TABLE II

PHOTOLYSIS OF ACETONE-d_6 IN THE PRESENCE OF n-BUTANE

t, min.	T, °C.	CD_4	CD_3H	CD_2H_2	CH_3D	CH_4	CD_2 Cor.	$\frac{CH_4}{CH_3D}$	k_{15}/k_4
5	250	17.6	185.2	(0.0)	(0.4)	(5)	10.48	...	4.21
10	250	33.1	351.7	0.7	(1.5)	(10)	10.59	...	4.26
4	303.5	13.7	127.1	0.3	10.9	104.3	9.24	9.57	3.60
10	303.5	43.0	391.6	1.2	32.6	249.1	9.07	9.17	3.51
3	355	13.2	108.5	0.4	29.7	256.3	8.18	8.63	3.08
6	355	29.5	240.3	3.2	61.7	530.6	8.11	8.60	3.04
3	397	12.6	96.2	0.9	50.3	392.0	7.60	7.53	2.79
6	397	37.1	279.9	6.1	132.7	1051.9	7.50	7.93	2.75
4	449	28.0	199.5	5.0	131.1	969.0	7.09	7.39	2.54

The pertinent data are given in Table II. From the slope of the Arrhenius plot for k_{15}/k_4, $E_4 - E_{15}$ is calculated to be 2.0 kcal. Since E_4 is 11.3 kcal.,[5,8] it follows that $E_{15} = 9.3$ kcal.

As in the acetone-d_6–n-butane-2,2,3,3-d_4 mixtures, these data indicate that CH_3 abstracts H and D with the same activation energy difference as does CD_3. It is of interest to note that the difference in energy of activation for the abstraction of secondary D and H by CD_3 from butane is 2.1 kcal., a value in excess of the zero point energy difference of H_2 and D_2. Some previous work[6,8] also indicates that zero point energy differences are not sufficient to account for the difference in rate of abstraction of D and H by methyl radicals.

It is of interest to calculate the ratio of preëxponential factors in the Arrhenius equations, A_3/A_{15}, corresponding to the abstraction of primary and secondary hydrogen. In this discussion we assume that $A_3 = A_{14}$.

As may be seen in Fig. 1, k_2/k_4 varies very little with temperature. From this observation A_3/A_4 may be calculated as 0.93.

From Fig. 2, $A_4/A_{15} = 1.61$, so that

$$\frac{A_4}{A_{15}} \times \frac{A_3}{A_4} = \frac{A_3}{A_{15}} = 1.50$$

This is the ratio of the number of primary hydrogen atoms to the number of secondary hydrogen atoms, so that the entropy of activation per hydrogen atom of the attack on primary hydrogen is the same as for the attack on secondary hydrogen.

We may also compare A_3/A_2, the ratio for the abstraction of primary hydrogen to the abstraction of secondary deuterium in butane-d_4.

From the intercepts in Fig. 1, $k_3/k_2 = 0.93$, independent of temperature. Thus $A_3/A_2 = 0.93$. This ratio is far from the ratio of the number of primary hydrogen atoms to secondary deuterium atoms in the butane-d_4. We can offer no explanation for this discrepancy at the present time. Since $E_{14} = 11.4$ kcal. and $E_{15} = 9.3$ kcal., it is concluded that the difference in activation energy for abstraction by CD_3 of primary and secondary H is 2.1 kcal. Considering the numerous approximations that were necessary in the work of Allen[9] at a single temperature, his estimate of 2.1 kcal. for the difference in abstraction activation energies of primary and secondary H from propane is remarkably close to our precisely measured value for the case of butane.

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[8] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **76**, 1416 (1954).

[9] A. O. Allen, *ibid.*, **63**, 708 (1941).

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

An Electron Diffraction Investigation of the Molecular Structure of 1,1,1-Trifluoroethane[1]

BY JAMES L. BRANDT AND R. L. LIVINGSTON

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The interatomic distances in methylfluoroform have been determined by electron diffraction using the visual correlation procedure. Sectored electron diffraction photographs were used in the interpretation of some of the features. The following results were obtained: C–F = 1.33 ± 0.02 Å., C–C = 1.52 ± 0.04 Å., and ∠CCF = 111.5° ± 1.5°.

Two previous electron diffraction investigations[2] of the structure of methylfluoroform gave the following conflicting results: C–C = 1.45 ± 0.04 Å. as compared to 1.53 ± 0.04 Å., C–F = 1.33 ± 0.03 Å. compared to C–F = 1.36 ± 0.02 Å. and ∠FCF = 108.5 ± 2° against 107 ± 3°. Edgell and Roberts,[3] in a microwave spectroscopic study, obtained a moment of inertia perpendicular to the threefold axis of 161.80 ± 0.07 × 10^{-40} g. cm.^{2}. They showed that this moment of inertia was compatible with the following parameters: C–C = 1.54 Å., C–F = 1.33 Å., C–H = 1.043 Å.,

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[1] From the Ph.D. thesis of James L. Brandt, Purdue Research Foundation Fellow in Chemistry, 1951–1952.

