Pennsylvania, supported by the Advanced Research Projects Agency, Office of the Secretary of Defense.

This paper is part of a thesis to be submitted by Mr Joseph Arbuckle to the Graduate School of Arts and Sciences of the University of Pennsylvania, Philadelphia, Pennsylvania, in partial fulfillment of the requirement for the Ph.D. degree.

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A Redetermination of the Orthorhombic IF_7 Structure

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(*Received* 7 *March* 1962)

The idealized molecular configuration in orthorhombic IF_7 has the point symmetry *mm* and can be derived from dodecahedral 8-coordination by allowing two atoms at one end of the $\bar{4}$ axis to coalesce into one. There are five bonds at 1·825 Å, $\sigma = 0{\cdot}03$ Å, and two bonds at 1·97 Å, $\sigma = 0{\cdot}04$ Å, in keeping with the chemical properties of IF_7 and IF_5. The same configuration has recently been observed in the ethylenediamine tetraacetoaquoferrate (III) ion. The revised structure was determined following a careful evaluation of the intensity data which entered into an earlier 3*d* Fourier difference analysis. Serious, non-calculable, systematic errors were found in the precession camera experiment. The most erroneous class of observations, the upper levels, were discarded. The zero levels were analyzed by least squares. The systematic errors for each zero level were treated as a separate problem in scaling and weighting analysis.

Introduction

Over a decade ago the writer and F. N. Bensey undertook a program of study of the polyfluoride branch of the interhalogen compounds. The crystal structures of ClF_3, BrF_3, and BrF_5 at low temperatures were determined in a relatively straightforward manner. The most interesting member of the group, IF_7, proved to be quite troublesome. In a preliminary report (Burbank & Bensey, 1953*b*) a structure was described which could have a symmetry no higher than that of the point group *mm*. This conclusion was unaltered in the final results of a 3*d* Fourier difference analysis (Burbank & Bensey, 1957*a*, *b*). The molecular structure found in the crystalline state was not in agreement with the interpretations given to a variety of other physical measurements.

Lord *et al.* (1950) studied the Raman spectra of the liquid and the infrared spectra of the gas, both at room temperature. Within the limited resolution of the spectra they stated that there was no noticeable departure from the selection rules for the point group symmetry D_{5h}, a pentagonal bipyramid. Gutowsky & Hoffman (1951) studied the nuclear magnetic resonance of the liquid at room temperature. The multiple F^{19} absorption lines were unexpectedly broad for a liquid. The simplest interpretation is that the F^{19} nuclei are in non-equivalent structural positions, which is not inconsistent with a D_{5h} structure. Overlap of individual lines prevented more detailed analysis. Bauer (1952) assumed a D_{5h} structure to analyze the electron diffraction of the gas at -65 °C. In a revised analysis of the same data LaVilla & Bauer (1960) considered it necessary to introduce displacements of the five girdle atoms in directions perpendicular to the plane of the girdle.

Donohue (1959) made the categorical statement that the interpretation of the crystal structure was incorrect and that the molecular symmetry in orthorhombic IF_7 was D_{5h}. Recently Lohr & Lipscomb (1962) have reported a recalculation based on the Burbank & Bensey (1957*a*) data using the Busing–Levy (1959*a*) least squares program. It is claimed that the recalculation provides a quantitative statistical basis for Donohue's statement. However, this claim is compromised by the following factors:

1. The data contain serious and unknown systematic errors.
2. Under these circumstances the weighting system used is entirely arbitrary.
3. A complete set of anisotropic thermal parameters was introduced under circumstances in which they can have no physical meaning and in which they may interact seriously with the positional parameters.

With the exception of the X-ray experiment all of the investigations described above were based on a single source of IF_7 prepared by M. A. Lynch in the course of a doctoral dissertation at MIT in 1948. The IF_7 used by Burbank & Bensey at Oak Ridge was prepared for them by W. B. Kenna and A. V. Faloon in 1952. The writer has no knowledge of any new source of IF_7 in the past ten years, nor of any likely to become available in the immediate future. In view of the conflicting opinions and results cited above, it seemed essential to make a critical re-examination of the *original unscaled* X-ray intensity data. The results of this activity are being reported for the following reasons:

1. To present evidence that the molecules in orthorhombic IF_7 are *not* pentagonal bipyramids nor are they of the form proposed by LaVilla & Bauer (1960).
2. To describe a molecular structure in orthorhombic IF_7 which is not without precedence for 7-coordination (Hoard, Lind & Silverton, 1961).
3. To illustrate the pitfalls that can beset the least squares method of analysis when the experimental data are encumbered with serious systematic error.

Interpretation of systematic errors

The experimental technique used to obtain the IF_7 diffraction data has been documented in detail (Burbank & Bensey, 1953*a*, 1957*a*). However, certain facts essential to the treatment that follows are not generally available (Burbank & Bensey, 1957*a*) and will be presented here.

Liquid IF_7 was sealed in a fluorothene (trifluoromonochloropolyethylene) capillary with a nominal inside diameter of 0·5 mm. The capillary was at room temperature when sealed. It was immediately placed in liquid nitrogen, transported to a precession camera and placed in a cold gas stream. The temperature of the specimen was never thereafter above 5 °C. for the duration of the experiment. Physical properties of the solid which have a bearing on this treatment are as follows: The vapor pressure of the solid reaches atmospheric at 4·5 °C. which is also the boiling point of the liquid. The solid will melt at 5–6 °C. under two atmospheres pressure. At —65 °C. the solid still has a vapor pressure of 10 mm.

