coming with Cr(II) ion. 2. Diphenylcarbazone reacts with Cr(III) and Cr(II) ions to form the same complex as observed above. No reaction occurs with chromium(VI) ion. 3. The stoichiometry of the reaction of chromium and the reagents is in a ratio of three moles of reagent to two moles of the metallic ion. 4. The highly absorbing chromium complex exists as a cationic species in aqueous solution. 5. The chromium complex is extracted, together with an anion, into non-aqueous media as a neutral molecule. 6. A chromium-(III)-diphenylcarbazone complex is postulated as the colored species in the reactions.

The above conclusions are the result of all of the experimental data obtained. This situation is unique in studies of the systems under consideration. Such a situation serves to clarify much of the unsatisfactory nature of the existing literature on the subject.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

The Molecular Structure of Perfluorotrimethylamine by Electron Diffraction[1]

BY R. L. LIVINGSTON AND G. VAUGHAN

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The molecular structure of perfluorotrimethylamine has been investigated by electron diffraction using the visual correlation procedure. The structural parameters, as determined by this investigation, are as follows: C–F = 1.32 ± 0.02 Å., C–N = 1.43 ± 0.03 Å., ∠FCF = 108.5 ± 2.0°, and ∠CNC = 114 ± 3°.

Introduction

Previous investigations of the structures of hexafluoropropene[2] and octafluorocyclobutane[3,4] in this Laboratory indicated, for these molecules, that the closest approach of fluorine atoms which are bonded to different carbon atoms is about 2.70 Å. or twice the van der Waals radius of fluorine. Preliminary calculations on perfluorotrimethylamine indicated that if a similar F··F distance prevailed in this compound, then rather unusual structural parameters would be encountered; hence an investigation of the molecular parameters of this compound was undertaken.

Experimental

The sample of perfluorotrimethylamine was supplied by Dr. W. H. Pearlson of the Minnesota Mining and Manufacturing Company. In the absence of any comparative data, their estimate of a purity greater than 98 mol per cent. was based on the constancy of the boiling point and the molecular weight over successive distillations. No known compounds were observed as impurities in the infrared spectrum.

The diffraction photographs were obtained in the usual way[5] using a camera designed and constructed by Professor H. J. Yearian of the Purdue Physics Department. The camera distance was about 107.1 mm., and the electron wave length, as determined from a transmission pattern of ZnO, was about 0.0588 Å. The recorded diffraction pattern of perfluorotrimethylamine extended to a q value of about 95.

Interpretation of the Diffraction Pattern.—The visual correlation method[5,6] and the radial distribution method[7,8] were used in interpretation of the diffraction pattern. The measurements of the diffraction features on three of the best plates are summarized in Table I. These values are based on measurements of each feature by two observers. The visual curve shown in Fig. 1 was based on independent interpretations of the patterns by three observers. The interpretations were in close agreement on all features except as noted below in the case of the eighth maximum and the ninth minimum. The portion of the curve in the interval $q = 0$ to $q = 20$ was copied directly from the most acceptable model as is customary.

Due to the diffuse nature of the eighth maximum and the ninth minimum, there was some doubt as to the exact shape of these features. However, it was the opinion of all observers that the maximum was asymmetric to the outside and that the indicated shapes of these features are approximately correct. Due consideration was given to this uncertainty in selecting acceptable models.

The radical distribution curve appearing in Fig. 1 was calculated using the equation[8]

$$rD(r) = \sum_{q=1}^{q_{max}} I(q)_0 \exp(-bq^2) \sin \frac{\pi q}{10} r \qquad (1)$$

The values $I(q)_0$ were read from the visual curve, Fig. 1, and the radial distribution curve was calculated on I.B.M. tabulators.[8] The peak at 1.37 Å. corresponds to the C–F and C–N distances and at 2.23 Å. corresponds to the N · · F distance and the F · · F distance in the CF_3 group. If preliminary calculations of models showed quantitative incompatibility with the curve with respect to these two peaks, further investigations of these models were abandoned. It was later demonstrated that none of these models was within the range of acceptability. In view of the complex nature of the vibrational problem for this molecule, as indicated later, a complete quantitative interpretation of the radial distribution was not attempted.

