

THE ELECTRON DIFFRACTION INVESTIGATION
OF DIFLUORODIBROMOSILANE

by

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INTRODUCTION

The electron diffraction investigations of the halides of the fourth, fifth, and sixth group elements (1) have shown many interatomic distances to be shorter than those given by Pauling and Huggins' table of empirical covalent bond radii (2), representing the distances between atoms in pure single bonds in the elements and in other bonds that have considerable ionic character. In the silicon fluorides, which are usually written formally as containing four two-electron bonds, large shortenings occur, and in SiF_4 , in which the interatomic distance is 5% less than that corresponding to a pure double bond, the explanation of anomalous shortenings applied by Brockway to the fluorochloromethanes (3) breaks down. This laboratory has undertaken careful electron diffraction studies of substances showing these unexpected shortenings in the hope that improved explanations may result from a larger accumulation of data. At present, for example, some explanations require postulating sets of resonance structures which altogether give to the atoms reversed orders of electronegativities which disagree with values obtained from electric moments and ionic resonance energies.

EXPERIMENTAL

Sample of the substance was supplied by Prof. Schumb of M. I. T., and was used without further purification. (4) The apparatus and technique used have been described by Brockway (5). The wave length of the electrons was determined at various times from transmission photographs of gold foil using the value $a = 4.070 \text{ \AA}$ for the edge of the cubic unit cell of gold. The camera distance was 10.84 cm. The substance boiled at 13.7° at one atmosphere

and was photographed at 0° C. Since the compound hydrolysed readily in moist air, necessary transferences between containers were carried inside a "dry" box, through which a slow current of dried air was passed. Of the three sets of five pictures taken the clearest eight were measured. Twenty-one features could be observed.

INTERPRETATION

Radial distribution functions $R(l) = \sum_n C_n \frac{\sin(l \cdot s_n)}{l \cdot s_n}$, where $C_n = f(I_n^\circ, s_n)$ with C_n here taken as $I_n^\circ \cdot s \cdot e^{-as^2}$, the "a" being so chosen as to make $e^{-as_{\max}^2} = 1/10$, were calculated (6), using the maxima and minima positions separately and then in combination. The coefficients were determined according to the procedure recommended by Schomaker (7). In the formula I_n° is the observed intensity of feature "n", $s_n = 4 \sin(\theta/2)/\lambda$ with θ equal to one half the scattering angle, and "l" the interatomic distance over which $R(l)$ is a radial distribution function. I_n° values vary from 1 to 10, depending upon how closely the peak in question comes to the smoothed envelope of the maxima and minima sets of peaks. Since succeeding careful examinations of the pictures resulted in slightly revised estimations of their appearance, a second and third recalculation of the radial distribution functions were made using slightly different interatomic distances in a few cases. A plot of the accepted function is labelled Fig. 1. The observed intensities and the calculated coefficients c_n for the maxima and minima are given in Table I. The positions of well resolved maxima on this curve represent values of the interatomic distances to within .02 Å. Sharp peaks are seen to occur at :

2.16	3.06	3.57	on the "maxima" curve,
2.16	3.11	3.59	on the "minima" curve,
2.16	3.09	3.58	on the complete curve.

Inasmuch as the radial distribution function was calculated using s_{obs} values for a wave length of .615 Å, whereas the actual wave length was .0611 Å, the

the observed "s" values are too small, the resulting distances too large. Application of the ratio 611/615 to the distances above gives the finally reckoned values of the interatomic distances to within .02 Å°. They are: l(Si-Br) = 2.15 Å°, l(F-Br) = 3.07 Å°, and l(Br-Br) = 3.555 Å°. An important peak at about 1.3 Å° on the maxima curve is cancelled out in the combined curve indicating its spurious nature; and a very low broad peak at 1.55 Å°, in which no reliance can be put, happens to coincide with the value 1.54 Å° assumed for the Si-F separation, although its position on the combined curve seems to arise accidentally by the cancellation of insignificant peaks and depressions in that region.

