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Concerning the Evidence for the Molecular Symmetry of IF₇

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(Received 3 May 1964 and in revised form 12 August 1964)

Additional refinements on the partial data from orthorhombic IF₇ show that it is not possible at the present time to demonstrate that the molecular symmetry is different from D_{5h}.

Introduction

In the most recent paper on the crystal structure of IF₇ (Burbank, 1962) it was stated that need for further discussion of the regular pentagonal bipyramidal (D_{5h}) structure for the molecule was obviated by certain evidence presented therein. The history of the crystal structure of this compound is as follows:

(1) In a short note, Burbank & Bensey (1957) stated at the outset, 'The crystal structure analysis of iodine heptafluoride is obscured by the possibility of systematic error and an inadequate treatment of thermal motion.' This note also included the statement regarding the space group that 'No evidence was found for the type of disorder which would give rise to *Abam* and *Aba2* was accepted as the correct space group.' In addition, refined positional and thermal parameters as obtained from a series of six three-dimensional Fourier difference syntheses were presented, and the resulting molecule was described as having an idealized description of 'five F atoms forming a tetragonal pyramid with the I atom situated *below* the base of the pyramid to which are added two more F atoms lying below the I atom',* a result which was stated to be 'in sharp contrast to the pentagonal bipyramid arrangement proposed by Lord *et al.* (1950) from a study of infrared and Raman spectra'. Standard errors in the bond distances were said to average 0.04 Å, with the effect of systematic errors unknown.

* This description is, of course, ambiguous.

(2) In Donohue (1959) it was then pointed out that the data (*i.e.* the positional parameters) given by Burbank & Bensey did in fact give a molecule which closely approximated a pentagonal bipyramid; it was shown that the parameters corresponded to bond angles which did not differ significantly from those for the ideal molecule, and that the seven I-F bond distances were all equal, within experimental error.

(3) Next, Burbank (1959), in commenting on (2), above, included extensive quotations from a U.S.A.E.C. Technical Report, the existence of which had not been mentioned in the previous note. It was stated that in the Technical Report the pentagonal bipyramidal model had in fact been considered, but rejected, in large part because the refinement led to an I-F(1) bond distance which was shorter than the other six bonds. This information was, of course, in sharp contrast to the discussion of (1).

(4) Lohr & Lipscomb (1962) then published the results of their least-squares refinement of the crystallographic data contained in the Technical Report. They stated that their results supported the position taken in (2), above, and 'that the X-ray data do not eliminate the pentagonal bipyramidal arrangement'. They further stated, on the basis of a statistical analysis, that 'the various sources of error, chiefly those in the intensity estimates, are nearly random.'

(5) Burbank (1962) then reported the results of still more refinement of the original data, this time by least squares. In the introduction to this paper, Burbank included the following: 'Donohue (1959) made the

categorical statement that the interpretation of the crystal structure by Burbank & Bensey (1957) was incorrect and that the molecular symmetry in orthorhombic IF_7 was D_{5h} . I wish to point out that nowhere in Donohue (1959) can be found a categorical statement that the molecular symmetry of IF_7 is D_{5h} . What *is* stated there is that 'the bond angles found experimentally do not differ significantly from those for the ideal (*i.e.* D_{5h}) molecule'; this is quite different from the statement attributed to me by Burbank. It should scarcely be necessary to add that the point here is *not* what the true symmetry of the IF_7 molecule is, but rather what one can state on the basis of the presently available X-ray data. At some future time, it may turn out, on the basis of additional data, that the correct symmetry is not D_{5h} , or it may turn out that it is D_{5h} . The discussion *now*, however, must be based on what the data of the Technical Report can be made to yield, since this is the only source of X-ray diffraction data on orthorhombic IF_7 .

Let us therefore examine these recent results of Burbank (1962), which, by the way, are different from any of those previously reported. There are a number of points which seem worthy of special comment:

(i) After stating that 'for the precession method it is known that the absorption effect is much more pronounced for upper levels than for zero levels. Therefore abandon the upper levels . . . ' Burbank adopts, in his new refinement, a discontinuous weighting function, by discarding the data from the 14 upper levels and retaining only the data from the 4 zero levels. This procedure is tantamount to retaining reflections which show the best agreement, and the resulting apparent improvement in the precision is thus, obviously, fictitious. Subsequent arguments based on the spuriously small standard errors must therefore be disregarded.

