

## An Electron Diffraction Study of the Molecular Structure of Dodecafluoro-cyclohexane in the Gas Phase

K. E. HJORTAAS

*Kjemisk institutt, Norges Lærerhøgskole, Trondheim, Norway \**

and

K. O. STRØMME

*Kjemisk institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway*

The molecular structure of dodecafluoro-cyclohexane ( $C_6F_{12}$ ) has been determined by the gas electron diffraction method. Bond distances and angles are:  $r(C-C)$ : 1.551 Å,  $r(C-F)$ : 1.337 Å,  $\angle CCC$ : 112.6°,  $\angle FCF$ : 109.1°.  $D_{3d}$  symmetry is assumed. The axial C—F bonds are bent 6.2° away from the chief axis of the carbon ring. The angle between a C—F bond and the plane through the bond carbon atom and the two adjacent ones is 53.7° for the axial and 55.4° for the equatorial position of the fluorine atom.

The purpose of this electron diffraction work was to obtain the molecular parameters of dodecafluoro-cyclohexane ( $C_6F_{12}$ ) as accurate as possible in order to compare with the accurate data reported for cyclohexane.<sup>1</sup> It was of particular interest to obtain detailed information of the bond angles. The molecule has previously been studied by Bastiansen *et al.*,<sup>2</sup> who obtained a C—F bond length of 1.38 Å on the basis of an undistorted molecular model, wherein the bond angles are tetrahedral, and an assumed C—C bond length of 1.54 Å. According to these authors a still better agreement with experimental data was obtainable if a minor distortion of the valency angles was assumed, leaving the symmetry of the model unchanged.

The data obtained in the present work have been used in an X-ray diffraction study of the disordered structure of dodecafluoro-cyclohexane in the cubic solid phase.<sup>3</sup>

\* Present address: Østfold tekniske skole, N-1700 Sarpsborg, Norway.

## THEORY

Theoretically,<sup>4</sup> a function for the molecular intensity may be deduced:

$$I_M^T(s) = k_s \frac{\varphi(s)}{s} \sum_{i=1}^N \frac{2n_i}{r_i} |f(s)|_m |f(s)|_n \cos(\eta(s)_m - \eta(s)_n) \exp(-\frac{1}{2}u_i^2 s^2) \text{sins}r_i$$

$s = (4\pi/\lambda) \sin\theta$ ,  $\lambda$  is wavelength of the electron beam,  $2\theta$  is the scattering angle. The scale factor  $k_s$  is introduced as the experimental intensities are on an arbitrary scale. The distance between the atoms  $m$  and  $n$  is denoted  $r_i$  ( $r_i = r_g(1)^5$ ),  $n_i$  is the multiplicity of this distance and  $u_i$  is the root-mean-square amplitude of vibration.  $|f(s)|$  and  $\eta(s)$  are related to the complex atomic electron scattering factor  $f(s)$ :

$$f(s) = |f(s)| \exp(i\eta(s))$$

The modification functions  $\varphi(s)$  is conveniently defined through the equation:<sup>4</sup>

$$\varphi(s) = \frac{s}{|f(s)|_k |f(s)|_i}$$

The experimental molecular intensities may be obtained by the usual procedure.<sup>4</sup> The photographic plates are exposed in the electron diffraction apparatus and then photometrically evaluated. The numerical values thus obtained are multiplied by the correction for using planar plates, the sector correction, the modification function  $\varphi(s)$  and  $s^4$ . From the numerical data thus obtained the corresponding values of the background curve are subtracted. These differences constitute the  $I_M^E(s)$  curve which corresponds to the  $I_M^T(s)$  curve.

