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# An Electron-diffraction Investigation of the Molecular Structure of Tris(trifluoromethyl)methane, $(CF_3)_3CH$, in the Vapour Phase

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The following values were found for bond lengths and angles: $r(C-C) = 1.537(3)$ Å, $r(F-C) = 1.334(2)$ Å, $\angle CCC = 112.9(0.2)°$, $\angle CCF = 110.9(0.2)°$, $\angle FCF = 108.0(0.2)°$, and $\angle HCC = 105.8(0.3)°$.

Values in parentheses are estimated standard deviations based upon least-squares refinements. Bond distances and angles are those consistent with the $r_a$ structure.

The investigation strongly indicates that the $CF_3$ groups are engaged in a rather large libration type of motion around the C–C bonds.

So far, no structural studies have been done on tris(trifluoromethyl)methane. The compound was synthesized [1] in 1963, and no later work relevant to this investigation has been published to the authors' knowledge.

One of us, E. T., intends to make an X-ray investigation of $CsC(CF_3)_3$, and we felt that information about the structure of $HC(CF_3)_3$ itself might be of interest in this connection.

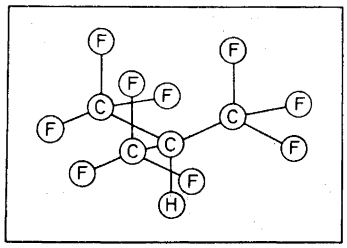


*Fig. 1.* Drawing of $CH(CF_3)_3$.

## EXPERIMENT AND TREATMENT OF DATA

The compound was synthesized and purified as described elsewhere.[1]

Diffraction photographs were obtained in the usual way with the Oslo apparatus.[2] The nozzle temperature was approximately 15°C. The electron

wavelength was determined from a gold foil diffraction pattern, and corrected according to an experiment with $CO_2$. Plates from two different nozzle-to-plate distances of about 48 cm (48.225) and 20 cm (20.091) were obtained. The electron wavelength was 0.06483 Å determined with a standard deviation of *ca.* 0.14 %.

Five plates for each camera distance were photometered, and the intensity data treated in the usual way.[3]

A statistical analysis of each set of data was carried out on the modified molecular intensity curves.[4,5] The general trend in the curves for standard deviations of the average intensities is the same as determined earlier in this laboratory.[4,5]

Individual curves for both sets of data show satisfactory mutual agreement. An average intensity curve for each set of data was calculated. The 48 cm data cover the $s$ range 1.75 – 18.50 Å$^{-1}$, with $\Delta s = 0.125$ Å$^{-1}$, and the 20 cm data cover the $s$ range 11.25 – 45.0 Å$^{-1}$ with $\Delta s = 0.25$ Å$^{-1}$.

Average molecular intensity curves, modified[3] by $s/|f_c|^2$ are presented in Fig. 2. The curves show satisfactory mutual agreement in the overlap region.

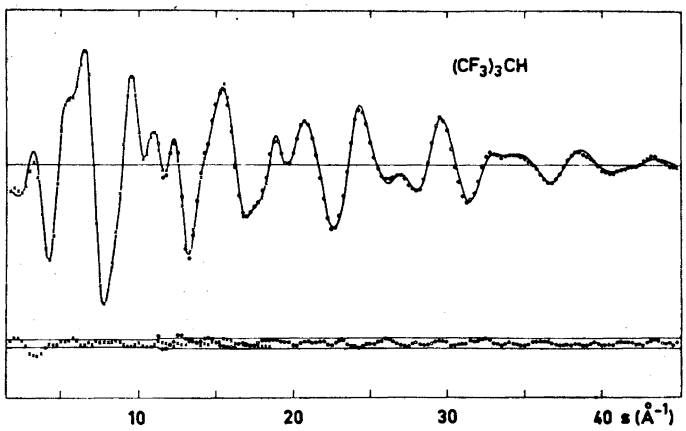


*Fig. 2.* 48 cm (×) and 20 cm (○) experimental average intensity curves. Residuals corresponding to parameters in Table 1 are plotted below together with the experimental error limits. On the 48 cm curve only every second point is plotted.

The experimental radial distribution (RD) function[3] is presented in Fig. 3.