The phase of IF_7 which freezes near 0 °C. was found to be body centered cubic. Data recorded at -110 °C. indicated a cell edge of 6·28 Å and two molecules/cell. Analysis showed that the cubic structure is highly disordered. A transition to an orthorhombic phase was found in the vicinity of -120 °C. Two of the orthorhombic axes are oriented along the diagonals of one face of the original cubic phase while the third axis is common to both phases. Special precautions were necessary to avoid obtaining several mutually orthogonal orientations of the orthorhombic phase instead of a single crystal. All the orthorhombic data were recorded on 4 zero levels and 14 associated upper levels from a single orientation of a single crystal which was maintained at -145 °C. The unit cell constants and symmetry are the following:

$a = 8{\cdot}74$ Å four molecules/cell
$b = 8{\cdot}87$ X-ray density 3·62 g.cm.$^{-3}$
$c = 6{\cdot}14$

Most probable space groups:

$$C_{2v}^{17} = Aba2 \quad \text{or} \quad D_{2h}^{18} = Abam\,.$$

After correction for *L.P* effects the data were scaled by making the sums of the intensities equal along the common lattice row where two levels intersect. When a reflection was observed on several different levels an average was taken of the several scaled values. In some instances as many as six values entered into such an average. Such is the origin of the data which were used for the Fourier analysis and for the Lohr & Lipscomb calculation.

In the absence of systematic error no scaling should be necessary at all since all levels were photographed with the same crystal under identical conditions. In actual fact scaling factors of 3 or 4 were required at some intersections. Further, it was sometimes found that the scaled values which were to be averaged were spread over a range of 2 to 1. These variations lie entirely outside of the precision obtainable in measuring the blackening of spots on films.

The most insidious type of error would be a progressive leakage of IF_7 from the fluorothene capillary during the several months of the experiment. It was possible to check key intensity measurements as a function of date recorded and to refute this possibility.

The most obvious systematic error is caused by absorption. Recently the absorption effect for the precession method has been worked out in considerable detail (Burbank & Knox, 1962). As a result several conclusions can be made concerning the IF_7 data. In the scaling procedure the intersections of lattice levels are of three types: upper level with upper level, upper level with zero level, and zero level with zero level. For a cylindrical specimen with absorption scaling will be required for the first two types of intersection, but not for zero level with zero level. This was not found to be the case for the IF_7 data. Therefore, if the discrepancies are caused by absorption alone the specimen is not cylindrical in cross section.

In general velocity and absorption effects cannot be separated in the precession method and must be combined into an over-all *LPA* correction. However, for the reflections that occur at the intersection of zero level with zero level the effects can be treated separately. Thus by trial it is possible to postulate various constant crystal cross sections which might give rise to absorption effects which would just account for the apparent scaling factors. A prismatic cross section was found, bounded by (100), (101), and $(10\bar{1})$ faces, which accomplished this. However, the prismatic crystal would not account for the scaling factors required for intersections involving upper levels.

One can next assume that the crystal is cylindrical but that extinction is severe. In this case there will be many upper level intersections involving larger Bragg angles and lower intensities where extinction should be relatively unimportant. *LPA* corrections calculated for a cylinder should remove the need for scaling factors for many upper level intersections. This was not found to be the case.

The most reasonable conclusion remaining is that the specimen was not of constant cross section. This is not inconsistent with the physical properties cited above. Appreciable gas pressure was probably always present during the solidification process. In such a case a capillary might not be filled with solid over its entire cross section, and the gap between solid and capillary might vary along the length of the capillary. It is suggested that the crystal might have assumed a wedge shape along the length of the capillary. Considering the optical properties of fluorothene this might occur without being obvious in the microscope used to observe crystal growth.

The most rational way to analyze data which contains severe absorption errors from a crystal of unknown shape would appear to be as follows. For the precession method it is known that the absorption effect is much more pronounced for upper levels than for zero levels (Burbank & Knox, 1962). Therefore, abandon the upper level data and apply least squares analysis utilizing the full matrix to the zero level data. The systematic errors may be quite different on each zero level. A separate scale factor should be refined for each level. Different weighting procedures will be required for each level. These must be deduced from analyses of the $w\Delta^2$ values obtained from a well refined structure. All thermal parameters will absorb systematic errors. This can be minimized by confining the thermal treatment to a single over-all B factor which is applied to all the levels.

Derivation of a refined structure

With seven F atoms per molecule the correct choice of space group depends on the presence or absence of disorder in orthorhombic IF_7. Space group *Abam* requires the molecular symmetry $2/m$ in an ordered structure. If the structure is ordered the space group is *Aba*2. The analysis commenced with a model based on the following assumptions:

1. An ordered structure.
2. Molecular symmetry D_{5h}.
3. Seven IF distances = 1·825 Å (LaVilla & Bauer, 1960). For a pentagonal bipyramid with I at 000, the five girdle atoms are defined by F_1 at $00z$, F_2, and F_3 at xyz. The two axial atoms are defined by F_4 at xyz with $z_4=0$. The only information retained from the Fourier analysis to define the initial model was the azimuthal orientation of the molecule around the C axis.

