

The Molecular Structure of Hexafluoro-2-butyne Determined by Gas Electron Diffraction

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The structure of hexafluoro-2-butyne has been determined by the electron-diffraction method. The most important parameters are: $r_a(\text{C}\equiv\text{C}) = 1.204$ (4) Å, $r_a(\text{C}-\text{C}) = 1.478$ (4) Å, $r_a(\text{C}-\text{F}) = 1.334$ (4) Å, $\angle\text{CCF} = 110.7$ (0.1)°. The final parameters are given in Table 1, column *e*, with the corresponding standard deviations in column *f*. The molecule exhibits essentially free internal rotation.

The barriers to internal rotation in 2-butyne, $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$, and derivatives are known to be much lower than in ethane. The barrier is so low that electron-diffraction data are compatible with essentially free rotation.^{1,2} Upper limits for the barrier in 2-butyne itself have been given as 0.10 kcal/mol³ and 0.03 kcal/mol.⁴ The upper limit for the barrier in $\text{CH}_3-\text{C}\equiv\text{C}-\text{SiH}_3$ has been estimated to only 0.003 kcal/mol.⁵ Based on IR and Raman spectra of hexafluoro-2-butyne, $\text{CF}_3-\text{C}\equiv\text{C}-\text{CF}_3$, it has been concluded that the effective point group for the vibrational function for this compound is D_{3d} ,⁶ which should not be strictly true if the barrier is extremely low.^{7,8} One of the reasons for the investigation of hexafluoro-2-butyne was to find if the electron-diffraction data gave any evidence for a barrier to rotation and if so, to establish the stable conformation. The bond lengths, particularly of the C-C bonds, are also of considerable interest.

A reinvestigation of 1,4-dibromo-2-butyne has been carried out simultaneously.⁹

EXPERIMENT AND THEORY

The sample of hexafluoro-2-butyne was obtained from Pierce Chemical Co., Rockford, Illinois, and used without further purification. The electron-diffraction photographs were obtained in the usual way with the Oslo apparatus.¹⁰ The electron wave length was 0.06464 Å and the nozzle temperature about 15°C. Pictures were recorded at two nozzle-to-plate distances, *i.e.* 48.179 and 20.208 cm, giving intensity data in the *s* ranges 1.75–20.0 Å⁻¹ and 7.25–44.0 Å⁻¹, respectively. The intensity data were read off at intervals

$\Delta s = 0.125 \text{ \AA}^{-1}$ and 0.25 \AA^{-1} . Six plates were used for each set. The data were corrected in the usual way,¹¹ and the modified molecular intensities were calculated using the modification function¹¹

$$s/|f_F'|^2$$

The background was subtracted from the curves obtained from the 12 plates separately. For the calculation of radial distribution curves (RD),¹¹ six composite intensity curves were calculated, combining data from two plates, one from each nozzle-to-plate distance. The average of these six curves was also calculated. Least-squares refinements were carried out either on data from each nozzle-to-plate distance separately, or simultaneously without combining to composite curves. The final results were obtained by simultaneously least-squares refinement on two average intensity curves each obtained from one set of plates.

The theoretical molecular intensities were calculated according to eqn. 10 of Ref. 11. The scattering amplitudes were calculated by the partial wave method^{11,12} using Hartree-Fock atomic potentials.¹³

STRUCTURE ANALYSIS AND REFINEMENT

The average composite intensity curve is shown in Fig. 1. The experimental RD function calculated by Fourier transformation of the intensity curve in

