in Supplementary Publication No. SUP 22044 (12 pp.).* The indices of resolution for the 21-, 11-, and 7-cm data were 0.81, 0.84, and 0.79. A composite data set, covering the range $3.8 \leqslant s \leqslant 48.4$ in increments of $\Delta s = \pi/10$, was obtained by blending together the three individual data sets. Radial distribution functions were calculated using a damping factor of $\exp(-0.0015s^2)$. Anharmonicity constants were taken to be 2.0 for bonded distances, 1.0 for non-bonded distances.[13] No corrections were applied for shrinkage effects.[14]

Nuclear magnetic resonance spectra were obtained in the continuous-wave (c.w.) mode using a Varian model A-56/60 n.m.r. spectrometer. The field was locked on an external water resonance, and the temperature was maintained within (±1 °C) with a Varian V-4343 variable-temperature accessory.

## RESULTS

*Structure Analysis*.—Several different molecular models were investigated during the course of this work. The simplest, adopted initially, imposed $C_3$ symmetry on the molecule and local $C_{3v}$ symmetry on each $CF_3$ group. This model requires nine geometrical parameters to define the structure, chosen to be the C–F, C–S, and S–N bond lengths together with six angles, an angle $\alpha$ between the molecular three-fold axis and an S–N bond, the N–S–C bond angle, an angle $\beta$ between the local three-fold axis of a $CF_3$ group and a C–F bond, an angle $\gamma$ defining the tilt of the $CF_3$ groups, an angle $\delta$ denoting the dihedral angle between an NSC plane and the plane containing the molecular three-fold axis and the N and S atoms, and finally an angle $\varepsilon$ referring to the conformation of the $CF_3$ groups. A non-zero angle of tilt $\gamma$ indicates that the three-fold axis of a $CF_3$ group is not collinear with the S–C bond, but lies in the NSC plane, such that a positive value of $\gamma$ decreases the $S^1 \cdots F^{11}$ distance. The atomic numbering scheme adopted is shown in Figure 1, which gives a view of the molecule using the final calculated structural parameters. If $0 < \delta < 180°$, $C^1$ is closer to $S^2$ than to $S^3$. A non-zero value of $\varepsilon$ implies that the $CF_3$ groups are twisted about their three-fold axes away from the staggered conformation, at which $\varepsilon = 0°$. For $0 < \varepsilon < 180°$, $F^{11}$ is closer to $S^3$ than to $S^2$. It will be convenient to refer hereafter to the three bond lengths, the N–S–C angle, and the angles $\alpha$, $\beta$, and $\gamma$ as the parameters defining the short-range structure of $N(SCF_3)_3$, that is essentially the distances within one $N(SCF_3)$ group. The angles $\delta$ and $\varepsilon$ determine the long-range structure, the disposition of one $N(SCF_3)$ group with respect to the others.

Experimental and final calculated molecular intensities are compared in Figure 2. Five distinct peaks arising from the bonded distances and principal 1,3 non-bonded distances may be seen in the experimental radial distribution function (Figure 3). The short-range structure of $N(SCF_3)_3$ was readily established, but some difficulty was experienced in finding suitable values of $\delta$ and $\varepsilon$, which are determined by the position and shape of the four less well defined features in the radial-distribution function, due to the many long non-bonded distances. Refinements with $\delta$ *ca.* 90° produced a very poor fit with the observed molecular-intensity data. Models with $\delta$ *ca.* 0° were much more successful, but the fit was appreciably less good than that normally obtained in this laboratory. The misfit was concentrated in distances over 3 Å in the radial-distribution function.

This problem was overcome by relaxing the constraint of $C_3$ molecular symmetry. Separate values of $\delta$ and $\varepsilon$ were refined for each $CF_3$ group, raising the number of independent geometrical parameters to 13 in all. A good fit was obtained only if two angles $\delta$ were *ca.* 0°, while the third was *ca.* 180°. Two angles $\varepsilon$ refined to values close to zero; the third was appreciably different from zero, but its uncertainty is large and we do not consider that a deviation from zero is unequivocally established.