The Busing–Levy (1959*a*) least squares program was used throughout on an IBM 7090 computer. The atomic scattering factors used for I were those of Thomas & Umeda (1957), corrected for dispersion by the method of Dauben & Templeton (1955), and for F those of Berghuis *et al.* (1955). In the initial absence of a refined structure all observations were given equal weight. For data with large systematic errors this would appear to introduce the least amount of predetermined bias in a weighting procedure. Later it became clear when the final weighting procedures were derived that this was indeed the case for the IF_7 data. Constant weights were used for all steps described in this section. All reflections of unobservable intensity were retained and assigned half the minimum locally observable intensity.

The structure was first treated as an 8 parameter problem, using only the $hk0$ reflections. The variables were one scale factor, one temperature factor, and the six x, y parameters. After refinement new values of z were computed, retaining the assumption that all IF = 1·825 Å. It was found that $|z_4| > 0$. Alternatively, one can assume that the five girdle IF = 1·825 Å, and the two axial IF are < 1·825 Å. Then z_4 can still be set equal to zero. Thus there are three models for further investigation with $z_4>0$, $z_4=0$, and $z_4<0$. The structure was next treated as an 8 parameter problem, using only the hkh, $0kl$, and $2h,k,h$ reflections. The variables were three scale factors, one temperature factor, and the four z parameters. After refinement the three models had become two. The $z_4=0$ and $z_4<0$ models both converged to $z_4<0$. There was little to choose between the two structures with $z_4<0$ and $z_4>0$ with respect to satisfactory convergence and the resulting interatomic distances. There is a strong implication that this has happened because the structure is really disordered with equal numbers of molecules directed along the $+C$ and $-C$ directions. This is consistent with the fact that orthorhombic IF_7 is formed from highly disordered cubic IF_7. Unless special precautions are taken in the phase transformation the axes a, b and c are freely permuted. It is quite likely that they are also permuted with respect to sign, i.e. $+C$ or $-C$. A reasonable description of a disordered orthorhombic phase is one containing a random assemblage of small regions, in any one of which the molecules are all directed either along $+C$ or $-C$. The scattering model used to represent the disorder consists of a centrosymmetric array of 14 half atoms. It is initially specified by superimposing two orientations, directed along $+C$ and $-C$, of the two *Aba*2 structures with $z_4<0$ and $z_4>0$ and averaging the parameters. The over-all symmetry is now *Abam*. Inherent in the new model is a 2-fold ambiguity. For the 10 half atoms which lie in the girdle plane there is no difficulty in selecting 5 which describe one orientation of the girdle atoms. For the remaining 4 half atoms it still must be determined which pair will correctly describe the axial atoms.

The structure was now treated as a 15 parameter problem using all the reflections. The variables were four scale factors, one temperature factor, and the ten positional parameters. In addition to the disordered structure both ordered structures were refined. Within the limits of standard errors the magnitudes of the parameters are equivalent in all cases. It is thus quite clear that if only a single ordered structure were investigated in detail, one would obtain scant suggestion of the presence of disorder.

To be certain that the conclusions concerning disorder were not a spurious result of a constant weighting procedure the 15 parameter problem was repeated with the Hughes (1941) weighting scheme for the disordered structure and the two ordered structures. Within the limits of standard errors the parameters are equivalent to the previous results. However, the Hughes weighting is decidedly inferior to constant weighting for this problem. If, on a relative scale, the largest F_o's be regarded as correctly weighted, then the smal F_o's are underweighted with constant weights. However, the small F_o's are much more drastically overweighted with the Hughes weights. As would be expected, the standard errors with the Hughes weights are larger than with constant weights.

In all of the preceding refinements, as well as those discussed below, convergence was always satisfactory, and the thermal parameter did not vary significantly.

In the discussion that follows the refined model is taken to be the disordered structure based on space group *Abam*.

Derivation of weighting procedure from $w\Delta^2$ analysis

Cruickshank *et al.* (1961) have emphasized that the usual least squares formula for estimating standard deviations is invalid unless the weights are correct. The requirement is that the averages of $w\Delta^2$ must be constant when the set of $w\Delta^2$ values is analyzed in any significant systematic fashion. For IF_7 average values of $w\Delta^2$ were analyzed in groups of increasing F_o, increasing ξ, and increasing τ, where ξ and τ are the the radial and angular cylindrical coordinates of the reciprocal lattice. Each of the four zero levels was examined as a separate problem. Because of the nature of the absorption effect (Burbank & Knox, 1962) a variation with τ cannot be discounted without examination. No systematic variation was found with either ξ or τ.

The variation of averages of $w\Delta^2$ with F_o was treated in terms of the values of Δ/σ which are supplied by the Busing–Levy program, where $w = 1/\sigma^2$. For a first approximation 6 constant values of σ were used, one each for $hk0_{\text{obs.}}$; $hk0_{\text{unobs.}}$; $hkh_{\text{obs.}}$; $0kl_{\text{obs.}}$; $2h,k,h_{\text{obs.}}$; and $2h,k,h_{\text{unobs.}}$. The average values of $w\Delta^2$ for each group are then equal. The values of σ on an approximately absolute scale are given in Table 1. Following a 15 parameter refinement the Δ/σ values for each group were plotted against F_o. For the four $F_{\text{obs.}}$ groups σ was fitted to a straight line of the form $a + b\, F_o$ by graphical means. In each case this was followed by a least squares fit to a straight line. For the two $F_{\text{unobs.}}$ groups σ was represented by a constant. The six functions of σ are given as the second entry in Table 1. Following another 15 parameter refinement the same process was repeated, leading to the third entry in Table 1, and followed by a final refinement. The improvement in weighting can be noted by the number of values of Δ/σ that exceeded 2 for each approximation. This number decreased from 17 to 7 to 4 for 157 observational equations. The estimates of standard error can be reduced appreciably by rejecting all $\Delta/\sigma > 2$. To be on the conservative side no rejection test was applied in deriving the results listed below.