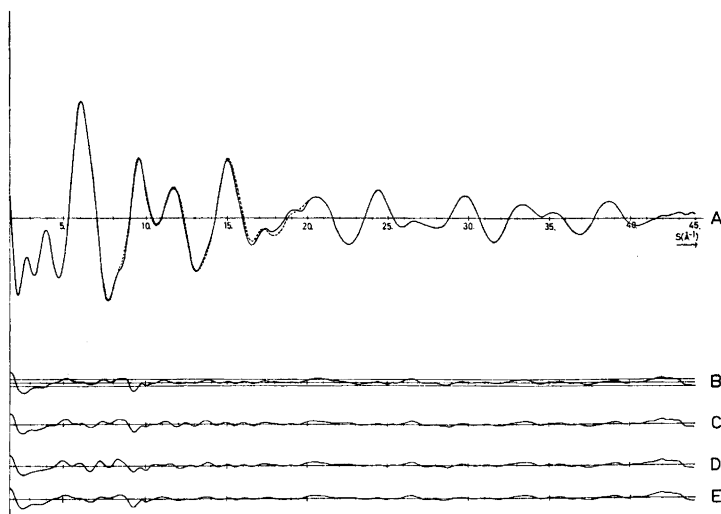


Fig. 1. Curve A shows the experimental composite intensity; the data corresponding to the short nozzle-to-plate distance are shown dotted in the overlap region. Curves B to E show the difference between experimental and theoretical intensities for various models. B: free internal rotation, the straight lines give the experimental uncertainty ($\pm 3 \times$ experimental standard deviation). C: eclipsed model. D: staggered model. E: restricted rotation, $V_3^\circ = 0.1 \text{ kcal/mol}$.

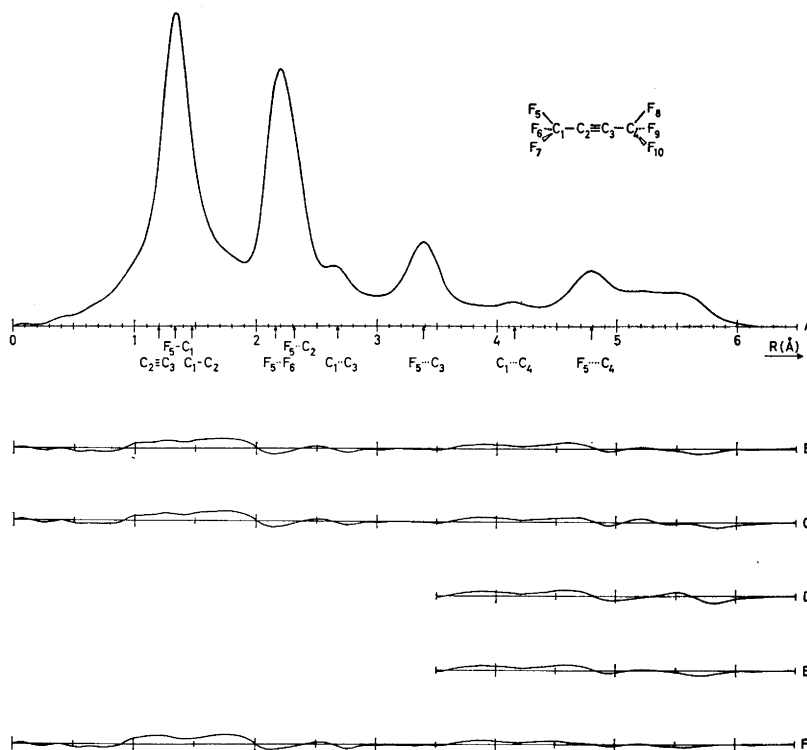


Fig. 2. Experimental radial distribution function (A) and curves showing the difference between experimental and various theoretical functions (B–F), ($k=0.0025 \text{ \AA}^2$). B: free internal rotation. C: eclipsed model. D: staggered model. E: restricted rotation, $V_3^\circ=0.1 \text{ kcal/mol}$. F: restricted rotation, $V_3^\circ=0.1 \text{ kcal/mol}$ and corrections for the shrinkage effects.

Fig. 1, is shown in Fig. 2. The bond distances contribute all to the first peak, while the $F \cdots F$ distances contribute to the outer part of the curve. This region thus contains the information about the internal rotation.

Determination of the molecular parameters. Various least-squares refinements of the molecular parameters were carried out. In most of the calculations all the non-bonded distances were obtained from the bond distances and $\angle CCF$. The shrinkage effect was neglected except in the final refinements. The molecule was assumed to have D_3 or higher symmetry. The torsional angle (ϕ) is defined to be zero for the eclipsed form (D_{3h} symmetry). The staggered form (D_{3d} symmetry) corresponds thus to $\phi = 60^\circ$.

Refinements were first carried out for an eclipsed and a staggered model, as well as for a model with freely rotating CF_3 groups. The theoretical intensity curve for free rotation was calculated by adding the contributions for 25 molecular models with different values of ϕ .¹⁵ The results obtained for the bond lengths, bond angles, and for the root-mean-square amplitudes of

vibration (u)¹⁴ for the distances with the exception of F \cdots F, were nearly the same in all cases.