Simplified theoretical intensity curves were calculated for various molecular models using the following formula:

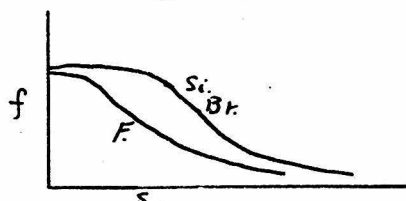
$$I(s) = \frac{1}{(Z-F)_{Si} \cdot (Z-F)_{Br}} \sum_{ij} (Z-F)_i (Z-F)_j \cdot e^{-A} \cdot \frac{\sin(sr_{ij})}{sr_{ij}}, \text{ where}$$

Z_i is the atomic number of atom "i", F_i is the scattering factor for X-rays (8), r_{ij} is the interatomic distance, s is $4 \sin(\theta/2)/\lambda$, A is $\frac{1}{2} \overline{dr_{ij}^2} \cdot s^2$, with $\overline{dr_{ij}^2}$ equal to half the mean square of the change in the distance between atoms i and j owing to thermal vibrations in the molecule. The omission of the atomic scattering terms, signified by the prime placed on the double summation to indicate omission of terms in which $i=j$, flattens the curve and makes the interference effects due to the molecular scattering appear as pronounced maxima and minima; and the omission of a factor $1/s^4$ from the above formula-such a factor appearing in the formula derived for molecular scattering-results in the simplified theoretical curves having the same general fall-off with increasing values of "s" as the visual curve.

The use of $(Z-F)_i$ in place of the more frequently used atomic number alone for the atom form factor for electrons is resorted to here because the scattering due to the electronic structure falls off as "s" increases faster for the lighter fluorine atoms than for the silicon or bromine atoms, which

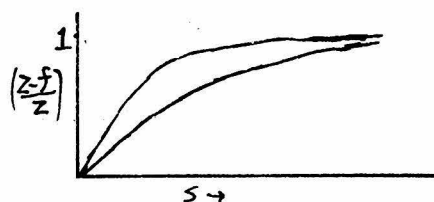
are in lower rows of the periodic table. That is, the effective nuclear scattering increases, as "s" increases, more rapidly for fluorine than for silicon or bromine, the asymptotic value at large values of "s" being $Z_i Z_j$. These facts are illustrated in the rough plots of Fig. 2, in which the curves for silicon and bromine are not much different and are represented as one.

Fig. 2-a



Scattering due to the Electronic Structure.

Fig. 2-b



The Deviation from Z_i of the Effective Nuclear Scattering for Electrons.

Neglect to consider the scattering due to the electronic structure results in the application of too small coefficients to the terms involving interaction of fluorine atoms in the inner region of the curve, say, from $s=2$ to $s=10$. In calculating the ordinate of the molecular intensity curve at each value of s , it is desired to weight the terms according to the relative atomic scattering factors for the interactions involved, but the dependence upon the average increase in the coefficients $(Z-F)_i, (Z-F)_j$, which the eye eliminates in the visual estimation of the appearance of the pattern, is here eliminated by dividing by an approximation to the average value of $(Z-F)_i (Z-F)_j$, here taken as $(Z-F)_{Br} \cdot (Z-F)_{Si}$.

The "temperature" factor e^{-A} in the molecular scattering formula, which must be used for the case of non-rigid molecules, was taken as $e^{-.001s^2}$ for the interaction Br against Br, and that of F against Br, the Si-F, F-F, and Si-Br separations being considered fixed. Since the calculation of this exponential coefficients from spectroscopic frequency values requires a normal coordinate treatment, summing for each interaction the displacement arising from each of the normal vibrations, the value $e^{-.001s^2}$ used was assumed to be equal to that obtained as an additional parameter in the electron diffraction

determination of the molecular structure of SiBr_4 , in which the effect of varying the temperature factor for Br-Br, referred to e^{-0} for Si-Br, was not mixed with the effect of varying the equilibrium structure parameter.