[2] R. W. Allen and L. F. Sutton, *Acta Cryst.*, **3**, 46 (1950).

[3] W. F. Edgell and A. Roberts, *J. Chem. Phys.*, **16**, 1002 (1948).

F–F = 2.16 Å., ∠ HCH = 109°28′. They also showed that a short C–C distance of 1.45 Å. with all other distances and angles as above gives $I_B = 154.07 \times 10^{-40}$ g. cm.^{2}. This short C–C distance required an unlikely C–F distance of 1.38 Å. in order to make $I_B = 161.7 \times 10^{-40}$ g. cm.^{2}.

Because the two electron diffraction investigations were in disaccord and the spectroscopic study was not consistent with either electron diffraction result, the present reinvestigation of the structure of methylfluoroform was undertaken.

Experimental

The sample of methylfluoroform (tabulated b.p. −46.8°[4]) was prepared by fluorination of 1-chloro-, 1,1-difluoroethane and distilled through a low temperature Hyd-Robot Podbielniak column. The middle fraction, boiling at −46.8° at 760 mm. pressure, was collected for photographing. The sample was estimated to have a purity in excess of 99%.

Electron diffraction photographs for the visual procedure were prepared in the usual manner[5] using an apparatus built by Dr. H. J. Yearian of the Purdue Physics Department. The camera distance was about 10.7 cm. and the wave length of the electron beam, as determined from transmission patterns of ZnO, was about 0.055 Å. The recorded diffraction pattern extended to a q value of about 105.

Sectored electron diffraction photographs were prepared following the procedure of Yearian and Barss[6] on the same apparatus as above. The camera distance for these photographs was about 16.0 cm. with the wave length of the electron beam about 0.055 Å. The diffraction pattern extended to a q value of about 70.

Visual Interpretation of the Pattern.—The visual correlation method[5,7] and the radial distribution method[8,9] were used in the interpretation of the recorded pattern. The radial distribution function was calculated from the equation[9]

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

by use of punched cards.[9] $I(q)$ is the visual intensity curve (Curve Vis, Fig. 2) which is drawn assuming no falling off of intensity with increasing q. The constant b was chosen so that $\exp.(-bq^2) = 0.10$ at $q = 105$. The terms for the range $q = 1$ to $q = 20$ were obtained from one of the acceptable theoretical intensity curves; the latter were calculated on I.B.M. tabulators from the equation[9]

$$I(q) = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}}\ \exp.\,(b_{ij}q^2)\ \sin\left(\frac{\pi}{10}\,qr_{ij}\right) \qquad (2)$$

All measurements and intensity estimates were made by two independent observers. The averages of these measurements and intensity estimates are given in Table I.

Theoretical intensity curves were calculated over the parameter field indicated in Fig. 1, for staggered models of 1,1,1-trifluoroethane in which the symmetry of the point group C_{3v} was assumed. The region most susceptible to changes in parameters extended from $q = 40$ to $q = 70$; this region includes a weakly resolved, diffuse doublet in the range $q = 58$ to $q = 70$ which was interpreted visually to have the character of broad, symmetric maxima of nearly equal intensity separated by a shallow minimum. Photographs obtained using a rotating sector confirmed this visual interpretation of the pattern in this region.

TABLE I

QUANTITATIVE ELECTRON DIFFRACTION DATA FOR 1,1,1-TRIFLUOROETHANE

Max.	Min.	I_0	q_0	$q\mathrm{V}/q_0$	$q\mathrm{W}/q_0$
1		+26	20.24	(0.969)	(0.959)
	2	−20	25.37	.982	.966
2		+12	30.31	1.010	.998
	3	− 6	24.65	0.996	.989
3		+ 8	38.42	.979	.968
	4	−15	43.23	.978	.960
4		+17	48.61	1.003	.979
	5	−20	55.17	0.988	.970
5		+ 6	59.64	(1.014)	(1.006)
	6	− 2	64.16	(0.990)	(0.984)
6		+ 6	68.34	(.980)	(.970)
	7	−20	73.11	.984	.973
7		+20	77.49	1.000	.987
	8	−16	82.77	0.999	.988
8		+ 5	86.17	.995	.986
	9	−18	91.05	.976	.970
9		+18	95.48	.987	.975
	10	−19	100.30	.997	.984
10		+ 8	105.03	1.005	.993
Av. (15 features)				0.992	0.979
Av. dev.				.009	.010

Values of $b_{ij} = 0.00016$ for the bonded C–H distance and $b_{ij} = 0.00030$ for the non-bonded C . . . H distance were used and the theoretical intensity curves were found to be quite insensitive to variation of vibration factors on the rotation dependent terms.