Table 1. *Functions of σ used in successive weighting procedures*

The scale is approximately absolute

$hk0_{\text{obs.}}$	$\sigma = 4\cdot9$	$4\cdot7 + 0\cdot029F_o$	$4\cdot7 + 0\cdot029F_o$
$hk0_{\text{unobs.}}$	$\sigma = 3\cdot3$	$4\cdot0$	$4\cdot2$
$hkh_{\text{obs.}}$	$\sigma = 4\cdot2$	$3\cdot4 + 0\cdot025F_o$	$3\cdot6 + 0\cdot026F_o$
$0kl_{\text{obs.}}$	$\sigma = 6\cdot3$	$4\cdot9 + 0\cdot044F_o$	$5\cdot4 + 0\cdot048F_o$
$2h, k, h_{\text{obs.}}$	$\sigma = 6\cdot2$	$5\cdot5 + 0\cdot034F_o$	$5\cdot4 + 0\cdot033F_o$
$2h, k, h_{\text{unobs.}}$	$\sigma = 3\cdot1$	$4\cdot0$	$3\cdot4$

A comparison of F_o versus F_c for the 6 groups of data is presented in Table 6.

Description of X-ray structure and statistical comparisons with the D_{5h} and LaVilla and Bauer models

The final parameters and their standard errors are listed in Table 2. The ambiguity in the disordered structure is evidenced by the ± sign preceding z_4. The two possible interpretations of the structure are illustrated in Fig. 1. The numbering of atoms corresponds to that used in all subsequent tables and discussion. Distances and angles which involve only girdle atoms or only axial atoms are the same for each interpretation. Distances and angles which involve both girdle and axial atoms are different for the two cases. All distances and angles within the molecule, for either interpretation, are listed in Table 3. These quantities and the associated standard errors were calculated with the Busing–Levy (1959*b*) function and error program in which the full matrix is used to compute the errors. Errors of 3 parts per 1000 in the cell parameters were included in the computations.

Table 2. *Final parameters for orthorhombic* IF_7

Atom	x	y	z
I	0	0	0
F_1	0	0	$0{\cdot}2942 \pm 0{\cdot}0080$
F_2	$0{\cdot}0717 \pm 0{\cdot}0028$	$0{\cdot}0869 \pm 0{\cdot}0022$	$-0{\cdot}2763 \pm 0{\cdot}0077$
F_3	$0{\cdot}1163 \pm 0{\cdot}0032$	$0{\cdot}1632 \pm 0{\cdot}0021$	$0{\cdot}0678 \pm 0{\cdot}0056$
F_4	$-0{\cdot}1673 \pm 0{\cdot}0028$	$0{\cdot}1234 \pm 0{\cdot}0021$	$\pm 0{\cdot}0495 \pm 0{\cdot}0066$

$B = 3{\cdot}43 \pm 0{\cdot}08$

σ of scale factors after normalization to unity:

$hk0 = 0{\cdot}018$
$hkh = 0{\cdot}018$
$0kl = 0{\cdot}030$
$2h, k, h \pm 0{\cdot}030$
unweighted $R = 0{\cdot}092$*
weighted $R = 0{\cdot}104$*
$[\Sigma w(F_o - F_c)^2/(m-n)]^{1/2} = 1{\cdot}002$

* All unobserved reflections included at one half minimum locally observable values.

If the molecular symmetry of orthorhombic IF_7 is D_{5h} a number of obvious equalities are imposed on the distances and angles. These have all been examined in an exhaustive manner.

Table 3. *Distances and angles in orthorhombic* IF_7

Bond	Observed
IF_1	$1{\cdot}81 \pm 0{\cdot}05$ Å
IF_2	$1{\cdot}97 \pm 0{\cdot}04$
IF_3	$1{\cdot}82 \pm 0{\cdot}02$
IF_4	$1{\cdot}85 \pm 0{\cdot}02$