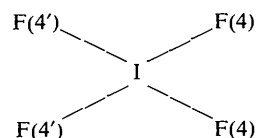
(ii) Burbank states, 'All thermal parameters will absorb systematic errors. This can be minimized by confining the thermal treatment to a single over-all B factor which is applied to all the levels.' It should be noted first, that it is not at all clear why, if all thermal parameters really do absorb systematic errors, they absorb them only on the zero levels and not on the upper levels (which were discarded because they were said to contain serious systematic errors), second, that the 'all' of the first sentence unaccountably becomes 'a single' in the second sentence, and finally, that restriction of the refinement to a single B means in practice that the determination of the thermal motion is confined to the iodine atom alone, and that the motions of the seven fluorine atoms are assumed to be not only isotropic but also identical with that of the iodine atom; the basis for these assumptions is tenuous, to say the least.

(iii) After a rather lengthy discussion, Burbank now decides that a disordered structure based on space group $Abam$ is the correct one, and bases his subsequent refinement and discussion of it on that model.

We do not attempt to reconcile this conclusion with the earlier one quoted in (1), above.

(iv) In the disordered structure now favored by Burbank, for every half fluorine atom at (xyz) there is also one at $(xy\bar{z})$. One consequence of this assumption, not pointed out by Burbank, is rather small separations between pairs of half fluorine atoms, the shortest of which is 0.4 Å between F(4) and F(4'), in the z direction. A least-squares treatment which forces the fluorine atoms to assume B values which are not only isotropic but also equal to that of the iodine atom automatically rejects (obviously) any allowance for anisotropy: the difference between, for example, two isotropic half-fluorine atoms separated by 0.4 Å in z and one anisotropic fluorine atom with a large B_{33} is not great, and would be difficult to detect, especially in the present case where the data being refined are not three-dimensional, but consist of four zones only, a situation which leads to serious problems in resolution.

(v) Burbank gives the F(4)–I–F(4') angle as 161.1° , $\sigma = 2.5^\circ$, and includes the difference of 7.6σ from 180° among his statistical arguments purporting to show the molecular symmetry is not D_{5h} . He has failed to notice, however, that the arrangement of the F(4) atoms in his disordered structure is as follows:



The angle 161.1° is obtained by choosing the top two or bottom two pairs of fluorine atoms; there is, on the other hand, no reason for not choosing opposite pairs in the disordered structure, in which case the angle is identically equal to 180° . Accordingly, the fact that the z coordinate of F(4) refines (with the above-mentioned restrictions) to a value different from zero is worthless in discussing the value of the angle F(4)–I–F(4') in relation to a molecular symmetry of D_{5h} .

(vi) In the original discussion of Burbank & Bensey (1957) it is stated, with regard to the I–F bond distances (with average standard errors of 0.04 Å), that 'the molecule has one short bond [I–F(1) = 1.71 Å]'. The latest discussion by Burbank (1962) is in sharp contrast to this, in that it is stated that 'the bonds I–F(1), I–F(3), and I–F(4) are equal in length and have the value 1.825 ± 0.03 Å, the 1.97 Å I–F(2) bond is longer.' Obviously, the results concerning these details of the molecular structure depend on how the data have been selected, and the presence in the literature of two conflicting answers from the same source does not exactly build confidence in either.

(vii) The agreement between the F_{obs} and F_{calc} in the case of the unobserved ($hk0$) reflections is far from satisfactory.