The reasons for eliminating models A, B and C can be seen by comparing curve C (Fig. 2) with the visual curve; the sixth maximum is too intense relative to the fifth, the intensity relationship between the seventh and eighth maxima is the reverse of that shown in the visual curve, and the ninth maximum has a higher degree of asymmetry than on the visual curve.

Curve F is shown to represent models D, E, F; it disagrees with the visual curves in the appearance of the fifth, sixth and eighth maxima and the seventh minimum.

Curve G is rejected because the fifth maximum has become a shelf on the inner portion of the sixth maximum. This discrepancy is common also to the curves for H, J, K and L and in curves J and L, the eighth maximum has entirely disappeared.

Although curve O disagrees with the visual curve in the appearance of the fifth and sixth maxima, model O is accepted as in borderline agreement with the visual curve. Models M and N, however, may be completely rejected because of the appearance of these features.

Models P, R and S are all rejected because of the appearance of the fifth and sixth maxima and the eighth maximum. Curve P is shown in Fig. 2

Since curve U disagrees only in the intensity relationship of the fifth and sixth maxima, it is accepted as in borderline agreement with the visual

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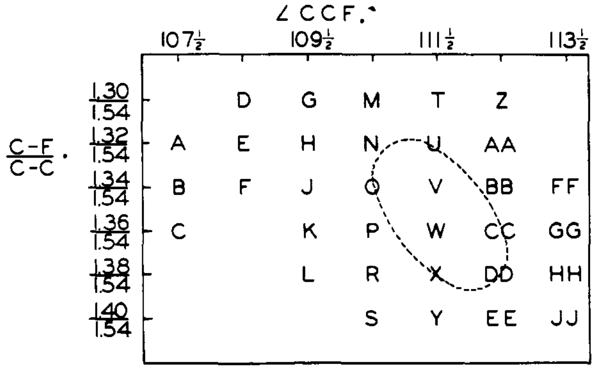

Fig. 1.—Parameters for calculated models of 1,1,1-trifluoroethane.

curve. Model T, however, may be completely rejected.

Models V and W are acceptable. Curve W is shown in Fig. 2.

Since the sixth minimum is so shallow in curve X, model X is only a borderline fit with the visual curve. Model Y is rejected because the sixth minimum has completely disappeared in its theoretical intensity curve.

Because the third maximum is so weak in curve CC, this model is accepted only as a borderline fit with the visual curve. For the same reason, model DD is also a borderline fit. Models Z, AA, BB and EE all may be rejected because the third maximum has disappeared entirely.

Models FF, GG, HH and JJ are all rejected. Curve JJ is chosen to show the over-all incompatibility of this group with the visual curve.

The area indicated by a dashed line in Fig. 1 shows the region of acceptability of models; the line is drawn through models whose theoretical intensity curves are in borderline agreement with the visual curve.

Table I summarizes the q_{calc}/q_0 values for models V and W. The quantitative results from the five borderline models were also taken into account; for all of these, the mean deviation from the average was less than 0.012.

Measurements on the first maximum were rejected because the central electron beam caused a general blackening of the plate in this area; the fifth and sixth maxima and the sixth minimum were also rejected because the diffuse nature of the pattern caused some doubt regarding the validity of the measurements of these features.

Table II lists the various sets of vibration factors used in this investigation. Since the rotation dependent terms contribute very little to the scattering expression, all sets give curves which are very similar; they contain vibration factors which were used to represent the vibrations of the C–F, C . . . F, and F . . . F distances in trifluoromethylacetylene.[10] Acceptable models may be calculated with any one of the sets A, B, C or D. Larger values of b_{ij} for the C . . . F and F . . . F completely destroy the agreement between the calculated and visual curves.