A radial distribution (RD) function may be defined:

$$\frac{\sigma(r)}{r} = \int_{s_1}^{s_2} I_M(s) \exp(-ks^2) \text{sins}r \, ds$$

$s_1$  is the minimum and  $s_2$  is the maximum  $s$  value.  $k$  is an artificial damping constant. The outer termination error of the integral is reduced by  $\exp(-ks^2)$ .<sup>4</sup>

The molecular parameters are refined by minimizing the sum:

$$\sum w(s) [I_M^E(s) - I_M^T(k_s, r_i, u_i, s)]^2$$

by the least squares method.<sup>6-9</sup> The weight function  $w(s)$  is defined by the equations:

$$\begin{aligned} w(s) &= \exp[-W_1(s' - s)^2] && \text{for } s < s' \\ w(s) &= 1.00 && \text{» } s' \leq s \leq s'' \\ w(s) &= \exp[-W_2(s - s'')^2] && \text{» } s > s'' \end{aligned}$$

$s'$ ,  $s''$ ,  $W_1$ , and  $W_2$  are constants.

## EXPERIMENTAL

The compound used was kindly supplied by Dr. Pedler, Department of Chemistry, University of Birmingham, England.

*Electron diffraction work.* The experimental data were obtained by A. Almenningen at the University of Oslo. Three nozzle-to-plate distances were used: 19, 48, and 186 (cm). The wavelength  $\lambda$  of the electron beam was about 0.064 Å. For each distance four exposed photographic plates were photometrically evaluated. The  $s$  ranges are: 7.5–45.0, 1.5–20.0 and 1.0–5.0 (Å<sup>-1</sup>). The average intensities were obtained from the plates for  $\Delta s = 0.25$  Å<sup>-1</sup>.

*Calculations.* For the calculation of the molecular intensities the modification function  $\varphi(s)$  was chosen:

$$\varphi(s) = \frac{s}{|f(s)|_C |f(s)|_F}$$

The final experimental RD curve was calculated using the theoretical intensity values for  $s < 1.0$  Å<sup>-1</sup> and the artificial damping constant  $k = 0.0009$  Å<sup>2</sup>.

The complex atomic electron scattering factors were calculated by T. G. Strand, Department of Chemistry, University of Oslo, using a program based on a work by J. L. Peacher and J. G. Wills.<sup>10</sup> For the least squares refinement of the molecular parameters on the observed and calculated intensities, a computer program written by H. M. Seip<sup>9</sup> was used. The constant  $s'$ ,  $s''$ ,  $W_1$ , and  $W_2$  of the weight function  $w(s)$  were chosen equal to 5.0 Å<sup>-1</sup>, 30.0 Å<sup>-1</sup>, 0.20 Å<sup>2</sup>, and 0.003 Å<sup>2</sup>, respectively. The calculations were performed on the UNIVAC 1107 computer at the Technical University of Norway.

## STRUCTURE INVESTIGATION

The final background curve was obtained by comparing successively calculated experimental and theoretical intensity and RD curves. Approximate values for the bond distances and for the distance between fluorine atoms attached to the same carbon atom, were easily obtained from the experimental RD curve. A molecular model of symmetry  $D_{3d}$  was worked out on the basis of these distances and tetrahedral angles. Values of root-mean-square amplitudes of vibration were estimated at this stage. The molecular parameters were changed according to successively calculated intensity and RD curves. RD curves were also calculated separately for each of the various overlapping interatomic distances in order to adjust their  $u$  values. In the least squares refinement groups of the molecular parameters were varied. The carbon atoms may be labelled C( $n$ ),  $n = 1, \dots, 6$ . The fluorine atoms which are axially ( $a$ ) or equatorially ( $e$ ) bonded to the carbon atom  $n$ , may be labelled F( $n, a$ ) and F( $n, e$ ), respectively. There are 20 non-equivalent interatomic distances in the molecule. In the least squares calculations five interatomic distances were chosen as "independent": the two bond distances and the three non-bonding distances C( $n$ )–F( $n+1, a$ ), C( $n$ )–F( $n+1, e$ ), and F( $n, e$ )–F( $n, a$ ). The distance C( $n$ )–C( $n+2$ ) was not chosen as "independent" because of its low multiplicity. The final parameter values with standard deviations are listed in Table 1. The theoretical intensity and RD curves based on these values, are shown in Fig. 1 and in Fig. 2, respectively. These figures also show the corresponding experimental curves.