The structural determination of perfluorotrimethylamine involves the evaluation of four param-

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TABLE I

q_c/q_0 VALUES FOR ACCEPTABLE MODELS OF PERFLUOROTRIMETHYLAMINE

Feature Max.	Feature Min.	q_0	Model M_{1E}	G_{2E}	H_{2E}	G_{3E}	H_{3E}	H_{2D}[a]	Wt.
2		20.10	0.914	1.021	1.021	0.904	...	0.980	0
	3	25.85	0.974	0.958	0.959	0.958	0.959	.962	0
3		30.37	1.031	1.025	1.015	1.031	1.023	.992	1
	4	34.31	1.004	0.999	0.995	1.002	0.997	.994	2
4		37.25	0.989	.982	.979	0.988	.985	1.004	0
	5	44.04	.987	.982	.978	.985	.984	0.963	2
5		48.07	.992	.980	.986	.987	.987	.992	5
	6	53.74	.982	.994	.984	.976	.979	.993	2
6		57.35	1.003	.996	.997	.992	.994	1.007	5
	7	61.36	0.974	.970	.970	.976	.976	0.977	2
7		64.85	0.986	.977	.979	.987	.991	1.006	0
	8	71.16	1.006	1.006	1.006	.995	.994	0.999	1
8		76.90	1.006	1.019	1.007	.991	.994	1.008	0
	9	88.77	0.965	1.021	1.009	1.019	1.010	1.009	0
9		95.91	.985	0.996	.998	0.984	0.995	0.997	1
Wt. mean			.995	0.990	.990	0.990	0.990	0.992	
Av. dev.			±0.010	±0.010	±0.009	±0.008	±0.007	±0.009	

[a] Although the qualitative agreement is not entirely satisfactory for this model, the ratios are included to demonstrate that this model is a fairly good approximation to the structure of this compound.

eters if one considers only rigid models with C_3 symmetry with the angular orientation of the CF_3 groups fixed relative to the axis of symmetry. In all models examined in this investigation, the angular orientation parameter was chosen so that equal values were obtained for the six shortest distances between fluorine atoms on different carbon atoms.

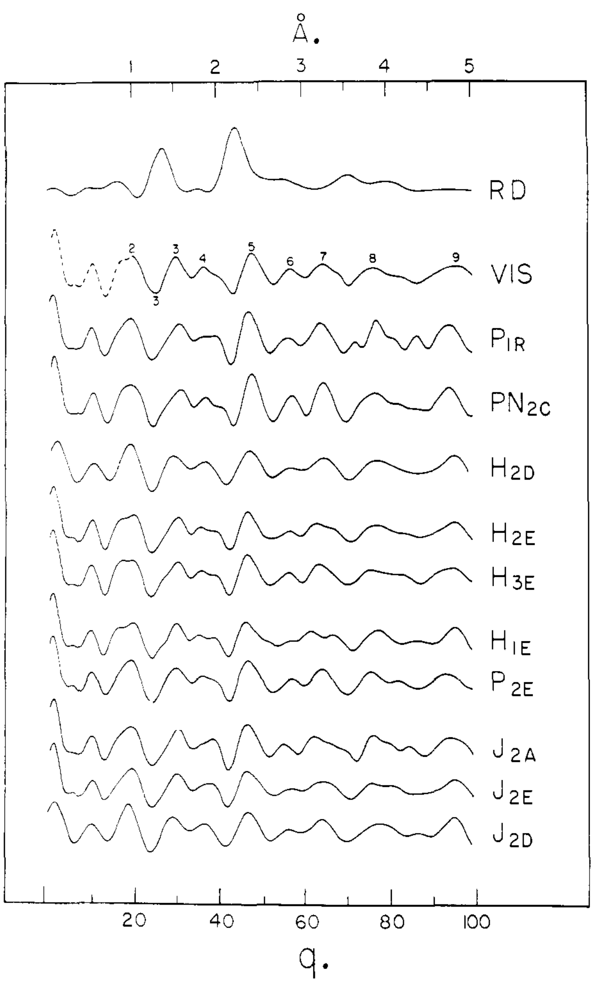

Fig. 1.—Radial distribution, visual and theoretical intensity curves for perfluorotrimethylamine.

The rigid models examined in this investigation covered the three parameter fields shown in Fig. 2.