Distance	Observed	Angle	Observed
Girdle nearest neighbors			
F_1F_3	$2{\cdot}25 \pm 0{\cdot}04$ Å	F_1IF_3	$76{\cdot}7 \pm 1{\cdot}1°$
F_3F_2	$2{\cdot}25 \pm 0{\cdot}06$	F_3IF_2	$73{\cdot}0 \pm 1{\cdot}4$
F_2F_2'	$1{\cdot}99 \pm 0{\cdot}05$	F_2IF_2'	$60{\cdot}7 \pm 1{\cdot}8$
Girdle second nearest neighbors			
F_1F_2	$3{\cdot}64 \pm 0{\cdot}06$	F_1IF_2	$149{\cdot}7 \pm 0{\cdot}9°$
F_3F_2'	$3{\cdot}47 \pm 0{\cdot}05$	F_3IF_2'	$133{\cdot}5 \pm 1{\cdot}4$
F_3F_3'	$3{\cdot}54 \pm 0{\cdot}05$	F_3IF_3'	$153{\cdot}5 \pm 2{\cdot}1$
Apex to Girdle, $z_4 < 0$			
F_4F_1	$2{\cdot}79 \pm 0{\cdot}05$	F_4IF_1	$99{\cdot}4 \pm 1{\cdot}2°$
F_4F_2	$2{\cdot}53 \pm 0{\cdot}05$	F_4IF_2	$83{\cdot}0 \pm 1{\cdot}3$
F_4F_2'	$2{\cdot}47 \pm 0{\cdot}04$	F_4IF_2'	$80{\cdot}7 \pm 1{\cdot}3$
F_4F_3	$2{\cdot}60 \pm 0{\cdot}04$	F_4IF_3	$90{\cdot}5 \pm 1{\cdot}0$
F_4F_3'	$2{\cdot}68 \pm 0{\cdot}03$	F_4IF_3'	$93{\cdot}8 \pm 1{\cdot}0$
F_4F_1	$2{\cdot}37 \pm 0{\cdot}04$	F_4IF_1	$80{\cdot}6 \pm 1{\cdot}2$
F_4F_2	$2{\cdot}91 \pm 0{\cdot}05$	F_4IF_2	$99{\cdot}3 \pm 1{\cdot}3$
F_4F_2'	$2{\cdot}86 \pm 0{\cdot}05$	F_4IF_2'	$97{\cdot}0 \pm 1{\cdot}3$
F_4F_3	$2{\cdot}51 \pm 0{\cdot}04$	F_4IF_3	$86{\cdot}2 \pm 1{\cdot}0$
F_4F_3'	$2{\cdot}58 \pm 0{\cdot}03$	F_4IF_3'	$89{\cdot}5 \pm 1{\cdot}0$
Apex to apex			
F_4F_4'	$3{\cdot}65 \pm 0{\cdot}05$	F_4IF_4'	$161{\cdot}1 \pm 2{\cdot}5$

The first statistical comparison to be made is *internal*, i.e., an examination of X-ray derived quantities that should be equal to each other for D_{5h} symmetry. The differences are expressed as multiples of σ and all values $\geq 3{\cdot}5\sigma$ are listed in Table 4.

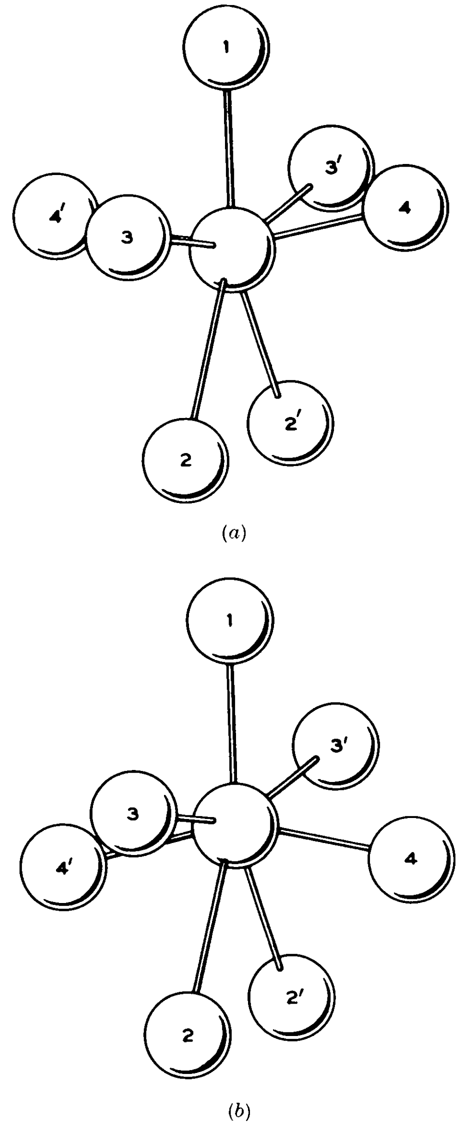

Fig. 1. (*a*) Interpretation of molecular structure in orthorhombic IF_7 if $z_4 > 0$. (*b*) Interpretation of molecular structure if $z_4 < 0$.

The second statistical comparison is *external*. X-ray derived quantities are compared with equivalent quantities in three idealized models that are free from error. The three models are D_{5h}, and LaVilla & Bauer's Model *A* and Model *B*. For Model *A* all 7 IF = 1·825 Å, for Model *B* 5 IF = 1·84 Å and 2 IF = 1·81 Å. In both cases 4 girdle atoms are displaced perpendicular to the girdle plane, F_3 and F_3' by +0·2 Å and −0·2 Å, F_2 and F_2' by −0·1 Å and +0·1 Å. Only angles can be compared for D_{5h}. Both distances and angles are compared for Model *A* and Model *B*. All differences $\geq 3{\cdot}5\sigma$ are summarized in Table 5.

It is the writer's opinion that sufficient evidence has been presented in Tables 4 and 5 to obviate the need for any further discussion of D_{5h}, Model *A*, or

Table 4. *Internal statistical comparison of X-ray derived quantities with each other*

Girdle nearest neighbors

Distances	Difference	Angles	Difference
F_1F_3, F_2F_2'	4·5σ	F_1IF_3, F_2IF_2'	7·7σ
F_3F_2, F_2F_2'	3·6σ	F_3IF_2, F_2IF_2'	4·2σ