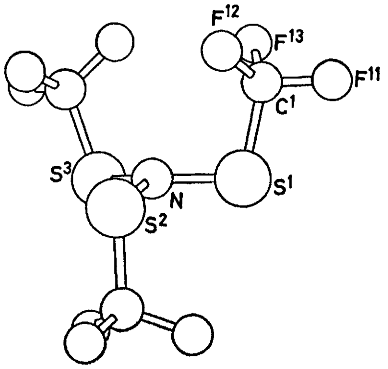

FIGURE 1 Perspective of the molecule $N(SCF_3)_3$ showing the atom-labelling scheme

Models were investigated in which one angle $\alpha$, for the $SCF_3$ group with angle $\delta$ *ca.* 180°, was less than 90° by the same amount as the other angles $\alpha$ exceeded 90°. These models provided a slightly poorer fit to the experimental data than did the simpler ones for which all the three angles $\alpha$ were constrained to be equal, but the difference in fit was not sufficiently large to enable us to exclude them with any confidence. We doubt that electron-diffraction data alone can rule out the presence of a small concentration of an isomer with all angles $\delta$ *ca.* 0°, although we did not investigate this point in any detail. The n.m.r. results discussed below provide no evidence for the existence of such an isomer in the liquid phase.

Amplitudes of vibration were refined satisfactorily for the bonded and principal 1,3 non-bonded distances, and the values appear reasonable. Attempts to refine amplitudes for the important 1,5 distances showed that these had large uncertainties, and that they were highly correlated with the angles $\delta$ and $\varepsilon$. Accordingly, we fixed the amplitudes for all the 1,4 and more remote distances, as well as for the 1,3 $C \cdots N$ distance, at the following values, which

---

* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[12] L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, 1971, **55**, 3055.

[13] L. S. Bartell, *J. Chem. Phys.*, 1955, **23**, 1219.

[14] O. Bastiansen and M. Traetteberg, *Acta Cryst.*, 1960, **13**, 1108; Y. Morino, *ibid.*, p. 1107.

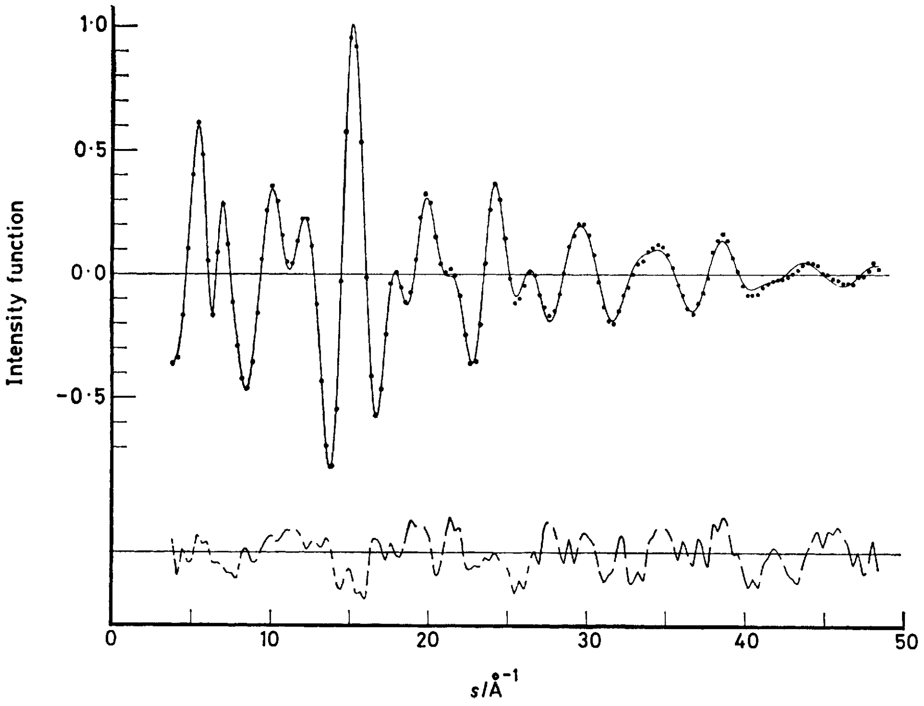

FIGURE 2 Experimental (●) and calculated [$sM(s)$] molecular intensity functions for $N(SCF_3)_3$. (— — —), $5\Delta sM(s)$. $\Delta sM(s) = sM(s)_{exp.} - sM(s)_{calc.}$