Further least-squares refinement

In view of the above points, as well as others which are not detailed here for reasons of brevity, it was decided to carry out additional least-squares refinement of the experimental data published by Burbank (1962). His weighting scheme and assumed disordered structure were used throughout, but the restrictions on the *B*'s were relaxed. Eight different refinements were carried out; in the first, ten positional and one thermal parameter were refined, duplicating Burbank, and results identical with those reported by him were obtained (!). In the subsequent refinements, the following (in addition to the scale factor) were chosen as variables:

- (1) 10 positional parameters plus 5 thermal parameters, *i.e.* one per (isotropic) atom.
- (2) same as (1), but with *z* of F(4)=0.
- (3) same as (2), but with F(4) anisotropic.
- (4) same as (2), but with F(1) anisotropic.

- (5) same as (2), but with both F(1) and F(4) anisotropic.
- (6) same as (2), but with all five atoms anisotropic.
- (7) same as (6), but with *z* of F(4) not restricted.

The results of these calculations are presented in Table 1, in which the following trends and comparisons are noted:

(1) When individual isotropic thermal motion of the fluorine atoms is allowed, *B* for iodine changes only slightly, as expected, from 3.43 ± 0.08 to 3.30 ± 0.07 , but the *B*'s for the fluorine atoms are larger, as expected, and quite different, at 7.8 ± 1.5 , 5.7 ± 0.7 , 5.0 ± 0.6 , and 4.7 ± 0.6 for F(1), F(2), F(3), and F(4), respectively. It may be noted that the smaller *B*'s are associated with the fluorine atoms with the smaller *z*'s. The reason for the apparent *z* dependence of *B* is not clear.

(2) Restricting the *z*-parameter of F(4) to zero had the expected effect of increasing its apparent *B*, to 5.5 ± 0.6 , a value very similar to those of F(2) and F(3), and not significantly different from that of F(1).