Girdle second nearest neighbors

		F_1IF_2, F_3IF_2'	7·8σ
		F_3IF_2', F_3IF_3'	6·1σ

Apex to girdle

	$z_4<0$	$z_4>0$		$z_4<0$	$z_4>0$
F_4F_1, F_4F_2		7·6σ	F_4IF_1, F_4IF_2	6·7σ	7·8σ
F_4F_1, F_4F_2'	4·2σ	7·1σ	F_4IF_1, F_4IF_2'	7·8σ	6·7σ
F_4F_1, F_4F_3	3·5σ		F_4IF_1, F_4IF_3	6·3σ	4·1σ
F_4F_1, F_4F_3'		4·8σ	F_4IF_1, F_4IF_3'	4·1σ	6·3σ
F_4F_2, F_4F_3		7·5σ	F_4IF_2, F_4IF_3	4·6σ	7·8σ
F_4F_2, F_4F_3'		6·1σ	F_4IF_2, F_4IF_3'	5·6σ	5·3σ
F_4F_2', F_4F_3		6·4σ	F_4IF_2', F_4IF_3	5·3σ	5·6σ
F_4F_2', F_4F_3'	4·1σ	5·8σ	F_4IF_2', F_4IF_3'	7·8σ	4·6σ

Table 5. *External statistical comparison of X-ray derived quantities with the equivalent quantities in three idealized models**

Girdle nearest neighbors

Distance	Difference		Angle	Difference		
	A	*B*		D_{5h}	*A*	*B*
			F_1IF_3	4·5σ	4·5σ	4·5σ
F_2F_2'	3·6σ	4·0σ	F_2IF_2'	6·3σ	6·3σ	6·3σ

Girdle second nearest neighbors

			F_1IF_2	6·3σ	6·3σ	6·3σ
			F_3IF_2'	7·7σ	6·8σ	6·8σ
			F_3IF_3'	4·5σ	4·5σ	4·5σ

Apex to girdle, $z_4<0$

F_4F_1	4·1σ	4·1σ	F_4IF_1	7·6σ	7·6σ	7·6σ
			F_4IF_2	5·3σ	7·7σ	7·7σ
			F_4IF_2'	7·2σ	4·8σ	4·8σ
F_4F_3	4·6σ	4·5σ	F_4IF_3		6·9σ	7·0σ
			F_4IF_3'	3·8σ		

Apex to girdle, $z_4>0$

F_4F_1	4·8σ	4·8σ	F_4IF_1	7·6σ	7·6σ	7·6σ
F_4F_2	5·3σ	5·3σ	F_4IF_2	7·2σ	4·8σ	4·8σ
F_4F_2'	7·7σ	7·6σ	F_4IF_2'	5·3σ	7·7σ	7·7σ
			F_4IF_3	3·8σ		
F_4F_3'	5·0σ	5·0σ	F_4IF_3'		6·9σ	7·0σ

Apex to apex

			F_4IF_4'	7·6σ	7·6σ	7·6σ

* The pentagonal bipyramid and LaVilla and Bauer's Model *A* and Model *B*.

Model *B* in connection with orthorhombic IF_7. It should be emphasized that the statistical comparisons can be made without any attempt to resolve the ambiguity of disorder.

Table 6. F_o *versus* F_c

Unobserved reflections listed at one half minimum locally observable values.

$hk0_{obs.}$

h	k	F_o	F_c
0	2	217	216
0	4	65	70
0	6	97	104
0	8	60	70
0	10	38	39
0	12	17	24
1	4	14	9
1	6	7	-16
1	8	6	- 4
2	0	217	228
2	2	193	203
2	4	147	147
2	6	91	88
2	8	56	53
2	10	35	38
2	12	23	23
3	2	63	-71
4	0	86	88
4	2	176	155
4	4	147	143
4	6	68	68
4	8	49	50
4	10	35	33
5	2	25	-30
5	4	12	-22
6	0	116	98
6	2	105	91
6	4	76	74
6	6	59	63
6	8	53	47
6	10	28	22
7	2	23	26
7	4	6	- 8
7	6	11	- 8
8	0	62	58
8	2	59	51
8	4	58	55
8	6	57	49
8	8	30	23
10	0	38	36
10	2	34	33
10	4	34	31
10	6	29	25
12	0	26	22
12	2	20	21

$hk0_{unobs.}$

h	k	F_o	F_c
1	2	1.4	-6.5
1	10	2.3	10.7
1	12	1.9	0.5
3	4	1.9	-4.1
3	6	2.3	4.6
3	8	2.3	1.6
3	10	2.3	7.3
3	12	0.0	-0.1
5	6	2.3	11.7
5	8	2.3	9.7
5	10	2.3	-2.8
7	8	2.3	4.0
7	10	1.4	0.6
9	2	2.3	3.3
9	4	2.3	5.8
9	6	2.3	-0.2
9	8	1.9	-3.2
11	2	2.3	-3.5
11	4	2.3	5.5

$hkh_{obs.}$

h	k	F_o	F_c
0	2	230	216
0	4	65	70
0	6	105	104
0	8	60	70
0	10	34	39
0	12	24	24
1	1	217	209
1	3	103	97
1	5	114	106
1	7	83	83
1	9	43	40
1	11	30	23
2	0	85	87
2	2	109	106
2	4	124	116
2	6	81	81
2	8	47	43
2	10	31	25

$hkh_{obs.}$

h	k	F_o	F_c
3	1	105	105
3	3	99	114
3	5	81	81
3	7	51	47
3	9	32	31
3	11	17	20
4	0	66	75
4	2	67	71
4	4	62	63
4	6	44	47
4	8	28	29
4	10	16	18
5	1	44	49
5	3	40	34
5	5	33	29
5	7	24	22
6	0	30	32
6	2	26	29
6	4	21	23
6	6	19	18
7	1	11	15