The assumption of this value of A in SiF_2Br_2 does not allow a more discriminating selection among a group of curves for slightly different models, all agreeing fairly well with the observed patterns for "s" less than 14, since some arbitrary temperature factor could make each a fair representation of the observed appearance. No one of the curves, furthermore, was clearly preferable to the others. It appeared that the correct model might be brought into correlation with the visual pattern by the use of an incorrect temperature factor. After all, in all but the very simplest molecules, the application of temperature factors does not merely produce a uniform dampening but rather changes the structure of the curve in the same way as might result from varying an equilibrium structure parameter, so as to make impossible a combined determination of all these parameters, particularly when some structural parameters are very unimportant and produce less radical changes in the curve for considerable parameter changes than are produced by changing the temperature factor. We did not feel that we should consider the equilibrium structure fixed completely by the radial distribution values and assumed values for the distances, so that the correlation method could be used for determining the temperature factor as a sole parameter.

The qualitative appearance of the intensity curves depends on four parameters, which could be taken to be the Si-F and Si-Br distances and the F-Si-F and Br-Si-Br angles. The value 215 \AA° was assumed for the SiBr distance, since it is the radial distribution value here and was also the final value that we report for this separation in the molecules SiHBr_3 and SiBr_4 . The value 1.54 \AA° obtained as the Si-F distance in SiF_4 (9) is assumed here for the Si-F distance, since the C-F distance is the same in CF_2Cl_2 and in CF_4 . (10).

TABLE I

Max	Min	I°	C_n	s_o	s_o'	$s_{calc} (D)$	s_{calc}/s_{obs}
	1	-	-	1.60	1.61		
1		$5\frac{1}{2}$	3.4	2.48	2.49		
	2	8	6	3.18	3.20	3.23	1.009
2		10	9	4.19	4.21	4.20	.997
	3	$6\frac{1}{2}$	8	5.11	5.14	5.30	1.031
3		5	7	6.23			
	4	1	1.4	6.66	6.70	6.50	.970
4		5	7	7.08			
	5	11	17	7.84	7.89	7.90	1.001
5		10	16	8.97	9.03	9.11	1.007
	6	5	8	10.04	10.10	10.23	1.014
6		$2\frac{1}{2}$	4	10.84	10.91	10.94	1.003
	7	$6\frac{1}{2}$	11	11.67	11.74	11.80	1.004
7		10	16	12.70	12.78	12.80	1.002
	8	10	16	13.66	13.74	13.90	1.012
8		6	9	14.81	14.90	14.92	1.003
	9	2	3	15.27			
9		2	3	15.64			
	10	6	8	17.02			
10		10	12	18.07	18.18	18.20	1.001
	11	8	8	19.55	19.67	19.70	1.001
11		8	7	21.12	21.25	21.33	1.004
	12	10	7	22.58	22.71	22.70	
12		10	6	23.82	23.96	24.	

(s_o' is s_o corrected to the wave length actually used)

Average value of Ratio (16 measurements) = 1.0035

Average Deviation = .007

Final Values: Si-F = 154.5 A°

Si-Br = 215.7 A°

Br-Br = 354 A°

F-F = 245 A°

(Quantitative comparison of s_o/s_o' at the 9th maxima and adjacent minima was not made because of uncertainty in the visual appearance in this region. The first maxima was not considered since it was considerably fogged by the central image.)