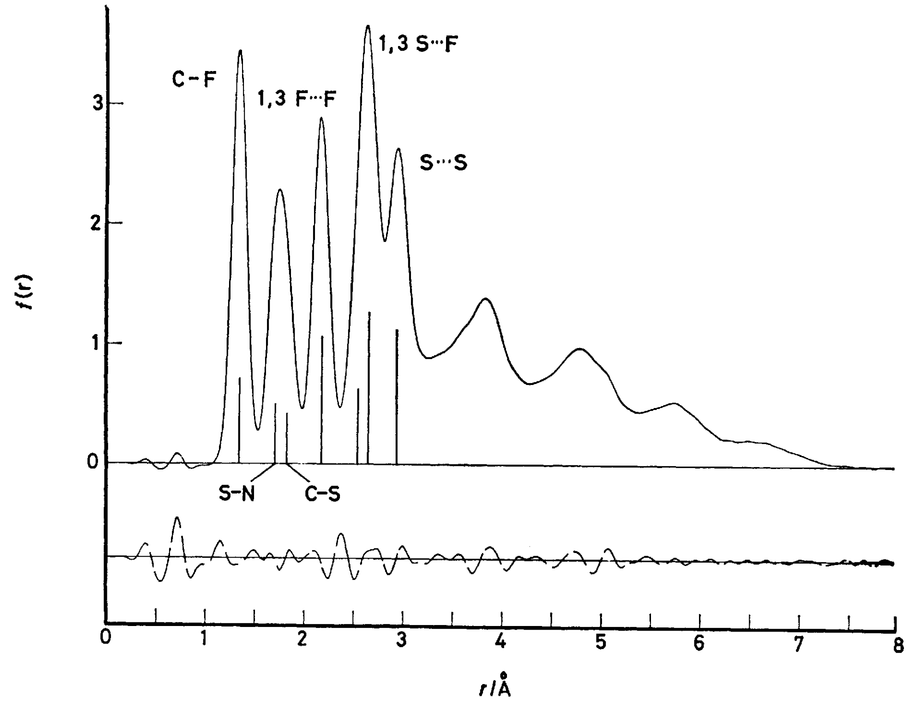

FIGURE 3 Experimental radial-distribution function for $N(SCF_3)_3$. (— — —), $4\Delta f(r)$. $\Delta f(r) = f(r)_{exp.} - f(r)_{calc}$

seemed to us to be plausible: N · · · C 0.08, C · · · S 0.14, N · · · F 0.16, S · · · F 0.20, C · · · F 0.20, and F · · · F 0.25 Å. Moderate variations in the more important of these amplitudes led to very small changes in the overall fit of the data, and to insignificant differences in the short-range geometrical parameters, but to large changes in both the values and standard deviations of the angles δ and ε. We did not think it profitable to attempt to find the ' best ' amplitude for each distinct distance, of which there are 89 in all. Since spectroscopic information on the low-frequency bending and torsional vibrations is completely lacking, and probably very difficult to obtain, any calculations of amplitudes of vibration would be based on arbitrary assumptions and of doubtful value. We consider that electron diffraction alone cannot establish with precision the conformation adopted by a molecule as complex as $N(SCF_3)_3$.

TABLE 2

Structural parameters[a] for $N(SCF_3)_3$

| | | |
|---|---|---|
| (*a*) Bond lengths ($r$/Å) | | |
| C–F | ($r_1$) | 1.336 (2) |
| C–S | ($r_2$) | 1.825 (6) |
| S–N | ($r_3$) | 1.705 (5) |
| (*b*) Angles (°) | | |
| S–N–S | | 118.8 (0.6) |
| N–S–C | (2) | 100.1 (1.0) |
| F–C–F | | 108.3 (0.3) |
| $CF_3$ tilt | (4) | 4.8 (0.6) |
| $\delta_1$ | (5) | 7 (9) |
| $\delta_2$ | (6) | 180 (5) |
| $\delta_3$ | (7) | −3 (8) |
| $\varepsilon_1$ | (8) | 0 (12) |
| $\varepsilon_2$ | (9) | −7 (9) |
| $\varepsilon_3$ | (10) | 25 (20) |
| (*c*) Amplitudes ($l$/Å) | | |
| C–F | ($l_1$) | 0.045 (3) |
| S–N | ($l_2$) | 0.053 (7) |
| C–S | ($l_3$) | 0.056 (9) |
| F · · · F 1,3 | ($l_4$) | 0.058 (3) |
| S · · · F 1,3 | ($l_5$) | 0.066 (6) |
| S · · · S | ($l_6$) | 0.072 (4) |
| $\sigma(I)/\bar{I}$[b] | | $7.44 \times 10^{-4}$ |

[a] See text for description of angles δ and ε. Uncertainties, given in units of the least significant digit, are 3σ, including random and suspected systematic errors, the effects of correlation between neighbouring data points ($\gamma \approx 1$ Å), and of several restrictive assumptions in the molecular model used. [b] Mean fractional standard deviation of diffraction intensity points.