TABLE II

VIBRATION FACTORS

	Set A $b_{ij} \times 10^5$	Set B $b_{ij} \times 10^5$	Set C $b_{ij} \times 10^5$	Set D $b_{ij} \times 10^5$
C–C	0	0	0	0
C–H	16	16	16	16
C. . .H	30	30	30	30
H. . .H	100	100	100	100
C–F	1.5	1.5	1.5	1.5
C. . .F	9.0	9.0	9.0	9.0
F. . .F	6.8	6.8	6.8	6.8
F. . .H (gauche)	30.9	30.9	30.9	62.5
F. . .H (*trans*)	0.5	10	50	0.5

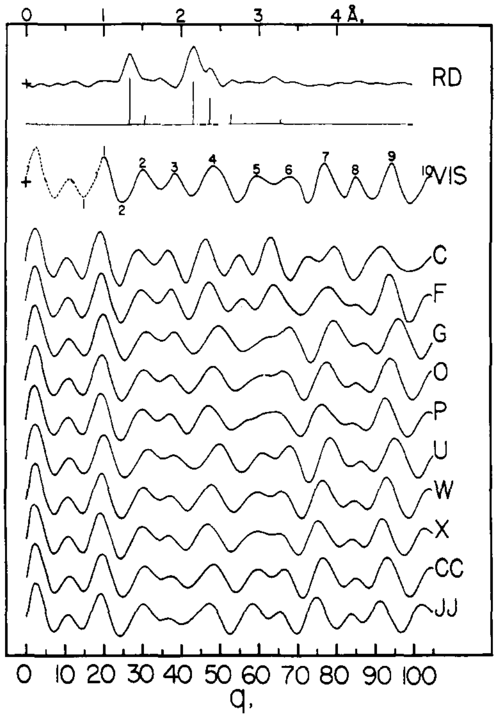

Fig. 2.—Radial distribution curve, visual intensity curve and theoretical intensity curves for 1,1,1-trifluoroethane.

The radial distribution function (curve RD, Fig. 2), calculated according to equation 1, gave three prominent peaks at 1.34, 2.17 and 2.36 Å. The values calculated for the C–C, gauche F . . . H, and *trans* F . . . H distances, and the CCF angle using these three values with C–H = 1.10 Å. and ∠ HCH = 109.5° are shown in Table III. This table also gives the quantitative results from the two entirely satisfactory models as well as the borderline models.

Table III also lists the final accepted values with limits of uncertainty for the interatomic distances in CF_3CH_3. The results obtained in this electron diffraction investigation gave a C–F distance compatible with one previous investigation[2] and a C–C distance compatible with a second investigation.[2] The parameters obtained in the present electron diffraction investigation give I_B = 163.00 $\times 10^{-40}$ g. cm.^{2} which is in very good agreement with the moment of inertia obtained by Edgell and Roberts.[3]

It is interesting to compare the C–F distance in CF_3CH_3 with that which has been found in other

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TABLE III

DISTANCES OBTAINED FROM q/q_0 VALUES

Distance, Å.	V	W	O	U	X	CC	DD
C–F	1.329	1.331	1.325	1.327	1.334	1.335	1.339
C–C	1.528	1.508	1.523	1.549	1.489	1.512	1.494
C...F	2.361	2.350	2.344	2.384	2.340	2.362	2.357
F...F	2.143	2.144	2.146	2.142	2.147	2.141	2.143
F...H (gauche)	2.639	2.614	2.620	2.665	2.601	2.641	2.619
F...H (*trans*)	3.283	3.261	3.263	3.243	3.239	3.280	3.259
∠CCF	111.5°	111.5°	110.5°	111.5°	111.5°	112.5°	112.5°

	Final results with limits of uncertainty Correlation procedure	Radial distribution
C–F, Å.	1.33 ± 0.02	1.33
C–C, Å.	1.52 ± .04	1.52[a]
C...F, Å.	2.36 ± .03	2.35
F...F, Å.	2.14 ± .02	2.16
F...H (gauche), Å.	2.63 ± .05	2.63[a]
F...H (*trans*), Å.	3.27 ± .05	3.27[a]
∠CCF	111.5° ± 1.5°	110.46[a]

[a] Calculated from three intense peaks assuming C–H = 1.10 Å. and ∠HCH = 109.5°.

molecules containing the CF_3 group. This distance is within 0.01 Å. of 1.33 Å. in CF_3H,[11] CF_3Cl,[12] CF_3CF_3,[13] CF_3CCH,[10] $F_3CC{\equiv}CCF_3$,[14] CF_3CN,[15] $N(CF_3)_3$,[16] $S_2(CF_3)_2$[17] and $S_3(CF_3)_2$.[17] In most of these cases the FCF angle is less than tetrahedral.

The C–C distance is apparently less than the value of 1.54 Å. which was found in ethane[18] although the uncertainty on the determination of this distance is quite large. Recent results on this same molecule,[19] obtained by a different electron diffraction technique which employs a rotating sector, indicate that this C–C distance is 1.512 ± 0.015 Å.; the results on the C–F distance and the ∠ FCF are essentially the same as obtained in the present investigation.

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