$0kl_{obs.}$

k	l	F_o	F_c
2	0	190	216
4	0	70	70
6	0	107	104
8	0	61	70
10	0	39	39
12	0	19	24
0	2	167	169
2	2	103	96
4	2	97	82
6	2	106	103
8	2	59	58
10	2	33	23
12	2	15	13
0	4	129	128
2	4	118	107
4	4	74	67
6	4	52	47
8	4	52	39
10	4	25	25

$0kl_{obs.}$

k	l	F_o	F_c
0	6	44	34
2	6	38	49
4	6	38	48
6	6	30	29
8	6	19	21
0	8	20	15
2	8	18	22
4	8	13	20

$2h,k,h_{obs.}$

h	k	F_o	F_c
0	2	205	216
0	4	65	70
0	6	99	104
0	8	69	70
0	10	34	39
0	12	22	24
1	3	24	-28
1	7	16	-21
2	0	92	76
2	2	110	106
2	4	97	91
2	6	65	46
2	8	44	36
2	10	31	25
4	0	30	30
4	2	30	33
4	4	28	33
4	6	25	24

$2h,k,h_{unobs.}$

h	k	F_o	F_c
1	1	2.7	-7.2
1	5	4.1	8.7
1	9	4.9	1.8
1	11	4.3	6.3
3	1	4.6	2.0
3	3	4.7	-2.1
3	5	4.9	-3.1
3	7	4.9	2.0
3	9	4.1	1.0

Resolution of the ambiguity in the disordered structure

The ambiguity in the disordered structure was resolved by considering the electron diffraction experiment of LaVilla & Bauer (1960). Their experimental facts are epitomized in two radial distribution curves, *RD''* and *RD'''* (their Fig. 3). *RD''* was based on the first 6 halos of their composite intensity curve while *RD'''* was based on the first 5 halos. *RD''* has a very high peak at 1·83 Å and two much lower peaks centered at 2·52 Å and 3·58 Å. The major change in *RD'''* is a shift of the 2·52 Å peak to 2·58 Å.

It was noted that the main peak in *RD''* or *RD'''* could be approximated by an isosceles triangle with a base of 0·6 Å. This offered a way to make an empirical correlation between the X-ray structure and the electron diffraction data. Each interatomic distance in the disordered structure was represented by an isosceles triangle with a base of 0·6 Å and a height of nZ_iZ_j/r_{ij} (LaVilla & Bauer, 1960), where Z_i and Z_j are the atomic numbers of the atoms involved, r_{ij} is the distance between them, and n is the number of times the distance occurs. Then all the triangles for a particular model were summed at intervals of 0·05 Å. The resulting synthetic radial distribution curves are illustrated in Fig. 2. The two curves are identical for the first peak at 1·84 Å and the last peak at 3·58 Å. The upper curve for $z_4<0$ has a middle peak centered at 2·55 Å. In the lower curve for $z_4>0$ the middle peak has split into two minor peaks at 2·35 Å and 2·87 Å. The $z_4<0$ curve has a remarkable

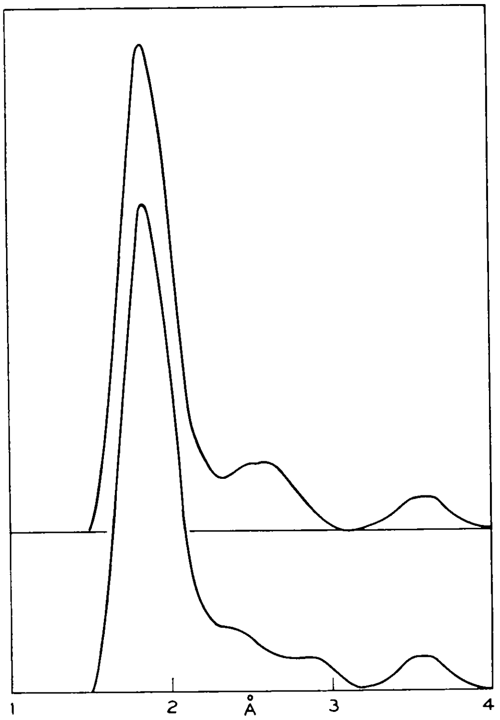

Fig. 2. Synthetic radial distribution curves for molecules in orthorhombic IF_7. Upper curve for $z_4 < 0$. Lower curve for $z_4 > 0$.

similarity to *RD''* and *RD'''* with respect to both peak positions and relative peak heights. The peak heights for *RD''* are in the ratio of 14·4 to 2·1 to 1·0. The peak heights for $z_4 < 0$ are in the ratio of 14·8 to 2·1 to 1·0. There seems to be no question as to the correct interpretation of the disordered structure.

The IF_7 molecule

If a molecular description is abstracted directly from the crystal structure, nine parameters are required, including four bond lengths, three bond angles, and two dihedral angles. These parameters and their standard errors are conveniently expressed in spherical coordinates with the I atom at the origin:

Atom	r (Å)	θ (°)	φ (°)
1	$1·81 \pm 0·05$		0
2, 2′	$1·97 \pm 0·04$	$(-90, 90) - 2·3 \pm 1·5$	$149·7 \pm 0·9$
3, 3′	$1·82 \pm 0·02$	$(-90, 90) + 1·8 \pm 1·0$	$76·7 \pm 1·1$
4, 4′	$1·85 \pm 0·02$	0, 180	$180 - 80·6 \pm 1·2$

The above description is the most objective possible for the X-ray results and incorporates no supplementary assumptions relating to symmetry, chemical properties, or statistics. Nevertheless, there is a strong tendency to seek for simplifying relations in any molecular description. For example, it will be noted that the θ-coordinates are close to the values required for *mm* symmetry and that the r-coordinates can be divided into a group of five and a group of two.