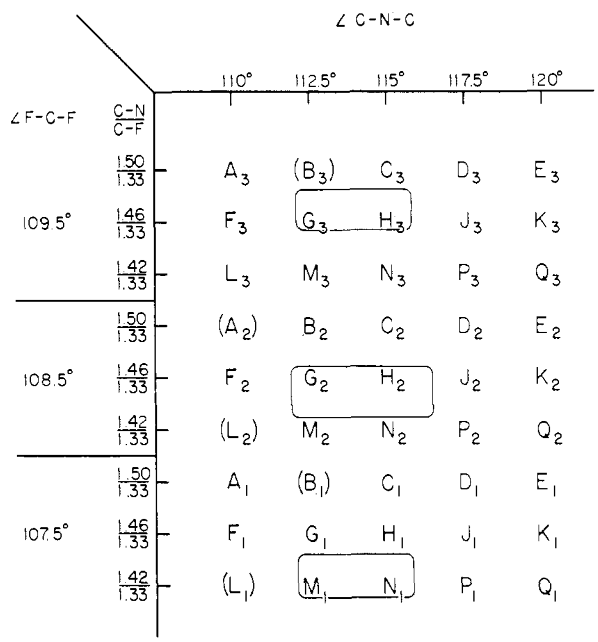

Fig. 2.—Parameters for calculated models for perfluorotrimethylamine.

In all models the C–F distance was 1.33 Å., and the values assumed for the remaining parameters are indicated on the chart. Curves were calculated on I.B.M. tabulators using the equation[8]

$$I(q) = \sum_i \sum_j{}' \frac{Z_i Z_j}{r_{ij}} \exp(-b_{ij}q^2) \sin \frac{\pi q}{10} r_{ij} \qquad (2)$$

None of the theoretical curves calculated for rigid models was in agreement with the visual curve, nor was there any indication that any other rigid models would prove satisfactory. Curve P_{1R} was selected as the rigid model curve in closest agreement with the visual curve. The obvious disagreements of the shapes of the fourth maximum and the eighth and ninth minima formed the basis for the rejection of this model. All other rigid model curves showed even greater discrepancies.

The effect of the three sets of b_{ij} values, designated A, B and C in Table II, was examined next. Preliminary calculations indicated that set C might prove to be satisfactory. Models D_1, J_1, P_1, CD_2, D_2, HJ_2, HP_2, J_2, JP_2, KQ_2, PN_2, P_2, D_3, P_3 and Q_3 were calculated using set C of the b_{ij} values; these models are designated as D_{1C}, J_{1C}, P_{1C}, CD_{2C}, etc. (The double letter designation refers to a model with parameters midway between those for models denoted by the individual letters.) The curve for model PN_{2C} was chosen as the most acceptable curve of this group and may be rejected on several counts. As seen in Fig. 1, the sixth and seventh minima are somewhat too deep, and the seventh maximum shows no shoulder and is too intense. Since all other models in this group gave rise to theoretical intensity curves which were in poorer agreement with the visual curve, all of these models are rejected. Extrapolation to $\angle CNC$ = 112.5° or 110° indicated that satisfactory curves could not be obtained using these b_{ij} values.

TABLE II

VALUES OF b_{ij} USED FOR PERFLUOROTRIMETHYLAMINE MODELS

Distance[a]	$b_{ij} \times 10^4$ A	B	C	D	E	F
C–F	0	0	0	0	0.16	0.16
C–N	0	0	0	0	0	0
$F_1 \cdot\cdot F_2$	0	0	0	0	0.68	0.68
$N \cdot\cdot F$	0	0	0	0	0.90	0.90
$C \cdot\cdot C$	0	0	0	0	0.68	0.68
$C_1 \cdot\cdot F_4$	0.25	0.56	0.80	∞	1.40	4.20
$C_1 \cdot\cdot F_5$	1.70	5.20	7.75	∞	1.40	4.20
$C_1 \cdot\cdot F_6$	0.25	0.56	0.80	∞	1.40	4.20
$C_1 \cdot\cdot F_7$	0.25	0.56	0.80	∞	1.40	4.20
$C_1 \cdot\cdot F_8$	1.30	2.55	4.75	∞	1.40	4.20
$C_1 \cdot\cdot F_9$	0.25	0.56	0.80	∞	1.40	4.20
$F_1 \cdot\cdot F_4$	0.56	0.80	1.01	∞	4.20	9.23
$F_1 \cdot\cdot F_5$	2.68	4.20	6.40	∞	4.20	9.23
$F_1 \cdot\cdot F_6$	0.80	1.01	1.37	∞	4.20	9.23
$F_1 \cdot\cdot F_8$	0.06	0.25	0.56	∞	4.20	9.23
$F_1 \cdot\cdot F_9$	0.06	0.25	0.56	∞	4.20	9.23
$F_2 \cdot\cdot F_5$	4.20	6.40	9.23	∞	4.20	9.23
$F_2 \cdot\cdot F_6$	1.80	1.01	1.37	∞	4.20	9.23
$F_3 \cdot\cdot F_5$	1.01	1.37	2.68	∞	4.20	9.23
$F_3 \cdot\cdot F_6$	1.37	2.68	4.20	∞	4.20	9.23