Final calculated values of the parameters are given in Table 2. Uncertainties quoted are 3σ, and include not only random errors and known possible systematic errors but also our estimates of the effects of correlation between neighbouring data points ($\gamma \approx 1$ Å),[9] correlations between various geometrical parameters, and the uncertainties introduced by fixing many amplitudes of vibration for the long non-bonded distances. Errors introduced by the neglect of shrinkage effects [14] have not been included. The correlation matrix is presented in Table 3. There are several moderately large elements connecting some of the short-range parameters, but none is particularly worrying. The largest elements are to be found among the angles δ and ε, since six parameters must be determined from the shape of four poorly defined features in the radial-distribution function. These correlations add to the difficulty of determining realistic uncertainties for the angles δ and ε.

*N.M.R. Spectrum.*—Since the conformation deduced from the diffraction data was unexpected, and might have been influenced by the choice of inappropriate amplitudes of vibration for the many long non-bonded distances, we thought it of interest to examine the $^{19}F$ n.m.r. spectrum of $N(SCF_3)_3$ at low temperatures. The sample used was dissolved in $CCl_3F$, giving a solution *ca.* 15% by volume. Representative results are presented in Figure 4. The sharp line seen at room temperature is appreciably broadened at −57 °C, and below −67 °C is split into two peaks which become progressively sharper as the temperature is decreased further. At −96.1 °C, the areas of the two peaks are in the ratio 2.03 : 1. Their chemical shifts are 51.7 p.p.m. for the larger peak and 53.3 p.p.m. for the smaller, relative to $CCl_3F$. No other features attributable to $N(SCF_3)_3$ were observed in the low-temperature spectrum within 500 Hz in either direction of the larger peak.

TABLE 3

Matrix of correlation coefficients for $N(SCF_3)_3$[a]

| | $r_1$ | $r_2$ | $r_3$ | <1[b] | <2 | <3[c] | <4 | <5 | <6 | <7 | <8 | <9 | <10 | $l_1$ | $l_2$ | $l_3$ | $l_4$ | $l_5$ | $l_6$ | $R$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| σ | 0.43 | 1.4 | 1.1 | 0.38 | 0.32 | 0.07 | 0.15 | 2.0 | 1.5 | 2.3 | 2.5 | 2.2 | 3.7 | 0.64 | 1.7 | 2.4 | 0.84 | 1.8 | 1.3 | 0.008 |
| $r_1$ | 100 | −50 | 4 | 3 | −2 | 64 | −11 | 6 | −3 | 10 | −7 | 3 | −10 | 3 | 17 | 9 | 4 | 12 | −6 | 1 |
| $r_2$ | | 100 | 7 | 4 | −16 | −69 | −16 | 4 | −15 | 4 | −11 | −1 | −5 | 1 | −28 | −10 | 2 | 8 | −5 | 3 |
| $r_3$ | | | 100 | 65 | −41 | −3 | −1 | −9 | −36 | 8 | −15 | −19 | −10 | 0 | 22 | 40 | −5 | 10 | 10 | −2 |
| <1 | | | | 100 | −64 | 6 | 11 | −4 | −56 | 35 | −26 | 10 | −38 | −7 | 9 | 20 | −9 | −12 | 19 | −15 |
| <2 | | | | | 100 | −5 | −7 | 33 | 26 | −3 | 10 | −43 | 5 | 11 | 2 | −8 | 13 | −7 | −17 | 21 |
| <3 | | | | | | 100 | −7 | 8 | 2 | 18 | −2 | 7 | −20 | −1 | 17 | 4 | 1 | 11 | −4 | −3 |
| <4 | | | | | | | 100 | −12 | 8 | −8 | 6 | 15 | 9 | 4 | 7 | 3 | 0 | −71 | 8 | 6 |
| <5 | | | | | | | | 100 | −6 | 85 | −37 | −43 | −78 | 12 | 1 | −1 | 16 | −5 | 0 | 22 |
| <6 | | | | | | | | | 100 | −19 | 54 | −58 | 20 | −8 | −8 | −16 | −6 | −10 | 2 | −13 |
| <7 | | | | | | | | | | 100 | −41— | 18 | −94 | 7 | 1 | 12 | 11 | −10 | 10 | 12 |
| <8 | | | | | | | | | | | 100 | −24 | 25 | −13 | −8 | −11 | −13 | −12 | 2 | −24 |
| <9 | | | | | | | | | | | | 100 | 28 | −7 | −8 | −10 | −7 | −5 | 7 | −13 |
| <10 | | | | | | | | | | | | | 100 | −10 | −1 | −1 | −14 | 7 | −10 | −17 |
| $l_1$ | | | | | | | | | | | | | | 100 | 15 | 11 | 29 | 15 | 4 | 58 |
| $l_2$ | | | | | | | | | | | | | | | 100 | 62 | 9 | 7 | 5 | 24 |
| $l_3$ | | | | | | | | | | | | | | | | 100 | 4 | 8 | 5 | 17 |
| $l_4$ | | | | | | | | | | | | | | | | | 100 | 12 | 2 | 50 |
| $l_5$ | | | | | | | | | | | | | | | | | | 100 | −8 | 26 |
| $l_6$ | | | | | | | | | | | | | | | | | | | 100 | 6 |
| $R$ | | | | | | | | | | | | | | | | | | | | 100 |