The problem of obtaining realistic standard deviations from an electron-diffraction investigation has been discussed previously.¹⁶ In this investigation we have carried out least-squares refinements on the average intensity curves both with a diagonal weight matrix and a weight matrix with non-zero off-diagonal elements of the type discussed previously.¹⁶

Table 1. Molecular parameters for F₃C-C≡C-CF₃. Distance (r_a) and amplitudes in Å, angles in degrees.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>
$r(\text{C}\equiv\text{C})$	1.191 (3)	1.193 (3)	1.194 (4)	1.201 (5)	1.204 (3)	4	1.198 (3)
$r(\text{C}-\text{C})$	1.472 (3)	1.471 (3)	1.467 (4)	1.481 (4)	1.478 (3)	4	1.470 (2)
$r(\text{C}-\text{F})$	1.331 (2)	1.333 (2)	1.331 (2)	1.333 (1)	1.334 (2)	2	1.331 (1)
$\angle\text{CCF}$	110.8(0.1)	110.8(0.1)	110.8(0.1)	—	110.7(0.1)	0.1	110.8(0.1)
$u(\text{C}\equiv\text{C})$	0.046 (4)	0.036 —	0.036 —	0.036 —	0.036 —	—	0.036 —
$u(\text{C}-\text{C})$	0.053 (3)	0.052 (3)	0.062 (6)	0.049 (3)	0.049 (3)	6	0.053 (4)
$u(\text{C}-\text{F})$	0.047 (1)	0.046 (1)	0.045 (1)	0.047 (1)	0.046 (1)	2	0.046 (1)
$u(\text{C}_2\cdots\text{F}_5)$	0.061 (1)	0.060 (1)	0.059 (2)		0.060 (1)	2	0.062 (1)
$u(\text{C}_3\cdots\text{F}_5)$	0.096 (3)	0.096 (3)	0.092 (3)		0.092 (2)	3	0.098 (2)
$u(\text{C}_4\cdots\text{F}_5)$	0.122 (5)	0.121 (5)	0.121 (5)		0.121 (5)	5	0.115 (6)
$u(\text{F}_5\cdots\text{F}_5)$	0.056 (1)	0.056 (1)	0.054 (1)		0.056 (1)	2	0.058 (1)
$u(\text{C}_1\cdots\text{C}_3)$	0.064 (6)	0.065 (6)	0.056 (6)		0.065 (6)	6	0.055 (5)
$u(\text{C}_1\cdots\text{C}_4)$	0.065(18)	0.065(19)	0.052(12)		0.063(17)	17	0.058 —

a. Shrinkage neglected, diagonal weight matrix, $u(\text{C}\equiv\text{C})$ refined.

b. Shrinkage neglected, diagonal weight matrix, $u(\text{C}\equiv\text{C})$ assumed.

c. Shrinkage neglected, off-diagonal elements included in the weight matrix, $u(\text{C}\equiv\text{C})$ assumed.

d. Bond distances refined independent of the non-bonded distances, diagonal weight matrix, $u(\text{C}\equiv\text{C})$ assumed.

e. Shrinkage included (see text), diagonal weight matrix, $u(\text{C}\equiv\text{C})$ assumed. The parameter values may be regarded as our final results.

f. Final standard deviations.

g. Results obtained by Bauer *et al.*²⁰

The results are compared in columns *b* and *c* in Table 1.* The differences in the parameters in these two columns are seen to be small. The values given in parentheses are acceptable standard deviations only if the applied weight matrix is a reasonably good approximation to the weight matrix obtained from the moment matrix for the observations. The values in column *c* should therefore be more realistic than the corresponding values in column *b*.

We have further carried out least-squares calculations on the intensity data obtained from each plate separately. The mean values and the corre-

* The results in Table 1 were actually obtained for a model with a small barrier to internal rotation ($V_3^\circ = 0.1$ kcal/mol, see p. 2980).

sponding standard deviations (σ_1) calculated from these results are given in Table 2. For comparison we have also given the standard deviations (σ_2) obtained by refining on the average curve applying a diagonal weight matrix.

Table 2. Mean values (distances and u values in Å, angles in degrees) and standard deviations obtained refining on the data from the two nozzle-to-plate distances separately. The shrinkage effect was neglected.