Theoretical molecular intensities were calculated according to eqn. 10 of Ref. 3. The scattering amplitudes were calculated by the partial wave method[3,6] using Hartree-Fock atomic potentials.[7]

## LEAST-SQUARES REFINEMENTS

The refinements[3] were carried out using the two average intensity curves simultaneously. The two curves had been scaled to each other prior to the refinements, and only one common scale factor was refined.

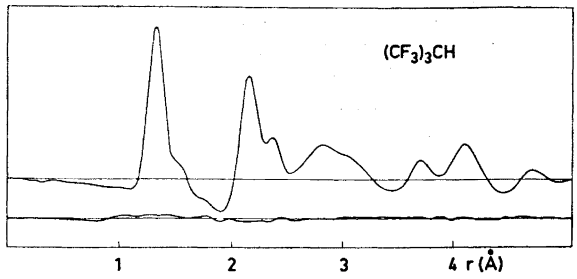


*Fig. 3.* Experimental radial distribution function (RD), and residuals corresponding to parameters in Table 1. An artificial damping constant equal to 0.0010 Å² has been applied.

For each set of data an individual weight matrix [4] including off-diagonal elements was applied. The diagonal weight [4] $w$ for the 48 cm data was given by $w=\exp(-0.13(s-6.0)^2)$ for $s<6.0$, $w=1$ for $6.0 \leq s \leq 16.0$, and $w=\exp(-0.13(s-16.0)^2)$ for $s>16.0$. The corresponding weight for the 19 cm data was given by $w=\exp(-0.13(s-14.0)^2)$ for $s<14.0$, $w=1$ for $14.0 \leq s \leq 35{,}0$, and $w=\exp(-0.0025(s-35.0)^2)$ for $s>35.0$.

Off-diagonal elements [4] of $\varrho^{-1}$ were $p_2=-0.65$ and $p_3=0.152$ for the 48 cm data, while $p_2=-0.61$ and $p_3=0.158$ for the 20 cm data. These values are in good agreement with the average values found for several sets of data from this laboratory.[4]

Eight parameters were used to define the geometry of the molecular model in the following way (Fig. 1); three bond distances, C–C, C–F, and C–H; two bond angles, CCC and CCF; and three angles of rotation for $CF_3$ groups around C–C bonds, $\omega_1$, $\omega_2$, and $\omega_3$.

When all $CF_3$ groups are staggered to the carbon skeleton $\omega_1=\omega_2=\omega_3=0°$.

The carbon skeleton is assumed to have a threefold symmetry axis coinciding with the C–H bond.

Each C–$CF_3$ group is assumed to have a threefold symmetry axis coinciding with the C–C bond.

A series of "rigid" models were tried in the refinements. It was not possible to obtain a good fit with the experimental data for a model having all $CF_3$ groups staggered ($\omega_1=\omega_2=\omega_3=0°$) to the carbon skeleton. A good fit was obtained with models where $\omega_1=\omega_2=\omega_3=\overline{\omega}$ and $\overline{\omega}$ being in the range of 14° to 22°. The best fit was obtained for $\overline{\omega}$ equal to 18°, and results corresponding to this refinement are presented in Table 1. Experimental and theoretical molecular intensity curves are presented in Fig. 2, and the experimental radial distribution (RD) function [3] is presented in Fig. 3.

The parameters in Table 1 are the final parameters. They are not exactly those obtained from refinements. An experiment with $CO_2$ gave a correction of −0.25 % in the $s$ scale. The distances in Table 1 are thus 0.25 % shorter than those found directly by refinements.

An uncertainty in the wavelength (0.14 %) is included in the standard deviations for distances in Table 1.

*Table 1.* Structure parameters ot tris(trifluoromethyl)methane with $\omega_1=\omega_2=\omega_3=18°$. The values in parentheses are estimated standard deviations. M is the multiplicity of the distance $r_a$, and $u$ is the root-mean-square amplitude of vibration of the distance. In the expressions for $R$-factors $V$ stands for residual and P for weight.