[a] Units for σ are $10^{-3}$ Å for distances and amplitudes of vibration, degrees for angles. $R$ is dimensionless. Matrix elements are given by $\rho_{ij} = (M_x)_{ij}/[(M_x)_{ii}(M_x)_{jj}]^{\frac{1}{2}}$, where $M$ is the zeroth order error matrix.[9] Only the upper half of the matrix is given. All entries, except for the standard deviations, have been multiplied by 100. The numbering of the parameters follows from Table 2, except where indicated. [b] Angle α. [c] Angle β. See text for definitions.

The most natural interpretation of these observations is that in the equilibrium conformation of $N(SCF_3)_3$, at least in solution in $CCl_3F$, one $CF_3$ group is in an environment different from the other two. Such a distinction would be expected if the values of two of the angles $\delta$ are 0° but the other is 180°, as deduced from the diffraction data. Torsional motion about the S–N bonds is sufficiently rapid at room temperature that the three $CF_3$ groups are equivalent on the relatively slow n.m.r. time scale, but at temperatures below *ca.* −65 °C the internal rotation is restricted to the extent that one $CF_3$ group is distinguishably different from the other two. We do not think that reduced torsional motion about the C–S bonds is responsible for the changed n.m.r. spectrum at low temperatures. Such a situation would lead to non-equivalence of the fluorines within a $CF_3$ group, and the resulting $AB_2$ or ABC spectrum would be far more complex than the simple two-line pattern observed. An approximate value of 6 ± 1 kcal $mol^{-1}$ was deduced for the barrier to rotation about an S–N bond from measurements of the line shapes [15] in the range −68.5 to −96.1 °C.*

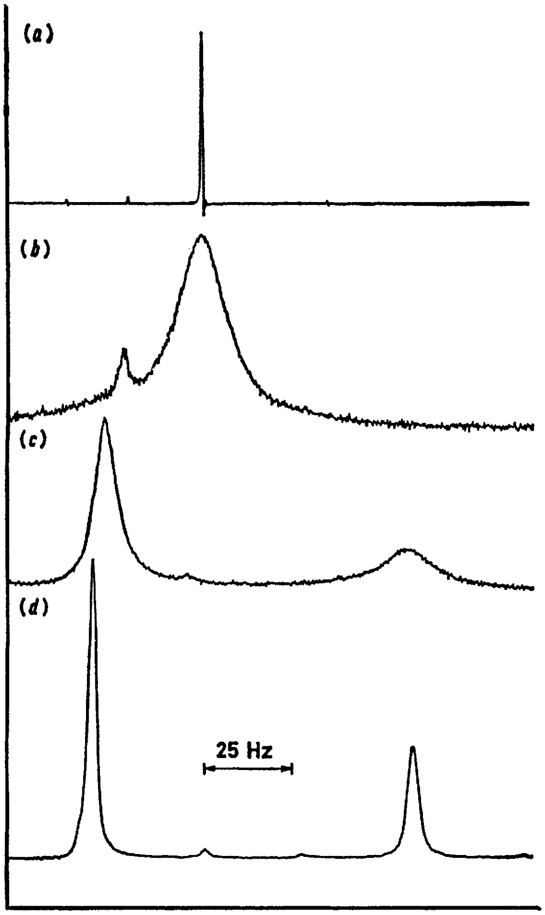

FIGURE 4 N.m.r. spectra of $N(SCF_3)_3$ in $CCl_3F$ at room temperature (*a*) and at −57.5 (*b*), 79.6 (*c*), and −96.1 °C (*d*)