Table 1. Results from the least squares refinement. The distances marked with asterisks were independent. Distances  $r_g(1)$ <sup>6</sup> and root-mean-squares amplitudes of vibration ( $u$ ) both with standard deviations ( $\sigma$ ) in Ångström units are listed. F( $n,a$ ) is axially and F( $n,e$ ) is equatorially bonded to C( $n$ ).  $n=1, \dots, 6$ .

	$r_g(1)$	$\sigma_r$	$u$	$\sigma_u$
C—C *	1.551	0.0007 0.0023 <sup>a</sup>	0.039	0.0016
C—F *	1.337	0.0005 0.0020 <sup>a</sup>	0.041	0.0005
C( $n$ )—C( $n+2$ )	2.580	0.0074	0.064	0.0059
C( $n$ )—C( $n+3$ )	3.010	0.0065	0.05	0.011
C( $n$ )—F( $n+1,a$ ) *	2.357	0.0020	0.065	0.0052
C( $n$ )—F( $n+1,e$ ) *	2.345	0.0021	0.058	0.0044
C( $n$ )—F( $n+2,a$ )	3.02	0.022	0.108	0.0060
C( $n$ )—F( $n+2,e$ )	3.721	0.0028	0.065	0.0020
C( $n$ )—F( $n+3,a$ )	3.59	0.018	0.17	0.022
C( $n$ )—F( $n+3,e$ )	4.190	0.0026	0.065	0.0062
F( $n,a$ )—F( $n,e$ ) *	2.177	0.0013	0.055	0.0014
F( $n,a$ )—F( $n+1,a$ )	3.495	0.0042	0.060	0.0024
F( $n,a$ )—F( $n+1,e$ )	2.64	0.008	0.096	0.0042
F( $n,a$ )—F( $n+2,a$ )	2.83	0.043	0.13	0.012
F( $n,a$ )—F( $n+2,e$ )	4.24	0.022	0.109	0.0052
F( $n,a$ )—F( $n+3,a$ )	4.50	0.025	0.14	0.22
F( $n,a$ )—F( $n+3,e$ )	4.49	0.015	0.16	0.12
F( $n,e$ )—F( $n+1,e$ )	2.79	0.0086	0.098	0.0085
F( $n,e$ )—F( $n+2,e$ )	4.673	0.0078	0.086	0.0064
F( $n,e$ )—F( $n+3,e$ )	5.443	0.0037	0.076	0.0090

$\angle$ CCC: 112.6°,  $\angle$ FCF: 109.1°,  $\angle$ FCF =  $\gamma_a + \gamma_e$ ,<sup>b</sup>  $\gamma_a = 53.7^\circ$ ,  $\gamma_e = 55.4^\circ$ .

Standard deviations: 0.34° ( $\angle$ CCC), 0.30° ( $\angle$ FCF), 0.22° ( $\gamma_a$ ), 0.21° ( $\gamma_e$ ).

<sup>a</sup> includes also uncertainty of wavelength.<sup>4</sup>

<sup>b</sup>  $\gamma_a$  and  $\gamma_e$  are the angles between the axial and the equatorial C—F bonds, respectively, and the plane through the actual bond carbon atom and the two adjacent ones.