Fourteen curves calculated for Si-Br =2.15 and Si-F=1.54 and systematically varying the two parameters F-Br and Br-Br over ranges of Br-Br from 3.49 to 3.61 and F-Br from 3.01 to 3.11 by intervals of about 1% in the distances are shown in Fig. 3. The F-F distance is of course fixed when the others distances are fixed and when such symmetry is assumed for the molecule as allows but one Si-Br distance. The contributions of the various internuclear separations to the molecular scattering are shown roughly by giving the values of the term coefficients at s=8: Si-Br=36; Br-Br=42; F-Br=52; Si-F=12; F-F=5. The temperature factors on the F-Br and the Br-Br terms reduce these coefficients to about (their) half the values given here by the time "s" equals 24. The structures corresponding to the curves calculated in Fig. 3 are shown in Table II

TABLE II

Theoretical Intensity Curves (Simplified) for SiF₂Br₂ with Scattering Factors and with Temperature Factors on Br-Br and F-Br terms.

All models have Si-F=1.54 and Si-Br= 2.15.

<u>Label</u>	l(Br-Br)	l(F-Br)	l(F-F)	-BrSiBr	-FSiBr	-FSiF.
A	3.57	3.05	2.41	112° 10'	110° 20'	102° 40'
B	3.57	3.08	2.28	112° 10'	112° 00'	95° 14'
C	3.57	3.11	2.12	112° 10'	113° 55'	87° 05'
D	3.53	3.05	2.44	110° 10'	110° 20'	104° 50'
E	3.53	3.08	2.32	110° 10'	112° 00'	97° 40'
F	3.53	3.11	2.18	110° 10'	113° 55'	90° 00'
G	3.61	3.05	2.36	114° 10'	110° 20'	100° 10'
H	3.61	3.08	2.22	114° 10'	112° 00'	92° 20'
J	3.61	3.11	2.06	114° 10'	113° 55'	83° 50'
M	3.49	3.05	2.47	108° 30'	110° 20'	106° 45'
N	3.49	3.08	2.36	108° 30'	112° 00'	99° 50'
P	3.49	3.01	2.60	108° 30'	108° 10'	115° 30'
Q	3.53	3.01	2.58	110° 10'	108° 10'	114° 00'
R	3.53	3.01	2.55	108° 10'	108° 10'	112° 05'

The considerations below result in taking the closed curve in Fig. 3as giving the ranges of F-Br and Br-Br parameters within which the correlations between observed patterns and theoretical curves are able to fix the structure of the SiF_2Br_2 molecule. The visual appearance of the photographs is given by the plot in Fig. 4.

Models G, Q, H, P, and J are eliminated because of poor correlation of the low sixth peak relative to the higher peaks on either side. C, H, and J are models with the seventh minimum too low relative to the sixth, while Q and P have these two minimum reversed.

Models Q, R, G, N, C, and F are eliminated on account of poor correlation of the maxima 2, 3-4 and 5. In Q, R, and G, the 5th maximum is higher than the second in disagreement with the pictures. In N, C, and F the 3-4 maximum is too high relative to the 5th. These may not deviate badly from the visual curve, since our estimation of the height of this peak may be low. It appeared to us to be broader than that given by any of the calculated curves, and at one time looked like a doublet with a very shallow minimum at the top, so that we may have overestimated the width of this peak at the expense of the height. These curves, are, however, eliminated by other considerations. Namely, N, C, and F do not agree well with respect to the relative depth of the third and fifth minima. These two minima are reversed in these structure.

Models G, H, J, and H have the 7th minimum lower than the eighth in disagreement with the pictures.

Only E, M, B, D, and A are left to be considered. When we look at the sequence M, D, A, and G, in which A has the 2nd and 5th maxima of equal height unlike the pictures, and G is ruled out previously, We decide that D is slightly preferable to M with regard to the 2-5 maxima, and the minima 3-5, M having 5th maximum no higher than the 3rd.

Considering the sequence Q, D, E, and F, it is hard to choose between D and E. D is better than E regarding the relative height of the 3-4 maximum, and the fifth maximum. Model F is in general somewhat worse than Q, suggesting that D may be slightly preferable to E. Model E has the 5th minimum no deeper than the 3rd, while D appears more like the observed patterns here.