	Short distance			Long distance		
	Mean value	σ_1^a	σ_2^b	Mean value	σ_1^a	σ_2^b
$r(\text{C}=\text{C})$	1.1894	0.0030	0.0071	1.200	0.0012	0.0038
$r(\text{C}-\text{C})$	1.4720	0.0045	0.0056	1.4685	0.0022	0.0028
$r(\text{C}-\text{F})$	1.334	0.0009	0.0013	1.3304	0.0005	0.0005
$\angle \text{CCF}$	110.77	0.36	0.19	110.69	0.7	0.7
$u(\text{C}-\text{F})$	0.067	0.009	0.005	0.045	0.001	0.001
$u(\text{C}_3 \cdots \text{F}_4)$	0.098	0.004	0.006	0.091	0.002	0.003
$u(\text{C}_4 \cdots \text{F}_5)$	0.120	0.003	0.011	0.125	0.005	0.008

^a σ_1 is the standard deviation for the mean of the results obtained for six intensity curves.

^b σ_2 is the standard deviation obtained by refining on the average of the six intensity curves with a diagonal weight matrix.

Though the neglect of the correlation between the experimental data implied in the use of a diagonal weight matrix should make σ_2 unrealistically small, Table 2 shows that σ_2 is larger than σ_1 for most parameters.

The results discussed so far suffer from neglect of the shrinkage effect. The bond lengths were therefore also refined considering the non-bonded distances as independent fixed parameters. The results are given in Table 1 *d*.

Both the average distances (r_g) and $r_a = r_g - u^2/r$ show shrinkage effects. The shrinkage may be estimated by calculation of r_α distances defined by¹⁷

$$r_\alpha \approx r_g - (\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle) / 2r = r_g - K / 2r \quad (1)$$

since there is no geometrical inconsistency in the r_α structure. Shrinkage parameters obtained using eqn. (1) and values for K calculated by Cyvin,¹⁸ were applied in least-squares calculations. The shrinkage for the F \cdots F distances was assumed independent of ϕ . The agreement between experimental and theoretical data was improved. The results are given in Table 1 column *e*. The inclusion of shrinkage is seen to lengthen the CC bonds, while the effects on the other parameters are small. Though the applied shrinkage parameters may be rather approximate, we feel that the results in column *e* are the most reliable ones.

The potential for internal rotation. As mentioned in the previous section, least-squares refinements were carried out both for eclipsed and staggered models, as well as for free rotation. The agreement obtained did not differ much in the three cases. A further study of the torsional potential was then carried out, using results obtained by Elvebredd.¹⁹ She calculated mean

amplitudes of vibration for hexafluorobutene from spectroscopic data, including the mean amplitudes for the F···F distances for various values of ϕ assuming no torsional oscillation. These u values, usually called framework amplitudes of vibration (u_{fr}), are a function of ϕ , *i.e.* to a good approximation¹⁹

$$u_{fr}(\phi)^2 = (\alpha + \beta \cos \phi + \gamma \cos^2 \phi) / r_{ij}(\phi)^2 \quad (2)$$

$r_{ij}(\phi)$ is the interatomic distance corresponding to ϕ , and α , β , and γ are constants. With $\alpha = 0.9358 \text{ \AA}^4$, $\beta = 0.5039 \text{ \AA}^4$, and $\gamma = -0.0020 \text{ \AA}^4$ u_{fr} ranges from 0.115 Å to 0.235 Å.*

The potential function for the internal rotation is probably to a very good approximation

$$V(\phi) = \frac{1}{2} V_3^\circ (1 + \cos 3\phi) \quad (3)$$

The electron-diffraction data contain information about the probability for finding ϕ in the range ϕ to $\phi + d\phi$; *i.e.* $P(\phi)d\phi$.¹⁵ Assuming the classical relation

$$P(\phi) = N \exp(-V(\phi)/RT) \quad (4)$$

to be valid, V_3° may be determined. Least-squares refinements of the molecular parameters were then carried out for various values of V_3° . The theoretical curves were calculated as for free rotation using eqn. (2), except that the weights for the molecular models were obtained from eqn. (4).

With a diagonal weight matrix a minimum in

$$S = \sum_s W_s (I_s^{\text{obs}} - \text{Scale} \times I_s^{\text{theor}})^2 \quad (5)$$

was found for $V_3^\circ = 0.1$ kcal/mol corresponding to a slight preference of the staggered form. However, the difference in S for $V_3^\circ = 0$ and $V_3^\circ = 0.1$ kcal/mol is only 0.1 %, which shows that the barrier is not significantly different from zero.