DISCUSSION

Normal values have been found for the C–F bond length and F–C–F bond angle in $N(SCF_3)_3$. The $r_g$(C–S) bond distance of 1.825(2) Å is somewhat longer than in $CF_3SH$,[16] for which an $r_g$ value of 1.802(5) Å has been reported. These two compounds appear to be the only $CF_3S$ derivatives for which precise gas-phase structural data are available. An *X*-ray study of $[OH_3][SO_3(CF_3)]$ [17] revealed a C–S bond length of 1.827(5) Å, similar to that in $N(SCF_3)_3$, although differences of oxidation state and phase render the significance of this comparison uncertain.

Perhaps the most striking aspect of this work is that the $NS_3$ skeleton of $N(SCF_3)_3$ is almost planar, with an S–N–S angle of 118.8(0.2)°. This aspect of the structure is fully consistent with the very low basicity of $N(SCF_3)_3$ [5] towards such species as $BF_3$. It is more difficult to interpret the virtual absence of a dipole moment,[5] in view of the asymmetric disposition of the $SCF_3$ groups. While the neglect of shrinkage corrections [14] will cause the S–N–S angle determined from our diffraction data to be smaller than the equilibrium angle, we doubt that this effect is sufficient to account for all of the deviation from planarity. A Si···Si shrinkage of *ca.* 0.007 Å is observed experimentally in $N(SiH_3)_3$;[2] inclusion of a correction of this magnitude for the S···S distance in $N(SCF_3)_3$ would increase the S–N–S angle from 118.8 to 119.2°. The angle between the approximate three-fold axis passing through the N atom and an S–N bond is 96.4(0.5)°; it would be reduced to 94.1° with the adoption of the shrinkage correction discussed above. In view of the asymmetry of non-bonded repulsions about the S atoms, a small deviation from planarity of the $NS_3$ skeleton could be anticipated if bonding forces alone favoured a planar skeleton. Small bond bendings of similar magnitudes and direction have been discussed by Hirshfeld.[18]

There is a widely held view [7] that the chief cause of the unusual stereochemistry found in such molecules as $N(SiH_3)_3$,[2] $O(SiH_3)_2$,[4] and $O(PF_2)_2$,[3] in which the bond angles around the central atom are larger than predicted by VSEPR theory,[1] is the existence of $p \longrightarrow d\pi$ bonding between the central donor atom and the second-row ligands. Such $\pi$ bonding is evidently favoured by planar geometry around N or by linear groups about O; furthermore, the stereochemical activity of the N or O lone pairs is reduced by $\pi$ delocalisation. More recently, in an extension of an idea put forward several years ago,[19] it has been suggested [8] that steric requirements of ligands determine the angular disposition of bonds in a molecule such as $N(SiH_3)_3$. Close examination of 1,3 non-bonded distances in a wide range of compounds shows that this concept cannot be lightly disregarded. A set of 'one-angle non-bonded radii' has been published by Glidewell,[8b] analogous to the familiar van der

---

* Throughout this paper: 1 cal = 4.184 J; 1 eV ≈ $1.60 \times 10^{-19}$ J; 1 Torr = (101 325/760) Pa.

[15] L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, 1959, **30**, 899.

[16] C. J. Marsden, *J. Mol. Structure*, 1974, **21**, 168.

[17] J. B. Spencer and J.-O. Lundgren, *Acta Cryst.*, 1973, **B29**, 1923.

[18] F. Hirshfeld, *Israel J. Chem.*, 1964, **2**, 87.

[19] L. S. Bartell, *J. Chem. Phys.*, 1960, **32**, 827.

Waals radii, but to be used for two atoms bonded to a common atom. One-angle radii are *ca.* 15—25% smaller than van der Waals radii.