[a] See Fig. 2 for the numbering of the atoms.

The effect of applying infinite b_{ij} values to the non-bonded C· · F distances and to all the F · · F distances, except those within each CF_3 group, was next examined. Set D of the b_{ij} values, Table II, was used in calculation of A_{2D}, C_{2D}, E_{2D}, F_{2D}, H_{2D}, K_{2D}, L_{2D}, N_{2D} and Q_{2D}. Curve H_{2D} is a representative curve of this group. The excellent qualitative agreement of this curve, except for the absence of the shoulders on the fourth and seventh maxima, indicates that the molecule is subject to rather severe vibrations of such a nature that the contributions of the longer non-bonded distances to the molecular scattering are relatively slight. However, these contributions cannot be ignored if completely satisfactory qualitative agreement with the visual curve is to be obtained.

In view of the relatively slight contributions of the non-bonded C · · F and long F· ·F distances as indicated above, sets E and F of the b_{ij} values, Table II, were then selected for examination, and preliminary calculations indicated that set E would probably be the more reasonable of the two sets. For $\angle FCF$ = 107.5°, models G_{1E}, H_{1E}, K_{1E} and M_{1E} were calculated; for $\angle FCF$ = 108.5°, models B_{2E}, C_{2E}, F_{2E}, G_{2E}, H_{2E}, J_{2E}, K_{2E}, M_{2E}, N_{2E}, P_{2E} and Q_{2E} were calculated; and for $\angle FCF$ = 109.5°, models G_{3E}, H_{3E}, and K_{3E} were calculated.

For convenience of discussion, the groupings of the models were made according to the qualitative similarity of the curves with regard to the major points of disagreement with the visual curve.

Curves M_{1E}, G_{2E}, H_{2E}, G_{3E} and H_{3E} were selected as the theoretical curves in qualitative agreement with the visual curve. Curves H_{2E} and H_{3E} are shown in Fig. 1. Curve H_{2E} shows the upper limit of acceptability for the prominence of the shelf on the fourth maximum, and curve H_{3E} shows the lower limit of acceptability for the prominence of the shoulder on the seventh maximum. It should be noted here that curve H_{2E} shows better agreement with the accepted visual interpretation of the shape of the eighth maximum and the ninth minimum than any other curve in this group. Some slight changes of slope on the inside of the third maximum were also observed on these curves but this was not considered as an adequate basis for rejection of models.

Curve H_{1E} is taken as being representative of the group of models G_{1E}, H_{1E}, K_{1E}, B_{2E} and C_{2E}. The appearance of a maximum in place of the observed shelf on the seventh maximum is the basis for the rejection of this group of models.

Of the group of curves F_{2E}, J_{2E}, K_{2E}, M_{2E}, N_{2E}, P_{2E}, Q_{2E} and K_{3E}, curve P_{2E} is in best agreement with the visual curve. Curve P_{2E} shows the seventh maximum as a nearly symmetrical feature; this curve is therefore rejected. The remainder of the curves in this group show at least this much disagreement and hence are also rejected.

Curves J_{2A}, J_{2D} and J_{2E} are included in order to show the effects of various b_{ij} values on the theoretical intensity curves. The selection of the sets of b_{ij} values shown in Table II was made as follows: the changes in interatomic distances in all rigid models were tabulated against 2.5° changes in the CNC angle, and the b_{ij} values for set A were then assigned roughly proportional to the change in interatomic distances. Larger values were assigned for sets B and C. In sets E and F, the values assigned for the first five distances were based on those used by Shoolery, *et al.*,[9] in the determination of the structure of trifluoromethylacetylene. The qualitative agreement shown by the models based on the b_{ij} values of set D indicated extensive

(9) J. N. Shoolery, R. G. Shulman, W. F. Sheehan, Jr., V. Schomaker and D. M. Yost, *J. Chem. Phys.*, **19**, 1364 (1951).

damping of the contributions from the longer non-bonded distances, and the b_{ij} values assigned to these distances in sets E and F were selected in an attempt to approximate the observed damping.