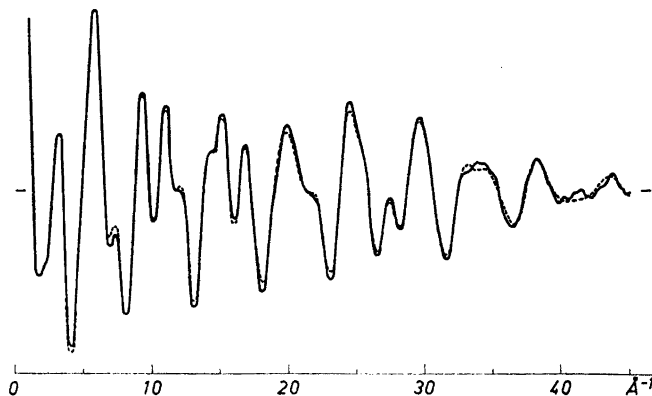


Fig. 1. Experimental and theoretical (dotted) molecular intensity curves.

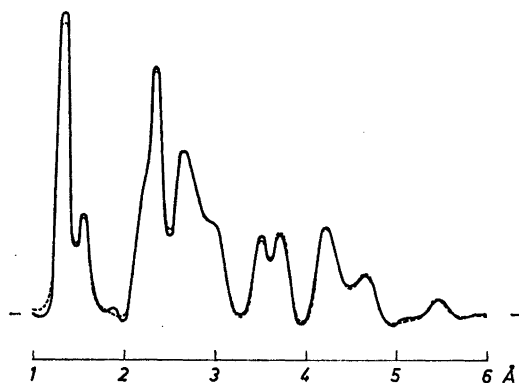


Fig. 2. Experimental and theoretical (dotted) radial distribution curves. Artificial damping constant:  $k=0.0009 \text{ \AA}^2$ .

By way of comparison, the theoretical intensity curve shown in Fig. 1, is redrawn in Fig. 3 (with a new scale factor) together with the curve based on the intensities:<sup>4</sup>

$$I_M(s) = k_s \sum_{i=1}^N \frac{n_i Z_m Z_n}{r_i} \exp(-\frac{1}{2} u_i^2 s^2) \sin sr_i$$

It may be seen that there is some difference between the two curves for small  $s$  values only.

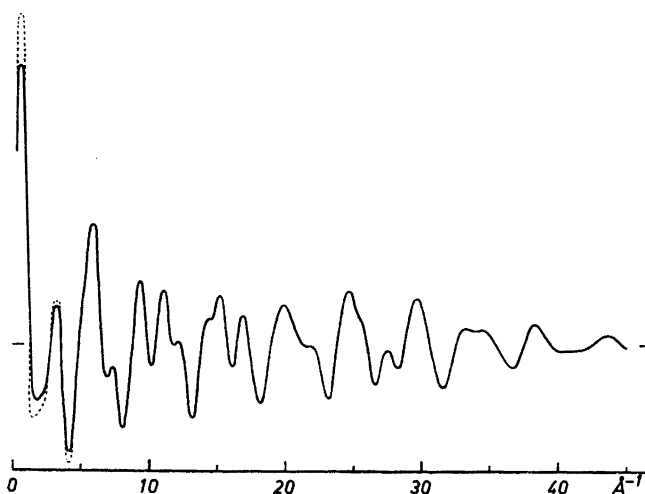


Fig. 3. Theoretical intensity curves. The final curve (Fig. 1) and the curve (dotted) based on the intensities:<sup>4</sup> cf. eqn. on p. 2967.

## DISCUSSION

The observed molecular configuration deviates significantly from an ideal model based on tetrahedral angles. The departure may be interpreted as an effect of repulsion between the fluorine substituents.