It is important to realise that the angles at a central atom are determined not only by the 1,3 non-bonded distances, but also by the bond lengths. Whilst fully admitting that such procedures are to a certain extent arbitrary and subjective, we believe we can show beyond reasonable doubt that the N–S distance in $N(SCF_3)_3$ is shorter than would be expected for a single bond. A comparison of the bond pairs N–S and N–Cl with C–S and C–Cl is instructive. The $r_s$(C–S) bond length in $SMe_2$ [20] of 1.802(2) Å is longer than the $r_s$(C–Cl) distance in $CH_3Cl$ [21] of 1.781(1)Å by 0.021 Å. However, the $r_g$(N–S) distance in $N(SCF_3)_3$ is 1.705(2) Å, which is 0.054 Å *shorter* than the $r_g$ (N–Cl) bond length of 1.759(2) Å in $NCl_3$.[6] Thus the shortening of the N–S bond in $N(SCF_3)_3$ compared to the value expected for a single bond is perhaps 0.075 Å. There is no unique choice of reference compounds for such comparisons, but our selection appears as reasonable as any. We consider it natural to account for this shortening in terms of $p \longrightarrow d\ \pi$ bonding between N and S. By the use of similar arguments, the N–Si bond length in $N(SiH_3)_3$ has been shown [6] to be 0.110 Å shorter than that expected for a single bond. These observations suggest that $p \longrightarrow d\ \pi$ bonding decreases in the order N–Si > N–S > N–Cl. If this is so, factors other than the energy of the *d* orbitals on the neutral acceptor atom must be involved, since the *d* orbitals on Cl are less diffuse and lower in energy than those on S prior to bonding. If $p \longrightarrow d\ \pi$ bonding is significant in N–Si and N–S bonds, species containing negative charges formally located on N and/or fewer than three acceptor ligands grouped around N would be expected to have shorter bonds than the parent, neutral, trisubstituted species. Available evidence is consistent with this idea. The observed N–Si bond lengths in the series $[N(SiMe_3)_2]^-$,[22] $NMe_2(SiH_3)$,[23] $NH(SiH_3)_2$,[24] and $N(SiH_3)_3$ [2] are 1.64(1), 1.716(4), 1.727(3), and 1.735(2) Å. N–S Bond distances in $[NH_2(SO_3)]^-$,[25] $[NH(SO_3)_2]^{2-}$,[26] $[N(SO_3)_3]^{3-}$,[27] and $[NH_3^+]$-$[SO_3^-]$ [28] are 1.666(6), 1.662(5), 1.71(2), and 1.76(2) Å.

Our interpretation of the evidence concerning bond angles in these systems is that steric considerations are of great importance. The S · · · S distance in $N(SCF_3)_3$ is 2.934(2) Å, close to the sum of the one-angle radii assigned by Glidewell,[8b] which is 2.90 Å. Glidewell stated explicitly [8b] that 'atoms in molecules are non-spherical,' and atoms are treated in his model as impenetrable objects, unable to approach each other more closely than the sum of the one-angle radii (or van der Waals radii, as the case may be). This model is remarkably successful in accounting for observed non-bonded distances, although it is a drastic approximation to the more complex physical situation. It is successful because bond angles can be deformed at a much lower energy cost than can bond lengths. The fact that 1,3 distances are typically 20% shorter than 1,4 or 1,5 distances is less an indication that atoms are 'smaller' in the 1,3 direction than a consequence of compromises between strong bonding forces pulling atoms together and relatively weak non-bonded interactions repelling them. Calculations of molecular structures based on Urey–Bradley force fields to which isotropic pairwise non-bonded interaction functions have been added have had pleasing success,[29] although few such calculations have yet been applied to inorganic systems.