| | $r_a$ (Å) | M | $u$ (Å) | |
|---|---|---|---|---|
| $r$(C−H) | 1.110(10) | 1 | 0.075[a] | Bond angles: |
| $r$(C−C) | 1.537(3) | 3 | 0.057[a] | |
| $r$(F−C) | 1.334(2) | 9 | 0.051(1) | CCC = 112.9°(0.2°) |
| | 2.37 | 9 | 0.069(1) | CCF = 110.9°(0.2°) |
| | 2.75, 2.82 | 3−3 | | FCF = 108.0°(0.2°) |
| $r$(F···C) | | | 0.116(4) | |
| | 3.06, 3.15 | 3−3 | | HCC = 105.8°(0.3°) |
| | 3.96, 3.72 | 3−3 | 0.077(3) | |
| | 2.16 | 9 | 0.061(1) | |
| | 2.70, 2.86 | 3−3 | 0.204(24) | |
| | 4.06, 4.07 | 3−3 | | $R$-factors: |
| $r$(F···F) | | | 0.111(3) | |
| | 4.14, 4.21 | 3−3 | | |
| | 4.72 | 3 | 0.082(4) | $R_1=\langle\|V\|\rangle/\langle\|I\|\rangle=0.074$ |
| | 2.87, 3.92 | 3−3 | 0.225(29) | $R_2=(\langle PV^2\rangle/\langle PI^2\rangle)^{\frac{1}{2}}=0.065$ |
| | 2.46, 2.73 | 3−3 | | $R_3=(\langle V'PV\rangle/\langle I'PI\rangle)^{\frac{1}{2}}=0.133$ |
| $r$(···H) | | | 0.200[a] | |
| | 3.25 | 3 | | |
| $r$(C···C) | 2.56 | 3 | 0.066[a] | |
| $r$(C···H) | 2.13 | 3 | 0.085[a] | |

[a] These parameters could not be refined along with the other parameters and the values reported are those assumed after some trial and error.

So far only one average angle of torsion has been determined ($\overline{\omega}=18°$) for the motion of $CF_3$ groups around the C−C bonds. The torsional motion may be very complicated and other "rigid" models with $\omega_1\neq\omega_2\neq\omega_3$ might have given a better fit to the experimental data.

Most of the non-bonded distances depend on the angles of rotation, and in the type of refinements carried out the torsional motion is reflected in the rather large $u$ values for some of those distances (Table 1).

It is possible in a rather approximate way to make an estimate of $u$ values for non-bonded distances assuming reasonable mean amplitudes of torsion. The equilibrium configuration of the molecular model was taken as the one with $\omega_1=\omega_2=\omega_3=0°$. Qualitatively this analysis gave the same distribution of $u$ values as determined in Table 1, if mean amplitudes of torsion as large as 10°−15° were used.

## ANALYSIS OF THE TORSIONAL MOTION

The electron scattering pattern from a molecule having three degrees of freedom ($\omega_1$, $\omega_2$, $\omega_3$), with respect to torsional motion is a function of an

angular probability distribution $P(\omega_1, \omega_2, \omega_3)$. It is assumed that the angular probability function is given by the classical expression [8,9]

$$P(\omega_2,\omega_2,\omega_3) = N_0 \exp(-E/RT)$$

$N_0$ is determined by the demand that $\sum P = 1$, where the summation is over all angular configurations of $\omega_1$, $\omega_2$, and $\omega_3$.

$E$ is the potential energy [10] for a certain configuration of $\omega_1$, $\omega_2$, and $\omega_3$.

$$E = V(\omega_1, \omega_2, \omega_3) + W(\omega_1, \omega_2, \omega_3)$$

The potential energy consists of two terms. $W$ is the energy expression for the sum of interactions between non-bonded substituents. Parameters for the function $W$ were taken from the literature.[10]

The function $V$ describes the restricting potential (in addition to the term $W$) around the C – C bonds in the following way:

$$V = \frac{V_0}{2} \sum_{i=1}^{3} (1 - \cos(3\omega_i))$$

The function $V$ was assumed to have a minimum value for $\omega_1 = \omega_2 = \omega_3 = 0°$ (all $CF_3$ groups staggered).

