

## ELECTRON DIFFRACTION STUDY OF THE MOLECULAR STRUCTURE OF TRIFLUOROMETHYL HYPOFLUORITE\*

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### ABSTRACT

The following structural parameters and estimated standard deviations were found for trifluoromethyl hypofluorite:  $r_g(\text{C-F}) = 1.319 \pm 0.003 \text{ \AA}$ ,  $r_g(\text{C-O}) = 1.395 \pm 0.006 \text{ \AA}$ ,  $r_g(\text{O-F}) = 1.421 \pm 0.006 \text{ \AA}$ ,  $\angle(\text{F-C-F}) = 109.4 \pm 1^\circ$ ,  $\angle(\text{C-O-F}) = 104.8 \pm 0.6^\circ$ , assuming a  $C_{3v}$  symmetry for the  $\text{CF}_3$  group, and a staggered conformation. Diffracted intensities indicate a bending of  $4.1 \pm 0.8^\circ$  of the C-O bond from the three-fold axis of the trifluoromethyl group and a torsional oscillation about the C-O bond corresponding to a potential barrier of  $2.5 \pm 0.5$  kcal/mole.

### INTRODUCTION

The unusual chemical and physical properties of highly fluorinated substances make them interesting subjects for investigation. As part of a continuing program of research on such compounds we report here an analysis of the structure of  $\text{CF}_3\text{OF}$ . Infrared studies have been published<sup>1,2</sup>, but detailed structure parameters have not been determined previously.

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\* Based on a dissertation by F. P. Diodati in partial fulfillment of requirements for the degree of Doctor en Física, Universidad de La Plata, 1970. For a tabulation of experimental intensity data for  $\text{CF}_3\text{OF}$ , order document No. 01144 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, N.Y. 10001, remitting \$1.00 for microfiche or \$3.00 for photocopies.

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## EXPERIMENTAL SECTION

A sample of  $\text{CF}_3\text{OF}$  was purchased from Penninsular Chemical Research, Inc. Impurities detected by chromatography and infrared analysis were removed according to procedures described in the literature<sup>1</sup>. A purification by low temperature filtration and successive distillations was performed until the infrared spectrum revealed no contaminants.

Electron diffraction patterns were taken with a unit described previously<sup>3</sup>. Patterns were recorded on Electron Image Plates at camera distances of 21-, 11-, and 7-cm using an  $r^3$  sector. The relation between exposure and absorbancy was assumed to be

$$A = A_0(1 - e^{-2cE})$$

according to which, with the additional criterion that  $E \approx A$  for weak exposure, it is possible to relate the calibration constants with the absorbancy at saturation of the emulsion. Carbon tetrachloride patterns, heavily exposed, yielded a value of  $5.55 \pm 0.05$  for  $A_0$ .

## ANALYSIS OF DATA

Following the usual procedure at the University of Michigan<sup>4</sup>, averaged experimental leveled intensities corresponding to the three camera ranges were calculated from the microphotometer readings of nine patterns. A range of  $4.4 < s < 51.2$  was covered.

After finding the proper graphical backgrounds for the three leveled intensities using the usual criteria, a blended intensity curve including all the experimental data was constructed. The final least-squares refinements were performed on this curve, adopting a value of  $a = 2 \text{ \AA}^{-1}$  for the asymmetry parameter for all bonded and nonbonded distances. A preliminary theoretical model available from a previous study of three patterns taken with a different unit\* proved helpful in the analysis.

An optimum weight matrix was not used, but instead, a diagonal weight matrix was adopted with elements proportional to  $s^2$  except for the beginning and final few points which were weighted more lightly.

As previously reported<sup>3</sup>, the effect of correlation between the experimental measurements was considered in the final standard deviations assigned.

A radial distribution function was calculated with the usual corrections<sup>5-8</sup>. In the Degard damping factor a value of 0.0015 for  $b$  was used. The elastic and inelastic atomic form factors were from refs. 9 and 10, respectively.

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During the process of the analysis it was necessary to impose some symmetry constraints, including for example, the assignment of  $C_{3v}$  to the trifluoromethyl group and  $C_s$  for the entire molecule. It was not feasible to derive more than one independent amplitude of vibration from each composite peak in the radial distribution curve.

A significantly improved fit resulted if the C–O bond was allowed to move away from the three-fold axis of  $CF_3$ , toward the  $CF_3$  fluorine in the  $C_s$  mirror plane, as is shown in Fig. 1. A further improvement was obtained if the OF group was assumed to be undergoing restricted rotation relative to the  $CF_3$  group. The torsional potential function<sup>11</sup> giving the optimum fit possessed minima at staggered conformations and a barrier of  $2.5 \pm 0.5$  kcal/mole.

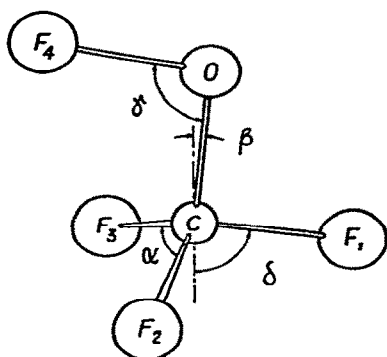


Fig. 1. Structural model for  $CF_3OF$ .