The statistical differences in the parameters can be summarized in the following statements:

The dihedral angle defined by F_2, I, F_2' and F_3, I, F_3' differs from 0° by $2·6\sigma$. The dihedral angle defined by F_2, I, F_2' and F_4, I, F_4' differs from 90° by $1·5\sigma$. The dihedral angle defined by F_3, I, F_3' and F_4, I, F_4' differs from 90° by $1·8\ \sigma$.

The angles F_3IF_3' and F_4IF_4' differ from each other by $2·0\sigma$.

The differences in bond lengths divide into two groups, the larger differences involving the IF_2 bond:

Bonds	Difference	Bonds	Difference
IF_2, IF_1	$2·3\sigma$	IF_1, IF_3	$0·2\sigma$
IF_2, IF_3	$3·1\sigma$	IF_1, IF_4	$0·8\sigma$
IF_2, IF_4	$2·4\sigma$	IF_3, IF_4	$1·0\sigma$

The writer believes that several simplifying assumptions are useful in describing the IF_7 molecule.

1. The molecular symmetry is *mm*.
2. The bonds IF_1, IF_3, and IF_4 are equal in length and have the value $1·825 \pm 0·03$ Å.
3. The 1·97 Å IF_2 bond is longer than the 1·825 Å bonds.
4. The angles F_3IF_3' and F_4IF_4' are equal and have the value $157·3 \pm 2·3$°.

The statistical differences quoted above are not decisive with respect to the third assumption where the difference is $2·9\sigma$. Nevertheless, on chemical grounds one would expect differentiation into five bonds of one type and two bonds of a different type. It is inconceivable that the seven observed bonds can be grouped into five and two in any other manner than the one assumed.

With the several assumptions a simplified four parameter description is obtained.

Atom	r (Å)	θ (°)	φ (°)
1	$1·825 \pm 0·03$		0
2, 2′	$1·97\ \ \pm 0·04$	$-90, 90$	$149·7 \pm 0·9$
3, 3′	$1·825 \pm 0·03$	$-90, 90$	$76·65 \pm 1·15$
4, 4′	$1·825 \pm 0·03$	0, 180	$180 - 76·65 \pm 1·15$

It is probably more than coincidence that the first analysis of the electron diffraction data (Bauer, 1952) led to 5 IF = 1·83 Å and 2 IF = 1·94 Å in good agreement with the bond lengths given above. The interpretation of such data depends only on the distances between atoms. The ingenuity of the investigator is sorely taxed to devise models which are simple enough to be manipulated. To appreciate the difficulties involved one need only recall that varying the position of a single atom alters *seven* interatomic distances in IF_7, and that these distances will be spread over the entire radial distribution curve. Only 2 and 3 parameter models were tested by LaVilla & Bauer (1960). A new analysis of the data with the 4 parameter *mm* model would be very desirable. It should be noted that there is a fundamental limitation to a new X-ray experiment even if the systematic errors are eliminated. The resolution of the disorder must still be based on the electron diffraction experiment.

The idealized description of IF_7 given above is essentially that reported by Hoard, Lind, & Silverton (1961) for the coordination around the Fe atom in rubidium ethylenediamine tetraacetoaquoferrate(III). The central 7-coordination involves 5 FeO bonds at an average distance of 2·055 Å and 2 FeN bonds at an average distance of 2·31 Å. It is remarkable to observe the grouping of 5 normal bond lengths and 2 longer lengths in both the complex ion and IF_7. Hoard *et al.* state that the experimentally established configuration is 'loosely describable' as a pentagonal bipyramid. The writer is of the opinion that the configuration is related fundamentally to the dodecahedral type of 8-coordination which was discovered by Hoard & Nordsieck (1939). If two atoms at one end of the $\bar{4}$ axis in dodecahedral 8-coordination are allowed to coalesce into one then the configuration of Fig. 1(*b*) results, where atom 1 represents the coalesced atoms. It is a geometric coincidence that the 72° angle of the pentagonal bipyramid is deceptively similar in magnitude to the 73° 42′ bond angle of dodecahedral 8-coordination.

The structure reported above is in keeping with the chemical behavior of IF_7. Atoms F_2 and F_2' are separated from each other by $1·99 \pm 0·05$ Å, and from I by $1·97 \pm 0·04$ Å. There appears to be some residual attraction between F_2 and F_2' and distinctly weakened bonding to the I atom. When the molecule dissociates the configuration of the 5 bonds at normal length should offer no obstacle to ready rearrangement to the tetragonal pyramid configuration known to exist for halogen pentafluorides (Lord *et al.* (1950), Gutowsky & Hoffman (1951), Burbank & Bensey (1957*c*)). At the same time the extreme fluorinating power of IF_7 may come about from the direct conversion of atoms F_2 and F_2' into atomic fluorine. Conversely, in the formation of IF_7 from IF_5 and molecular fluorine the configuration of IF_5 requires little rearrangement to achieve the configuration which is stable for IF_7.

I am indebted to several people for their generous assistance. First, Frank N. Bensey who provided me with all of the data and facts remaining on file at Oak Ridge. Second, Miss Noel Vaughan, who carried out the initial IBM calculations and guided me in the use of the 7090 computer. Finally, Prof. I. Fankuchen who offered valuable criticisms following a preliminary presentation of this material at a meeting of the Point Group at The Polytechnic Institute of Brooklyn.

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