Theoretical intensities, $T(s)$, were calculated according to the following expression

$$T(s) = \sum_{\text{config.}} P(\omega_1, \omega_2, \omega_3) I(s; \omega_1, \omega_2, \omega_3)$$

$I$ is the theoretical intensity (calculated from eqn. 10 of Ref. 3) for one particular configuration, and the summation being over all configurations of the $\omega$-angles. Configurations were included in the range $-60° \leq \omega_i \leq +60°$

*Table 2.* Energies and angular probabilities for different configurations in $CH(CF_3)_3$. $\omega_1$, $\omega_2$, and $\omega_3$ define the angular configurations in such a way that $\omega_1 = \omega_2 = \omega_3 = 0°$ corresponds to all $CF_3$ groups being staggered. G is the multiplicity of a configuration. $E$ is the energy (in kcal/mol) relative to the energy of the configuration $\omega_1 = \omega_2 = \omega_3 = 15°$. P is the angular probability and $P' = P\,G$. Configurations corresponding to an angular probability P′ of less than 0.3 % are not given. The parameter $V_0 = 0$ kcal/mol.

| $\omega_1$ | $\omega_2$ | $\omega_3$ | G | $E$ | P′(%) | $\omega_1$ | $\omega_2$ | $\omega_3$ | G | $E$ | P′(%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 1 | 0.43 | 1.5 | 20 | 10 | 10 | 6 | 0.23 | 12.6 |
| 10 | 0 | −10 | 3 | 1.25 | 1.0 | 20 | 20 | 0 | 6 | 1.15 | 2.5 |
| 10 | −10 | 0 | 3 | 1.32 | 0.9 | 20 | 20 | 10 | 6 | 0.25 | 12.0 |
| 10 | 0 | 0 | 6 | 0.66 | 5.9 | 20 | 20 | 20 | 2 | 0.21 | 4.3 |
| 10 | 10 | −10 | 6 | 1.59 | 1.2 | 30 | 0 | 0 | 6 | 1.80 | 0.8 |
| 10 | 10 | 0 | 6 | 0.56 | 7.0 | 30 | 10 | 0 | 6 | 1.37 | 1.7 |
| 10 | 10 | 10 | 2 | 0.13 | 4.9 | 30 | 20 | 0 | 6 | 1.78 | 0.8 |
| 20 | 0 | −10 | 6 | 2.17 | 0.4 | 30 | 0 | −10 | 6 | 1.41 | 1.6 |
| 20 | 10 | −10 | 6 | 2.26 | 0.4 | 30 | 10 | 10 | 6 | 0.66 | 5.9 |
| 20 | −10 | 0 | 6 | 2.37 | 0.3 | 30 | 20 | 10 | 6 | 0.80 | 4.6 |
| 20 | 0 | 0 | 6 | 1.22 | 2.2 | 30 | 0 | 20 | 6 | 1.77 | 0.8 |
| 20 | 10 | 0 | 6 | 0.87 | 4.1 | 30 | 10 | 20 | 6 | 0.77 | 4.6 |
| 20 | −10 | 10 | 6 | 2.41 | 0.3 | 30 | 20 | 20 | 6 | 0.88 | 4.0 |
| 20 | 0 | 10 | 6 | 0.91 | 3.8 | 60 | 0 | 0 | 6 | 2.23 | 0.4 |

(i = 1, 2, 3) in steps of 10°. Many of these configurations have the same potential energy and the multiplicity G was introduced to simplify the calculations (Table 2). The number of $E$ values needed is thus drastically reduced.

Several angular probability distributions were computed by changing the value of $V_0$ in the function $V$ ($0 \leq V_0 \leq 3.5$ kcal/mol). The energy parameters [10] in the function $W$ were not changed.

Bond lengths and angles obtained in the refinement corresponding to Table 1 were used to define the geometry.

The theoretical intensity, T($s$), is the one expected from a mixture of hypothetical molecules with different angular configurations, each undergoing small amplitudes of vibration about the equilibrium configuration.[9] The root-mean-square amplitude of vibration needed in the calculation of theoretical intensities is $u_{fr.}$ (framework amplitude), the one resulting from all modes of vibration except libration.[8,9] For distances that vary with the angular configuration the framework amplitude is a different one for each configuration.

In some molecules $u_{fr.}$ may be obtained from spectroscopic information.[11,12] In this case we had to assume that $u_{fr.}$ is independent of the angular configuration. Framework amplitudes were estimated from the $u$ values in Table 1, assuming a mean amplitude of libration for each $CF_3$ group of 10°.

Theoretical intensities, T($s$), were fitted to the experimental ones by a least-squares refinement adjusting only a scale factor. Intensities beyond $s = 30$ Å$^{-1}$ were not considered in this type of refinement. Theoretical radial distribution (RD) curves are compared to the experimental one in Fig. 4.