The fact that the sixth maximum is too high in A, and the 5th maximum is as high as the second make B preferable to A as a model.

Finally, Model D is to be preferred to B, since the 7th and 8th minima are equal in depth in B, while D has a deeper eighth minimum as shown by the photographs.

These observations thus lead to the conclusions stated above. Accordingly, the position of the maxima and minima on curve D are indicated by vertical lines and are used to obtain the values " s_{calc} " shown in Fig. 1. s_0 designates "s" values, corrected to the true wave length, and s_c/s_0 gives the ratio by which assumed interatomic distances in the chosen model must be multiplied in order to give the observed distances by the quantitative correlation method.

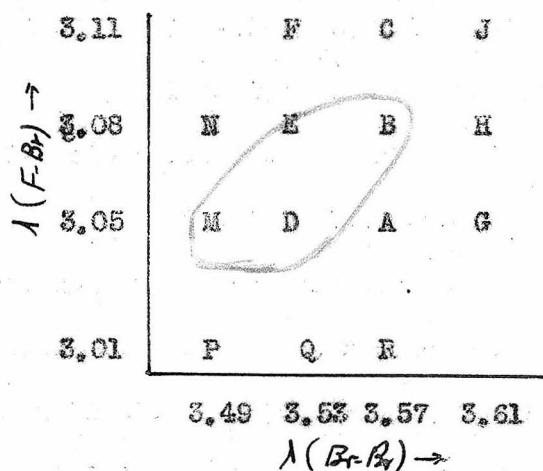
Table III gives the values of s_0 for the region from the tenth to the twelfth maximum set beside values of s_{calc} , using Model K in Fig. 3, which considered only two terms, representing the Si-Br and Si-F interactions. The average value of the ratio is 1.000±, giving an independently determined Si-Br distance of 2.15, that assumed in calculating curve K. The visual curve did not look sufficiently like the theoretical curve with infinite temperature factors until the tenth maximum was reached. The twelfth maximum was not considered because not much confidence was put in its exact observed location.

Figure 3.

A two dimensional plot locating the models assumed for SiF_2Br_2 in which the Si-Br and Si-F distances are fixed, and in which F-Br and Br-Br are allowed to vary.

$$\text{Si-Br} = 2.15 \quad \text{Si-F} = 1.54 \text{ \AA}$$

Ordinate $l(\text{F-Br})$; Abscissa $l(\text{Br-Br})$.



$l(\text{F-Br})$ is determined to within $\pm 0.03 \text{ \AA}$
 $l(\text{Br-Br})$ is determined to within $\pm 0.05 \text{ \AA}$
 by the correlation method.

The values of the equilibrium separations finally decided upon are given below with the limits of accuracy claimed.

- | | |
|---|--|
| $l(\text{Si-Br}) = 2.15 \pm 0.02 \text{ \AA}$ | $\angle \text{Br-Si-Br} = 110 \pm 1 \frac{1}{2}^\circ$ |
| $l(\text{Si-F}) = 1.54 \text{ assumed}$ | $\angle \text{Br-Si-F} = 110 \pm 1 \frac{1}{2}^\circ$ |
| $l(\text{Br-Br}) = 3.55 \pm 0.05 \text{ \AA}$ | $\angle \text{F-Si-F} = 105 \pm 9^\circ$ |
| $l(\text{F-Br}) = 3.06 \text{ \AA}$ | |
| $l(\text{F-F}) = 2.45 \pm 15 \text{ \AA}$ | |