The barrier to internal rotation about an S–N bond in $N(SCF_3)_3$ has been inferred from our n.m.r. results to be 6 ± 1 kcal mol$^{-1}$. We carried out molecular-orbital calculations at the extended-Hückel level,[30] endeavouring to elucidate the influence of $p \longrightarrow d\ \pi$ bonding on the magnitude of this barrier. For the sake of economy and simplicity, we studied a hypothetical model compound $N(SF)_3$ with a planar $NS_3$ skeleton. VOIP for the orbitals on N as well as for the 3*s* and 3*p* orbitals on S were taken from the work of Basch *et al.*,[31] but for the orbitals on F were reduced from those of a free atom, in an attempt to simulate more closely the effective electronegativity of a $CF_3$ group. Orbital exponents used for N, F, and the 3*s* and 3*p* orbitals on S were those of Clementi and Raimondi.[32] The 3*d* orbitals on S were assigned VOIP of 6 eV and exponents to 1.1. It was found that the energy difference between a conformation corresponding to that observed experimentally for $N(SCF_3)_3$ and the potential maximum occurring when one fluorine atom lies in the $NS_3$ plane was 9 kcal mol$^{-1}$, which is of the same order of magnitude as the experimental value. Inspection of the individual overlap populations showed that the main destabilising factor for a conformation in which $\delta_1 = 90°$ was the complete elimination of $\pi$ overlap between the lone pair $p_z$ orbital on N and the $3p_z$ orbital on S (the *z* axis being taken as the molecular three-fold axis). The $p \longrightarrow d\ \pi$-bonding population was in fact slightly greater in the high-energy conformation than in that analogous to the experimental structure of $N(SCF_3)_3$, for which the $\sigma$- and $\pi$-bond populations were 0.671 and 0.175, respectively. These

---

[20] L. Pierce and M. Hayashi, *J. Chem. Phys.*, 1961, **35**, 479.

[21] C. C. Costain, *J. Chem. Phys.*, 1958, **29**, 864.

[22] A. M. Domingos and G. M. Sheldrick, *Acta Cryst.*, 1974, **B30**, 517.

[23] C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Structure*, 1970, **6**, 231.

[24] D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. J. Aylett, I. A. Ellis, and J. J. Monaghan, *J. Chem. Soc.* (*A*), 1969, 1224.

[25] G. W. Cox, T. M. Sabine, V. M. Padmanabhan, Nguyen Tu Ban, M. K. Chung, and A. S. Surjadi, *Acta Cryst.*, 1967, **23**, 578.

[26] G. A. Jeffrey and D. W. Jones, *Acta Cryst.*, 1956, **9**, 283.

[27] J. V. Tillack and C. H. L. Kennard, *J. Chem. Soc.* (*A*), 1970, 1637.

[28] R. L. Sass, *Acta Cryst.*, 1960, **13**, 320.

[29] S. Fitzwater and L. S. Bartell, *J. Amer. Chem. Soc.*, 1976, **98**, 5107; E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, 1967, **47**, 3736.

[30] R. Hoffmann, *J. Chem. Phys.*, 1965, **39**, 1397.

[31] H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, 1965, **3**, 458.

[32] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 1963, **38**, 2686.

calculations therefore reinforce the arguments presented above that $p \longrightarrow d\ \pi$ bonding is an important influence on the N–S bond lengths in $N(SCF_3)_3$, although it does not appear to be crucial in determining the conformation adopted. Estimates were made of the magnitude of the contribution of 1,5 S $\cdots$ F non-bonded repulsions to the barrier to internal rotation. A fluorine–fluorine non-bonded potential derived in this laboratory [33] was modified for the greater size of S than of F; the indications are that repulsive 1,5 S $\cdots$ F interactions in a relaxed transition state between conformers are less than 1 kcal $mol^{-1}$.

We are unable to account to our satisfaction for the 'asymmetric' conformation adopted by $N(SCF_3)_3$, which contains NSC planes roughly perpendicular to the $S_3$ plane, apparently with two $CF_3$ groups above that plane and one below it, as shown in Figure 1. A hypothetical 'symmetric' conformation with all $\delta$ and $\varepsilon$ angles *ca.* 0° but with other parameters as reported in Table 2 would possess no unfavourably short non-bonded distances. It may be that the greater entropy associated with the unsymmetrical conformation plays an important role. We suspect that our diffraction data are insensitive to the presence of modest amounts of the symmetrical conformer. No evidence for such a conformer was obtained from the n.m.r. spectra at low temperatures. Whether the reduction in temperature of the gaseous sample as it expands into the evacuated specimen chamber of the diffraction unit has a significant effect on the conformational equilibrium is not known. In the absence of any energy preference or vibrational-frequency distinction between the symmetric and asymmetric conformers, a population of *ca.* 25 mol % symmetric conformer would be expected because there are only one-third as many ways of realising it.

We thank Mr. F. Bennis for assistance in obtaining the n.m.r. spectra, Dr. R. Sharp for helpful discussions thereof, The University of Michigan Computing Center for a generous allocation of computing time, and the National Science Foundation (U.S.A.) for support.

[7/024 *Received, 6th January,* 1977]

---

[33] L. S. Bartell and S. Woehler, unpublished work.