In view of the complexity of an empirical determination of such a large number of b_{ij} values, no further examinations of models were made. However, it was felt that the b_{ij} values of set E are at least of the proper order of magnitude, and the closed areas shown in Fig. 2 represent the parameter volume in which the most acceptable models, based on set E, are located. In assigning the limits shown, allowances were made in the selection of acceptable models for further variations of the b_{ij} values.

Based on the foregoing discussions, models M_{1E}, G_{2E}, H_{2E}, G_{3E} and H_{3E} are accepted as satisfactory fits. The q_c/q_0 values for these models are summarized in Table I.

The weightings assigned to each feature indicate the estimated reliability of that feature in the determination of the q_c/q_0 ratios. Zero weightings are assigned to the inner features where the intensity of the background is of sufficient magnitude to make measurements unreliable. Low weightings were assigned to asymmetric features on which reproducible measurements could not be made and to the outer features where the pattern is so weak that reliable measurements are not generally obtained.

Table III summarizes the parameters calculated from the mean q_c/q_0 values, and the accepted values of these parameters and the limits of acceptability as determined by this investigation are included in the table.

TABLE III

STRUCTURAL PARAMETERS AS DETERMINED FROM q_c/q_0 VALUES[a]

Parameter	Model M_{1E}	G_{2E}	H_{2E}	G_{3E}	H_{3E}
C–F	1.323	1.317	1.317	1.317	1.317
C–N	1.413	1.445	1.445	1.445	1.445
∠CNC, deg.	112.5	112.5	115	112.5	115
∠FCF, deg.	107.5	108.5	108.5	109.5	109.5
F··F[b]	2.580	2.595	2.613	2.563	2.578

FINAL RESULTS WITH LIMITS OF ACCEPTABILITY

Parameter	Result
C–F	1.32 ± 0.02
C–N	1.43 ± 0.03
∠CNC, deg.	114 ± 3
∠FCF, deg.	108.5 ± 2.0
F··F[b]	2.59 ± 0.04

[a] All values for interatomic distances quoted in ångström units. [b] Closest approach of fluorine atoms on different carbon atoms.

Discussion of Results

The distance of 2.59 ± 0.04 Å. obtained for perfluorotrimethylamine for the closest approach of fluorine atoms attached to different carbon atoms is appreciably less than the value of 2.70 Å. found in hexafluoropropene[2] and octafluorocyclobutane,[3,4] indicating that the minimum distance of approach of 2.70 Å. does not hold for all organic fluorides. As previously mentioned, the vibration factors required to generate intensity curves in satisfactory agreement with the visual curve indicate rather large intramolecular vibrational amplitudes.

The CNC angle reported here as 114 ± 3° is larger than the value of 109 ± 2° obtained for trimethylamine[10] and the C–N distance appears to be appreciably larger than the corresponding distance in $(CH_3)_3N$ (1.47 ± 0.01 Å.).

Comparisons between the structure of the CF_3 group in $(CF_3)_3N$ and in other molecules seem to be worthwhile. A recent investigation of CHF_3 by electron diffraction[11] gave 1.334 ± 0.005 Å. for the C–F distance and 108°30′ ± 30′ for the ∠FCF; the microwave results[12] of 1.332 Å. and 108°48′, respectively, agree quite favorably with these values. An electron diffraction investigation of the structure of CF_3CF_3[13] yielded C–F = 1.330 ± 0.015 Å. and ∠FCF = 108.5 ± 1.5°. The values resulting from a combination of electron diffraction and microwave techniques on $CF_3C{\equiv}CH$[9] are C–F = 1.335 ± 0.010 Å. and ∠FCF = 107.5 ± 1°. FCF angles less than tetrahedral have also been obtained in CF_3CH_3,[14] CF_3CN[15] and $CF_3C{\equiv}CCF_3$.[16] In all cases, the C–F distances appear to be somewhat larger than the C–F distance of 1.32 ± 0.02 Å. obtained for $(CF_3)_3N$, but the FCF angles are in close agreement.

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