Fig. 4. The Visual Appearance of SiF_2Br_2 Diffraction Patterns

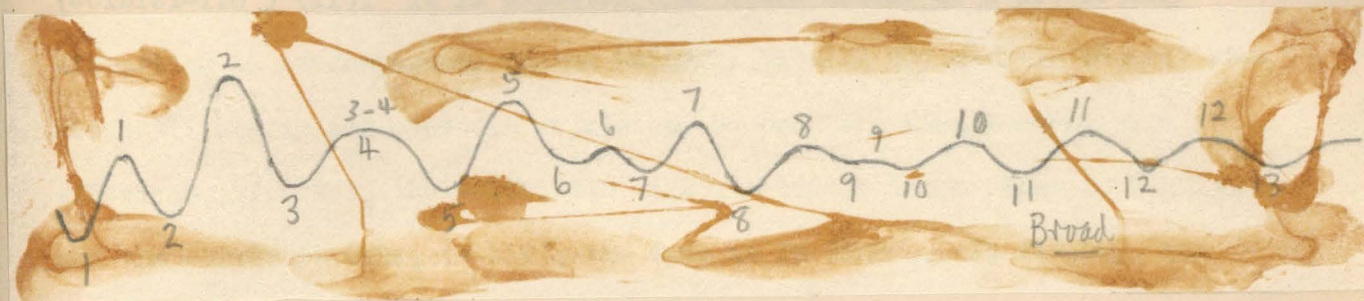


Table III

Max	Min	s_o^1	$s_{\text{calc}}(K)$	$s_{\text{calc}}/s_{\text{obs}}$
10		18.18	18.14	.998
	11	19.67	19.64	.998
11		21.25	21.27	1.001
	12	22.71	22.80	1.004
12 a		23.96	24.20	1.010
Average of 4 values:				1.000+

a-Not considered because of difficulty of measurement.

$$l(\text{Si-Br}) = 2.15\text{\AA}$$

DISCUSSION

There is very little distortion from tetrahedral angles for $\angle\text{BrSiBr}$ in SiF_2Br_2 , just as there is little in SiHBr_3 ($\angle\text{BrSiBr}=110^\circ 30'$) or in SiHCl_3 ($\angle\text{ClSiCl}=110^\circ$) (11). It is expected that there should be a little more distortion in corresponding carbon halides, because the smaller central atom makes the steric and electric repulsions between non-bonded atoms more effective. In CHCl_3 the $\angle\text{ClCCl}=112^\circ$ (12), a little larger than in SiHCl_3 , and the $\angle\text{BrCBr}$ in CHBr_3 is 110° , the same as in SiHBr_3 . In SiF_2Br_2 , the $\angle\text{FSiBr}$ shows little distortion also. The angles F-Br and Br-Br are equal, but the number of separations of type F-Br is four against one Br-Br separation, so that the F-Br repulsions may well be less as expected than those between Br-Br. The small angle $\angle\text{FSiF}$ ($105+9^\circ$), compared to $\angle\text{FCCl}=110^\circ$ in CF_2Cl_2 , also bears out Brockway's observation for the substituted methanes that steric effects rather than differences in electronegativities fix the bond angles in compounds of this type. Fluorine with electronegativity $\chi=4$, which is higher than that of bromine $\chi=2.8$, should produce a larger angle than F-Br or Br-Br angles. The reverse is observed. The larger uncertainty for $\angle\text{FSiF}$ in SiF_2Br_2 ($=9^\circ$), compared to $+2^\circ$ for $\angle\text{FCF}$ in CF_2Cl_2 is necessary because the heavier central silicon atom makes smaller the relative contribution of the F-F interaction to the theoretical scattering intensity, and the replacement of Cl by Br, still further reduces the sensitivity of the theoretical curve to small changes in the F-F angle parameter.

The observed distances for SiF and SiBr separations are compared below with the single bond and double bond values of the normal radii sums obtained from Pauling's Book, The Nature of the Chemical Bond, p154.