The CCC bond angle obtained ( $112.6^\circ$ , standard deviation ( $\sigma$ ):  $0.36^\circ$ ) is not significantly different from the one reported for cyclohexane ( $111.55 \pm 0.15^\circ$ ).<sup>1</sup> The FCF bond angle obtained ( $109.1^\circ$ ,  $\sigma=0.30^\circ$ ), compares well with the corresponding values for fluoroform ( $108.8 \pm 0.75^\circ$ )<sup>11</sup> and for difluoromethane ( $108.5^\circ$ ).<sup>11</sup> The axial C—F bond is bent  $6.2^\circ$  away from the direction of the three fold axis in the mirror plane of the molecule. The axial C—F bond makes the angle  $53.7^\circ$  ( $\sigma=0.22^\circ$ ) with the plane through the carbon atom inherent in the bond, and the two adjacent ones. The equatorial C—F bond makes the angle  $55.4^\circ$  ( $\sigma=0.21^\circ$ ) with the same plane. The directions of the C—F bonds might be explained to be due to the non-bonding repulsions. The distance between  $F(n,e)$  and  $F(n\pm 1,a)$  ( $2.64 \text{ \AA}$ ) is shorter than the sum of the van der Waals' radii of the fluorine atoms ( $2.70 \text{ \AA}$ ).<sup>12</sup> However, repulsions between these atoms might not to any great extent affect the direction of the  $C(n)$ — $F(n,e)$  bond as the component of the repulsive force vertical to the bond direction should be rather small. Repulsions between  $F(n,e)$  and  $F(n-1,e)$  and  $F(n+1,e)$  (distance:  $2.79 \text{ \AA}$ ) might neither be expected to affect seriously the  $C(n)$ — $F(n,e)$  bond direction. As to the direction of this bond repulsions between  $F(n,e)$  and  $F(n,a)$  (distance:  $2.177 \text{ \AA}$ ) might be expected to be of greater importance. The atoms  $C(n)$ ,  $F(n,a)$ ,  $F(n-1,e)$ , and  $F(n+1,e)$  are not far from being coplanar. Therefore, despite the short  $F(n,a)$ — $F(n\pm 1,e)$  distance ( $2.64 \text{ \AA}$ ), repulsions between these fluorine atoms might not greatly affect the direction of the  $C(n)$ — $F(n,a)$  bond. The distance ( $2.83 \text{ \AA}$ ) between fluorine atoms which are axially bonded on the same side of the carbon ring, is obtained somewhat greater than the sum of the van der Waals' radii of the fluorine atoms. Repulsions between these fluorine atoms, however, would work almost vertically to the  $C(n)$ — $F(n,a)$  bond directions. Accordingly, it seems reasonable that the directions of these bonds deviate somewhat outward from the direction of the three fold axis and in the planes of symmetry of the molecule.

The C—C bond distance obtained ( $1.551 \text{ \AA}$ ,  $\sigma=0.0023 \text{ \AA}$ ) is rather long compared to the one reported for cyclohexane ( $1.528 \pm 0.005 \text{ \AA}$ ).<sup>1</sup> This might be expected, however, when greater non-bonding repulsions are assumed for the fluorine compound than for cyclohexane itself. Considering the strong electronegative character of the fluorine atoms, a small negative excess charge on these and a small positive excess charge on each of the carbon atoms might be expected. Positively charged carbon atoms might enhance the effect from non-bonding repulsions on the C—C bond length. It might be mentioned that the reported C—C bond length ( $1.564 \text{ \AA}$ ) of hexachloroethane<sup>13</sup> is definitely greater than the C—C distance reported for ethane ( $1.536 \text{ \AA}$ ).<sup>14</sup> One of the C—C bond distances of the molecule of the perhydroanthracene isomer, m.p.  $121^\circ\text{C}$ , was found equal to  $1.554 \text{ \AA}$ , whereas the mean value of the C—C bond lengths is  $1.538 \text{ \AA}$ . This bond lengthening was also attributed to non-bonding repulsions.<sup>15</sup> The C—F bond distance ( $1.337 \text{ \AA}$ ,  $\sigma=0.0020 \text{ \AA}$ ) is

reasonable compared with the reported average value of the C—F bond distances in paraffinic poly fluorine compounds (as well as in olefinic fluorine compounds):  $1.333 \pm 0.005 \text{ \AA}$ .<sup>11</sup>

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