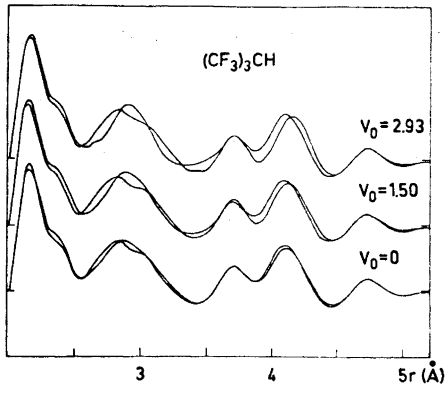


*Fig. 4.* Radial distribution (RD) curves calculated for different probability distributions. The experimental RD curve is plotted together with each of the theoretical ones. An artificial damping constant equal to 0.0010 Å$^2$ has been applied.

The best fit was obtained with the angular probability distribution corresponding to $V_0 = 0$ kcal/mol, this being only slightly better than the fit obtained with $V_0 = 0.5$ kcal/mol.

The angular probabilities were calculated at a temperature $T = 288$ K (the nozzle temperature).

Before attempting any interpretation of the results obtained we want to point out the following:

The parameters in the energy expression[10] for non-bonded interactions were not changed, only $V_0$ was varied to obtain the angular probabilities used in the refinements. Several approximations are involved in the calculation of theoretical intensities.

We therefore present $V_0$ as a formal parameter, and we do not claim that the separation of the total potential energy into two terms $V$ and $W$ is anything more than a convenient way of building up an expression for the energy to be tested. However, the fit obtained between experimental and theoretical intensities seems to indicate that the total potential energy is not too unrealistic.

In Table 2 is presented a list of configurations, their multiplicities (G), potential energies ($E$), and the corresponding angular probabilities ($P' = P\,G$) calculated with $V_0 = 0$ kcal/mol. The probability distribution in Table 2 yielded an rms angle, $\langle\omega^2\rangle^{\frac{1}{2}}$, of about 17°. A minimum in the energy function was found for values of $\omega_1$, $\omega_2$ and $\omega_3$ being nearly equal to 15°.

## CONCLUSIONS

The electron diffraction intensities are consistent with two types of models.

In the simplest model only an average angle of torsion was used to analyze the torsional motion, together with the average $u$ values for those distances being dependent of the torsional angle ("rigid" model).

A more complicated model is the one where the theoretical intensities are the weighted average of intensities from several angular configurations ("dynamical" model).

Electron diffraction can really not distinguish between the two models. Both of them strongly indicate that the $CF_3$ groups are engaged in a rather large libration type of motion around the C – C bonds. The energy calculations yielded an r.m.s. angle of about 17° for the dynamical model that gave the best fit with experimental intensities (Table 2).

Nothing in the analysis indicates that the assumptions of a threefold symmetry axis for the carbon skeleton and the $C-CF_3$ groups are wrong.

There is nothing controversial about the bond distances and angles found in this molecule.

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## REFERENCES

1. Andreades, S. *J. Am. Chem. Soc.* **86** (1964) 2003.
2. Bastiansen, O., Hassel, O. and Risberg, F. *Acta Chem. Scand.* **9** (1955) 232.
3. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* **23** (1969) 3224.
4. Seip, H. M., Strand, T. G. and Stølevik, R. *Chem. Phys. Letters* **3** (1969) 617.
5. Markov, P. and Stølevik, R. *Acta Chem. Scand.* **24** (1970) 2525.
6. Peacher, J. and Wills, J. C. *J. Chem. Phys.* **46** (1967) 4809.

7. Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* **40** (1964) 1686.
8. Almenningen, A., Hartman, A. O. and Seip, H. M. *Acta Chem. Scand.* **22** (1968) 1013.
9. Haaland, A. and Nilsson, J. E. *Acta Chem. Scand.* **22** (1968) 2653.
10. Abraham, R. J. and Parry, K. *J. Chem. Soc.* **B 1970** 539.
11. Cyvin, S. J., Elvebredd, I., Cyvin, B. N., Brunvoll, J. and Hagen, G. *Acta Chem. Scand.* **21** (1967) 2405.
12. Morino, Y. and Hirota, E. J. *J. Chem. Phys.* **28** (1958) 185.

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