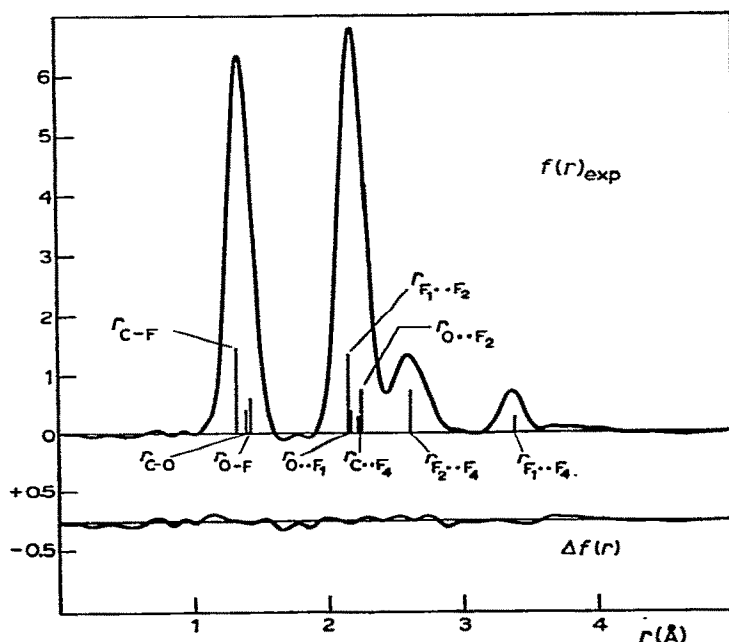


Fig. 2. Experimental radial distribution function for  $CF_3OF$ ;  $\Delta f(r) = f(r)_{exp} - f(r)_{calc}$ .

## RESULTS

The difficulties imposed by the poor resolution of the internuclear distances, as illustrated in Fig. 2, are worth noting. From four peaks must be determined six geometric parameters (or seven, including the mean torsional twist angle). From this unpromising starting point it proved to be possible to extract a unique structure, with errors only several-fold larger than normal, by virtue of the restrictions imposed by geometric consistency. As a check, the structure refinements were made from a variety of different initial structures.

Table 1 gives the results of the analysis. Indices of resolution are lower than usual, probably due to the method of developing the plates. Table 2 lists the values of the correlation coefficients between the independent structure parameters. Fig. 3 shows the experimental and theoretical reduced intensity functions,  $sM(s)$ , and the difference between them.

TABLE 1

STRUCTURAL PARAMETERS AND ESTIMATED STANDARD ERRORS FOR CF<sub>3</sub>OF

	$r_g(\text{Å})$		$l_g(\text{Å})$	Angles (degrees)
C-F	1.319±0.003	C-F, C-O; O-F	0.046±0.005	$\alpha = 109.4 \pm 1.0$
C-O	1.395±0.006	F <sub>1</sub> ··· F <sub>2</sub> , F ··· O; C ··· F	0.061±0.006	$\beta = 4.1 \pm 0.8$
O-F	1.421±0.006	F <sub>2</sub> ··· F <sub>4</sub>	0.061±0.009	$\gamma = 104.8 \pm 0.6$
C ··· F <sub>4</sub>	2.230±0.009	F <sub>1</sub> ··· F <sub>4</sub>	0.061±0.009	
O ··· F <sub>1</sub>	2.160±0.015			
O ··· F <sub>2</sub>	2.244±0.007	Indices of resolution	21-cm data = 0.82	
F <sub>1</sub> ··· F <sub>2</sub>	2.153±0.008		11-cm data = 0.85	
F <sub>2</sub> ··· F <sub>4</sub>	2.608±0.010		7-cm data = 0.75	
F <sub>1</sub> ··· F <sub>4</sub>	3.383±0.010			

TABLE 2

DIAGONAL ELEMENTS OF ZEROth ORDER ERROR MATRIX<sup>a</sup> AND MATRIX OF CORRELATION COEFFICIENTS<sup>b</sup> FOR CF<sub>3</sub>OF

	$r_{C-O}$	$r_{C-F}$	$r_{O-F}$	$\beta$	$\delta$	$\gamma$	$l_{C-F}$	$l_{F_1-F_2}$	$R$
$\sigma(\theta_1)^{a,b}$	3.15	0.82	2.87	395.70	260.00	323.80	1.06	1.55	4.82
$r_{C-O}$	1.00	-0.66	-0.72	0.00.24	-0.00.12	-0.00.29	-0.34	-0.52	-0.15
$r_{C-F}$		1.00	0.60	-0.00.21	-0.00.24	-0.00.24	0.34	0.14	0.13
$r_{O-F}$			1.00	-0.00.31	-0.00.11	-0.00.04	-0.02	0.36	0.23
$\beta$				1.00	-0.00.72	-0.00.17	-0.01	-0.25	-0.09
$\delta$					1.00	-0.00.53	-0.07	0.57	0.06
$\gamma$						1.00	0.10	0.34	-0.04
$l_{C-F}$							1.00	0.27	0.42
$l_{F_1-F_2}$								1.00	0.41
$R$									1.00

<sup>a</sup> Corresponds to  $M_x^\circ$  of L. S. BARTELL, *Acta Cryst.*, 25 (1969) S76. Values are  $\times 10^3$  based on 150 points interpolated from 336 data points. Units for distances and amplitudes are in Å, for angles, in degrees.