The difficulty in determining a very low barrier in a molecule of this type by electron diffraction is also illustrated in Fig. 3, which shows the contribution from the torsional dependent F···F distances to the RD curve. To obtain the experimental curve all the ϕ -independent contributions were subtracted from the experimental intensity curve, and the resulting function was Fourier transformed. The theoretical curves corresponding to $V_3^\circ = 0$, 0.1, and 0.25 kcal/mol, are seen to be very similar.

DISCUSSION

In a simultaneous investigation by Bauer *et al.*²⁰ it was concluded that the molecule has free internal rotation. This conclusion is not contradicted by our results. However, Bauer *et al.* assumed $u_{fr}(\phi) = \text{constant}$. Fig. 3 illustrates the importance of varying u_{fr} with ϕ . The theoretical RD curves, including only ϕ -dependent F···F distances, are shown calculated for constant $u_{fr}(\phi) = 0.179 \text{ \AA}$ and with $u_{fr}(\phi)$ given by eqn. (2). The probability distribution (eqn. (3)) was in both cases calculated with $V_3^\circ = 0.1$ kcal/mol.

* These values for α , β , and γ differ somewhat from those given by Elvebredd partly because of a small difference in molecular parameters and partly because of a small error in Ref. 19.

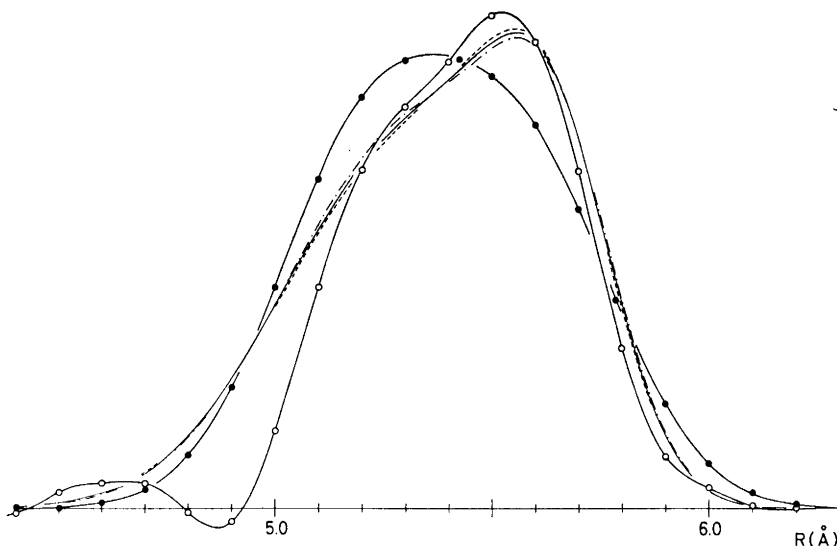


Fig. 3. Radial distribution functions for the torsional dependent F...F distances ($k = 0.0025 \text{ \AA}^2$). O, experimental; all the others are theoretical; ●, $V_3^\circ = 0.1 \text{ kcal/mol}$ and $u_{\text{tr}}(\phi) = 0.179 \text{ \AA}$ independent of ϕ . ---, free internal rotation and $u_{\text{tr}}(\phi)$ given by eqn. (2). —, $V_3^\circ = 0.10 \text{ kcal/mol}$ and $u_{\text{tr}}(\phi)$ given by eqn. (2). - · - · - ·, $V_3^\circ = 0.25 \text{ kcal/mol}$ and $u_{\text{tr}}(\phi)$ given by eqn. (2).

Table 1 includes results of the investigation by Bauer *et al.*²⁰ Since shrinkage was neglected in their investigation, the parameters in column *g* should be compared to the values in column *c* rather than to our final results in *e*. The agreement is seen to be satisfactory. Sheehan and Schomaker²¹ reported 1.22 Å, 1.465 Å, and 1.34 Å for the bond distances.

The parameters in Table 1, column *e*, may be compared to the results obtained for 2-butyne, where Kuchitsu *et al.*¹⁷ found $r_a(\text{C}\equiv\text{C}) = 1.212 \text{ \AA}$ and $r_a(\text{C}-\text{C}) = 1.466 \text{ \AA}$. Our results indicate thus a lengthening of the single bond and a shortening of the triple bond in hexafluorobutyne compared to 2-butyne.

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