Separation	Observed	Single Bond Radius Sum	Double Bond Radius Sum	Triple Bond Radius Sum
SiF	1.54	1.81	1.62	1.49 ?
SiBr	2.15	2.31	2.12	-

The SiBr distance is shortened by an amount equal to 84% of the difference between pure double bond and single bond lengths, and using the empirical curve of interatomic distance against proportion of single bond- double bond character obtained for a series of carbon compounds of known bond character (13a), we find that SiBr has about 40% double bond character, to be compared with about the same value similarly obtained for the SiCl bond in SiCl_4 , studied by Brockway and Wall. The now accepted reasons for this type of shortening are the tendency of atoms to form double bonds and the tendency of atoms to ionize off a central atom, leaving an additional orbital free for multiple bond formation with other attached atoms. The second factor still applies to central atoms not located in the first row of the periodic table, whose octets may be exceeded, and whose (in this case) 3d orbitals lead to only slightly higher-lying energy states, because the correct over-all order of electronegativities is preserved only when the contribution of ionic structures, most of which obey the octet rule, is larger than that of doubly-bonded structures without ionized atoms, which have more than eight electrons about the central atom. It must be said, however, that the electronegativity difference is not the direct factor involved, because it is really harder for fluorine to ionize as a positive ion than for chlorine. The fact that fluorine forms double bonds more readily must be correlated with actual energy calculations as to the preferential stability of double bonds over single bonds for various elements.

The SiBr shortening and that of SiCl in SiHCl_3 and in SiHBr_3 are about the same. We should expect that the greater polarization of Br over Cl: (R in $\text{cm}^2\text{-mol}$ refraction = 9.30 for Cl, 12.14 for Br; with α -vol. polarizability equal to $.394R \cdot 10^{-24}$) would result in the pulling out of electrons from the attached donor Br with greater ease to form a double bond. Of course the available number of orbitals in the case of Cl and Br need not be considered since these are not acceptor atoms. On this score, of course, fluorine

should form double bonds most reluctantly. Perhaps the factor suggested by Gregg, Hampson et al (14), the weakening of the ionic character of the bond by the increasing polarization possible in Br over that in Cl, balances the factor involving double bond formation.

The Si-F shortening requires contributions of structures with triple bonds, viz:- $\text{Si}=\text{F}^{++}$, which are unlikely for two reasons. The large value 429 kcal./mol for the ionization energy of fluorine, which measures its reluctance to become a positive ion by losing an electron, makes a literal acceptance of a double or even a single formal plus charge on fluorine unlikely. In addition, elements in the periodic table below the first row do not form triple bonds. Perhaps the distance is affected by the ionic character of the bond. For the Si-F bond the electronegativity difference is $\Delta\chi = 2.2$, (high compared ^{t.} 1.2 for SiCl, 1.0 for SiBr, 1.5 for CF, .5 for CCl, .3 for CBr); corresponds to almost 70% of ionic character using the empirical curve of amount of ionic character plotted against the electronegativities differences of the atoms involved (15). But considerable amounts of polar character have been shown to have little effect on the bond distance (16,17). The observed distances in the methyl compounds of Si, Ge, Sn, Pb, N, S, and Hg where double bonding could not occur owing to the absence of extra available orbitals on the attached group, checked with the radius sums obtained from the elements. The fluorine radius in methyl fluoride was observed to be in agreement with the extrapolated radius of fluorine.

The effect of formal charge has not yet been considered. It is the effective nuclear charge that determines the decrease in the covalent radius in the sequence C-N-O-F in a given row of the periodic table. Now this periodic decrease is then due to a factor which is the actual nuclear charge minus the screening of the electrons. The screening of a valence electron is .4 of a unit charge. (18). When the nuclear charge Z increases by one unit, the effective nuclear charge increases by only .6, due to the .4