Table 1. Results of various refinements

		BB*	B**	(1)	(2)	(3)	(4)	(5)	(6)	(7)	LL***
F(1)	<i>z</i>	2777	2942(80)†	2812(155)	2827(160)	2799(159)	2903(162)	2906(150)	2952(127)	2964(123)	288(6)
F(2)	<i>x</i>	0862	0717(28)	0714(34)	0709(36)	0709(35)	0733(37)	0754(38)	0705(31)	0700(30)	071(6)
	<i>y</i>	0974	0869(22)	0907(29)	0914(30)	0918(30)	0903(29)	0927(31)	0866(31)	0864(31)	077(11)
	<i>-z</i>	2361	2763(77)	2731(108)	2734(112)	2736(107)	2644(116)	2571(126)	2496(99)	2509(99)	242(14)
F(3)	<i>x</i>	1235	1163(32)	1180(35)	1181(37)	1186(35)	1180(34)	1170(34)	1165(30)	1169(30)	113(4)
	<i>y</i>	1566	1632(21)	1627(23)	1622(24)	1623(23)	1625(23)	1632(22)	1625(18)	1624(18)	157(4)
	<i>z</i>	0585	0678(56)	0686(69)	0764(65)	0669(68)	0924(64)	0918(65)	0974(84)	0989(80)	057(4)
F(4)	<i>-x</i>	1695	1673(28)	1668(29)	1663(30)	1670(25)	1628(28)	1659(22)	1656(19)	1661(20)	167(3)
	<i>y</i>	1189	1234(21)	1227(23)	1227(25)	1226(24)	1234(22)	1215(21)	1218(18)	1215(19)	123(5)
	<i>z</i>	0310	0495(66)	0438(83)	—	—	—	—	—	0379(81)	001(17)
F(1)	<i>B</i> or <i>B</i> ₁₁		3.43(0.08)	7.8(1.5)	7.9(1.6)	7.9(1.5)	0.8(0.9)	1.0(0.9)	9.7(3.9)	10.2(4.0)	
	<i>B</i> ₂₂						10.7(2.9)	11.2(3.0)	27.7(8.3)	28.6(8.5)	
	<i>B</i> ₃₃						11.6(5.6)	10.7(5.1)	5.5(4.1)	5.0(4.1)	
	<i>B</i> ₁₂						1.0(2.4)	2.0(2.5)	-25.2(9.5)	-26.9(10.0)	
F(2)	<i>B</i> or <i>B</i> ₁₁		3.43(0.08)	5.7(0.7)	5.9(0.8)	5.8(0.7)	5.9(0.7)	6.6(0.8)	5.3(1.3)	5.1(2.8)	
	<i>B</i> ₂₂								7.3(1.3)	7.4(1.2)	
	<i>B</i> ₃₃								6.7(2.4)	6.2(2.1)	
	<i>B</i> ₁₂								6.8(2.5)	6.6(2.4)	
	<i>B</i> ₁₃								0.3(3.0)	-2.9(3.9)	
	<i>B</i> ₂₃								2.5(4.5)	1.6(4.2)	
F(3)	<i>B</i> or <i>B</i> ₁₁		3.43(0.08)	5.0(0.6)	5.0(0.6)	5.0(0.6)	5.0(0.5)	5.0(0.5)	5.5(1.1)	5.4(1.1)	
	<i>B</i> ₂₂								4.3(0.6)	4.3(0.6)	
	<i>B</i> ₃₃								13.4(4.7)	11.3(4.1)	
	<i>B</i> ₁₂								-4.6(1.7)	-4.6(1.7)	
	<i>B</i> ₁₃								3.7(5.0)	3.8(4.6)	
	<i>B</i> ₂₃								-5.3(3.8)	5.0(3.4)	
F(4)	<i>B</i> or <i>B</i> ₁₁		3.43(0.08)	4.7(0.6)	5.5(0.6)	3.0(0.9)	5.4(0.9)	3.5(0.9)	3.2(0.7)	3.2(0.7)	
	<i>B</i> ₂₂					5.5(0.9)		5.9(0.8)	5.9(0.7)	5.9(0.7)	
	<i>B</i> ₃₃					13.7(3.9)		7.8(2.1)	8.1(2.1)	4.0(3.5)	
	<i>B</i> ₁₂					1.7(1.6)		5.8(1.6)	5.5(1.3)	5.4(1.3)	
	<i>B</i> ₁₃									-3.2(3.3)	
	<i>B</i> ₂₃									-3.3(3.4)	
I	<i>B</i> or <i>B</i> ₁₁		3.43(0.08)	3.30(0.07)	3.30(0.07)	3.30(0.07)	3.36(0.07)	3.36(0.07)	2.87(0.12)	2.87(0.12)	
	<i>B</i> ₂₂								3.22(0.06)	3.22(0.06)	
	<i>B</i> ₃₃								4.03(0.14)	4.03(0.14)	
	<i>B</i> ₁₂								0.31(0.19)	0.31(0.19)	
$\Sigma w\Delta^2$		146	114	120	110	103	92	57	56		
<i>R</i>		9.2	7.9	8.3	7.8	7.7	7.3	6.0	6.0		
No. Variables		12	16	15	18	18	21	33	36		
$(\Sigma w\Delta^2/m-s)^{\ddagger}$		1.00	0.90	0.91	0.89	0.86	0.82	0.68	0.68		

* Burbank and Bensey (1957).

** Burbank (1962).

*** Lohr and Lipscomb (1962).

† Standard errors in parentheses.

(3) Allowing F(4) to assume thermal anisotropy gives a markedly anisotropic F(4), but the B 's of the other four atoms are unchanged.

(4) Allowing F(1) instead of F(4) to assume thermal anisotropy gives a somewhat unnatural F(1), and unchanged B 's for the other four atoms, but z of F(3) takes an unexpected leap of 0.0255 (0.16 Å), or 4σ .

(5) When both F(1) and F(4) are allowed to become anisotropic, their resulting anisotropies, with the exception of B_{33} and B_{12} of F(4), are virtually the same as when these atoms were individually anisotropic.

(6) Allowing all atoms to be anisotropic gives very anisotropic F(1) and F(3), moderately anisotropic F(2) and F(4), and an almost isotropic iodine. This last result strongly suggests that some of the previous peculiar results were not caused by neglect of iodine anisotropy.

(7) Allowing z of F(4) to be different from zero produces no significant changes in any of the other parameters.