<sup>b</sup> Correspond to the  $\rho_{ij}$  of ref. 18. Correlations for  $l_{F_2-F_4}$  and  $l_{F_1-F_2}$  have not been listed because they are significantly smaller.

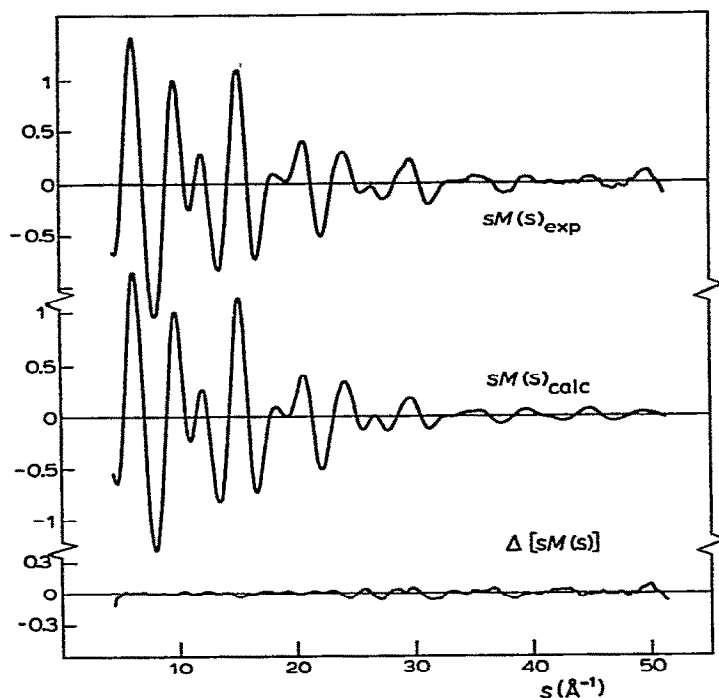


Fig. 3. Experimental and calculated reduced molecular intensity functions for  $\text{CF}_3\text{OF}$ ;  $\Delta [sM(s)] = sM(s)_{\text{exp}} - sM(s)_{\text{calc}}$ .

#### DISCUSSION

Comparisons between the structure parameters of  $\text{CF}_3\text{OF}$  and those of selected molecules are instructive. For example, the C-F bonds do not differ significantly in length from those in  $\text{CF}_4$  ( $1.323 \pm 0.005 \text{ \AA}$ ), but are shorter than those in  $\text{CF}_3$  groups attached to less electronegative atoms, cf.  $\text{CF}_3\text{Cl}$  ( $1.328 \pm 0.002 \text{ \AA}$ )<sup>12-14</sup> and  $\text{CF}_3\text{CH}_3$  ( $1.335 \pm 0.005 \text{ \AA}$ ). Similarly, the C-O bond length is  $0.033 \text{ \AA}$  shorter than that in methanol ( $1.428 \pm 0.003 \text{ \AA}$ )<sup>15</sup>. The C-O bond tilts away from the  $\text{CF}_3$  axis by about the same amount as reported for methanol (refs. 16-18).

The above trends are qualitatively in accord with the double-bond-no-bond resonance theory<sup>19</sup>, and with Gillespie's valence shell electron pair theory<sup>20</sup>. To complete the comparison between experiment and simple models on a basis more amenable to numerical analysis, extended Hückel molecular orbital calculations<sup>21</sup> were performed on  $\text{CF}_3\text{OF}$  and  $\text{CH}_3\text{OH}$ . Orbital exponents were taken from Clementi and Raimondi<sup>22</sup> together with the valence orbital ionization potentials (VOIP's) of Basch et al.<sup>23</sup>. Using zero charge VOIP's and identical C-O bond lengths as input parameters for  $\text{CF}_3\text{OF}$  and  $\text{CH}_3\text{OH}$ , we obtained a 10% greater C-O overlap population for  $\text{CF}_3\text{OF}$  than for  $\text{CH}_3\text{OH}$ , consistent with the shorter bond

in the former molecule. Adopting ligand charges for the voip's of  $\text{CF}_3\text{OF}$  to yield an MO gross population of 2.6 valence electrons on the carbon, and placing the C–O bond on the  $\text{CF}_3$  axis, we computed that the staggered conformation was 1.7 kcal/mole more stable than the eclipsed form, in fair agreement with the present experiment.

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