screening of the added electron. When an atom loses an electron, such as fluorine in $\text{Si}=\text{F}^+$, its formal charge being increased by one, its actual charge is unchanged, but its effective nuclear charge is increased by .4 owing to the removal of the electron. This is $2/3$ of the increase of the effective nuclear charge noticed in moving one element to the right in the periodic table, and hence the effect of this unit formal charge on the covalent radius should be to decrease it by $2/3$ of the difference between the covalent radius of the element in question and its first neighbor to the right in the periodic table. A negative formal charge would similarly increase the covalent radius. The $.04\text{\AA}$ decrease in the N-O distance in nitrate ion below that given by the type of single bond-double bond resonance was attributed to the increase of the formal charge on nitrogen(19). More recently, the $.04\text{\AA}$ decrease in the C-C bond distance in acetaldehyde below the covalent radius sum was attributed partly to the contribution of a resonating structure with a single C-C bond, but with a formal charge on one atom: $\text{H}_3-\overset{+}{\text{C}}-\overset{-}{\text{C}}-\overset{\cdot\cdot}{\text{O}}$. Incidentally, where ordinary partial ionic character occurs in a bond, with the bonded atoms possessing equal and opposite charges, the decreased radius of the atom with positive formal charge is just offset by the increased radius of the atom with negative formal charge.

Since we wish to explain a shortening in the Si-F distance of 1.62-1.54 or $.08\text{\AA}$ below the value for a pure double bond, we should be obliged to consider contributions in considerable amount of the energetic structures with fluorine having double positive formal charges, viz.: $\text{Si}=\text{F}^{++}$, since the formal charge effect is only $.04\text{\AA}$ for one unit of charge. It is difficult to say to what extent the resonance hybrid is formed from ionic structures and from multiply bonded structures, since we do not know much about the energy of multiple bonds.

The covalent radius of fluorine assumed in the preceding discussion may be in error. The value $.64\text{\AA}$ was obtained from the extrapolated curve of the covalent radii of the first row elements against their position in the row, and from an accepted value of the radius found in methyl fluoride as investigated by electron diffraction, despite the fact that the value obtained directly from fluorine by the same technique came out to be $.73\text{\AA}$, or 14% higher. Recently Brockway's value of the internuclear distance in fluorine has been confirmed by Rogers (22,23). Further investigations in this laboratory of the structures of H_2O_2 and NH_2NH_2 have shown tentatively that the values of the nitrogen and oxygen covalent radii have been given too low, and that the extrapolation of fluorine from the revised curve may lead to the value actually found for it. This curve, although we do not understand it well enough to predict it, must be continuous since the various factors responsible for the changing radius are varying continuously from element to element. Sutherland has reported a revised value for the C-F distance in methyl fluoride 1.385 corresponding to a fluorine radius of $.61\text{\AA}$ (21,24). When we take all these facts into account, including the anomalously long distances in OF_2 , we might as ^{well} admit that molecular fluorine is a normal covalent bond, and that the fluorine bond distances cannot be satisfactorily correlated with other covalent radii on the simple basis of the additivity of covalent bond radii. Consequently, little but general confusion describes the situation of trying to interpret the experimental distances. It would certainly be worthwhile to obtain experimental values of the fluorine radius from NF_3 , again from BH_3F , and to investigate the situation in the fluoroethylenes. We plan to determine the Si-F distance in SiF_3Br to avoid the assumption made necessary here. Fluoroform and silicofluoroform remain also to be investigated.

SUMMARY

The molecular structure of the molecule SiF_2Br_2 has been investigated by electron diffraction methods. The Si-F distance was assumed to be 1.54\AA . The Si-Br distance was found to be $2.15 \pm 0.02\text{\AA}$, with practically tetrahedral Br-Si-Br and F-Si-Br angles, and with the F-Si-F angle $104^\circ 50'$ with a large uncertainty of $+9^\circ$.

An explanation of the anomalous shortenings of the Si-Br and Si-F distances has been repeated and added to a bit, but the failure of the experimental distances to obey the rule of additivity of normal covalent bond radii is such that only a full treatment of the matter considering some factors such as double bond energies about which we know little would seem adequate to bring order into the present confusion.

REFERENCES

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