Discussion

A complete statistical discussion of the interatomic distances and bond angles resulting from the above seven refinements would not only be excessively lengthy, but is unnecessary. In view of the rather large differences in some of the parameters among the various refinements it is obvious that not much significance can be attached to their standard errors, nor to the significance of differences between calculated molecular quantities and those expected for a particular model. If the systematic errors mentioned by Burbank (but denied by Lohr & Lipscomb) are present in the data, a statistical treatment of the results of Table 2 may be dubious. It is of interest, nevertheless, to apply the Hamilton (1965) test to some of the results. Of the many possibilities, the following are chosen:

Hypothesis 1: A single (isotropic) B value for the molecule is preferable to individual isotropic B 's for each atom. The appropriate ratio of generalized weighted \mathcal{R} factors is $\sqrt{146/114} = 1.132$. The dimension of the hypothesis is 4, and the number of degrees of freedom is 141. Interpolation of Table 1 of Hamilton gives:

$$\mathcal{R}_{4,141,0.005} = 1.054.$$

The hypothesis may therefore be strongly rejected.

Hypothesis 2: The z parameter of F(4) is zero.

Case 1, isotropic atoms: The value of $\mathcal{R} = \sqrt{120/114} = 1.026$, while $\mathcal{R}_{1,141,0.005} = 1.029$, and $\mathcal{R}_{1,141,0.010} = 1.024$. The probability of error if the hypothesis is rejected is between 0.5% and 1%, and customary practice would be to term it somewhere between 'possibly significant' and 'significant'.

Case 2, anisotropic atoms: The value of $\mathcal{R} = \sqrt{57/56} < 1.016$, while $\mathcal{R}_{3,122,0.250} = 1.017$. If the hypothesis is rejected, the probability of error is therefore approximately 25%, and usual practice would not require its rejection.

It is concluded that the results do not rule out a model having z of F(4) = 0.

Hypothesis 3: All atoms vibrate isotropically. The appropriate \mathcal{R} is $\sqrt{120/57} = 1.451$ and $\mathcal{P}_{18,124,0.005} = 1.2$. It is accordingly quite certain that there is anisotropic motion.

On the other hand, it is possible that the presumed systematic errors have in fact been absorbed by the thermal parameters, in which case a statistical treatment of the positional parameters would be more meaningful than that of the thermal parameters. As an example, the results obtained from refinement 6 are summarized in Table 2.

Table 2. *Molecular quantities resulting from refinement 6*

Quantity	Value $\pm \sigma$	Difference from D_{5h} model
I-F(1)	$1.81 \pm 0.08 \text{ \AA}$	0.4σ
I-F(2)	$1.82 \pm 0.05 \text{ \AA}$	0.5σ
I-F(3)	$1.87 \pm 0.03 \text{ \AA}$	0.9σ
F(1)-I-F(3)	$71.3 \pm 1.5^\circ$	0.5σ
F(2)-I-F(3)	$76.0 \pm 2.0^\circ$	2.0σ
F(2)-I-F(2)	$65.5 \pm 2.6^\circ$	2.5σ
F(3)-I-F(4)	$88.5 \pm 0.9^\circ$	1.7σ
F(2)-I-F(4)	$91.0 \pm 0.9^\circ$	1.1σ

It might be said that the data of Table 2 prove, by statistics, that the IF₇ molecule has symmetry D_{5h} , within the limits of the determination. An alternate, and much to be preferred, conclusion to be drawn is that it is not possible, with the experimental data now available, to demonstrate that the symmetry of the IF₇ molecule is different from D_{5h} . Because IF₇ can now be obtained commercially, perhaps new data, which are obviously needed to settle this question, will become available at some time in the future. Meanwhile, it would seem prudent to refrain from discussing the molecule in terms of a pentagonal bipyramid, a coalesced dodecahedron, or, for that matter, any other particular model. Although this conclusion unfortunately may appear to be rather negative, it is also unexceptionable.

This work was aided by a grant from the National Science Foundation. Most of the calculations were carried out at the Western Data Processing Center, with the invaluable assistance of Dr Aimery Caron. I wish to thank Dr Walter Hamilton for enlightening and stimulating discussion.

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