

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 845]

An Electron Diffraction Investigation of the Molecular Structures of Silicon Tetrabromide, Tribromosilane, and Dibromodifluorosilane

BY RALPH SPITZER, W. J. HOWELL, JR., AND VERNER SCHOMAKER

Introduction.—The bond lengths in the halides of the fourth, fifth, and sixth group elements are in general considerably shorter than the sums of the corresponding Pauling-Huggins covalent radii.¹ This discrepancy appears to be partially resolved by the introduction of a correction for the partial ionic character of the bonds²; however, large disparities remain for the second row fluorides, while for the heavier halides the agreement is not precise. For the bromosilanes considered in this paper, the Si-Br distances are found to be 2.16 ± 0.03 Å., 0.06 Å. shorter than the distance calculated by Schomaker and Stevenson.² The bond-angle values reported here are all approximately tetrahedral with the exception of that for F-Si-F in SiF_2Br_2 , which seems to be decidedly less than tetrahedral. This value may be in error, however, as noted below.

We have found approximate values for the relative amplitudes of vibration $\overline{\delta l_{ij}^2} - \overline{\delta l_{\text{Si-Br}}^2}$ in silicon tetrabromide and tribromosilane which should be helpful in connection with the spectroscopic data for the consideration of the normal modes of vibration and vibrational potential functions of these molecules.

Experimental.—The apparatus and technique employed have been described by Brockway.³ The wave length of the electrons was determined from transmission photographs of gold foil ($a_0 = 4.070$ Å.), and was about 0.06 Å.

We are indebted to Professor W. C. Schumb of the Massachusetts Institute of Technology for supplying us with the samples used.

Interpretation.—In interpreting the photographs the correlation method was used in conjunction with the radial distribution method described by Schomaker.⁴ The simplified theoretical intensity curves for the various models were calculated according to the formula

$$I(s) = \frac{1}{(Z_{\text{Si}} - f_{\text{Si}})(Z_{\text{Br}} - f_{\text{Br}})} \sum_{ij}' (Z_i - f_i)(Z_j - f_j) e^{-a_{ij}s^2} \frac{\sin l_{ij}s}{l_{ij}s} \quad (1)$$

in which account is taken of the variation with s of the relative scattering powers of the various atoms and of the effect of the harmonic vibrations of the molecule. Z_i is the atomic number of atom i ; f_i , the atom form factor⁵; l_{ij} , the interatomic distance; a_{ij} , one-half the mean square amplitude of vibration of atom i against atom j ; and $s = 4\pi/\lambda \sin \varphi/2$ where λ is the electron wave length and φ is the scattering angle. Since the calculation of a_{ij} from spectroscopic data is not feasible at present for polyatomic molecules having large moments of inertia, an attempt was made to determine these temperature-factor constants by including them as parameters in the correlation treatment. $a_{\text{Si-Br}}$ was arbitrarily set equal to zero, so that the quantities actually determined are $a_{ij} - a_{\text{Si-Br}}$; for brevity we call these quantities a_{ij} . The values reported refer to the effective temperature of the scattering gas, about 25° for SiHBr_3 and SiF_2Cl_2 , and about 100° for SiBr_4 .

The radial distribution formula used was

$$D(l) = \sum_n C_n \frac{\sin s_n l}{s_n l}$$

with

$$C_n = I_n s_n e^{-as_n^2}$$

and

$$e^{-as_{\text{max}}^2} = 0.1$$

where I_n is a relative intensity, estimated for the various peaks so as to show no average dependence on s , and s_{max} is for the last observable feature on the photograph.

Silicon Tetrabromide.—The two parameters to be determined were l , the Si-Br distance, and a , the temperature-factor constant for Br-Br vibration. The molecule was assumed to have the symmetry of a regular tetrahedron.

The photographs showed a rather heavy background which tended to make the measurements less precise than usual. The difficulty of meas-

(1) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).
 (2) V. Schomaker and D. P. Stevenson, *THIS JOURNAL*, **63**, 37 (1941).
 (3) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).
 (4) V. Schomaker, Thesis, California Institute of Technology, 1938; American Chemical Society meeting, Baltimore, Md., April, 1939.

(5) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

urement was enhanced by the slight, but deceptive, asymmetry of some of the peaks. In all, twenty-six features were measured and used in the radial distribution curve; of these, the first five and last six were rejected in the quantitative comparison with theoretical intensity functions since it was felt that these measurements were less reliable than the others. The observed values of s are given in Table I, together with values of I_n

Max.	Min.	I_n	C_n	s_0	$s_{\text{caled.}}$	s/s_0
	1	-3	-2	1.54		
1		2	2	2.39		
	2	-2	-2	3.25		
2		7	10	4.11		
	3	-10	-17	5.00	4.94	(0.988)
3		5	10	5.99	5.91	.987
	4	-5	-10	6.78	6.75	.996
4		4	9	7.63	7.54	.988
	5	-10	-23	8.53	8.42	.987
5		10	24	9.45	9.42	.997
	6	-7	-17	10.37	10.39	1.002
6		4	10	11.19	11.31	1.011
	7	-3	-7	12.08	11.95	0.989
7		6	14	12.71	12.89	1.014
	8	-10	-22	13.84	13.90	1.005
8		10	21	14.68	14.87	1.014
	9	-3	-6	15.65	15.76	1.007
9		4	7	16.49	16.41	0.995
	10	-7	-11	17.26	17.34	1.005
10		10	15	18.23	18.35	1.007
	11	-10	-13	19.41	19.44	(1.002) ^a
11		5	6	20.19	20.24	(1.002)
	12	-1	-1	21.05	21.05	(1.000)
12		5	5	21.60	21.70	(1.005)
	13	-6	-5	22.85	22.77	(0.996)
13		9	7	23.71	23.97	(1.011)
			Average			1.000
			Average deviation			0.008
			$l_{\text{Si-Br}}$			2.145 Å.

^a Ratios enclosed in parentheses were not used in the quantitative comparison.

and C_n used in the radial distribution function, and values of $s_{\text{caled.}}$ s_0 . The curves were calculated for $l_{\text{Si-Br}}$ equal to 2.145 Å.

The curves D, E and F (Fig. 1) correspond to $a = 0, 0.001$ and 0.003 , respectively. None of the curves shows marked disagreement with the photographs; the best correlation would be attained with some curve between B and C. This fixes the value of a between 0.001 and 0.003. Figure 1a shows the radial distribution curve for silicon tetrabromide.

The average value for the Si-Br distance obtained from fifteen features by the correlation method was 2.145 Å. with an average deviation

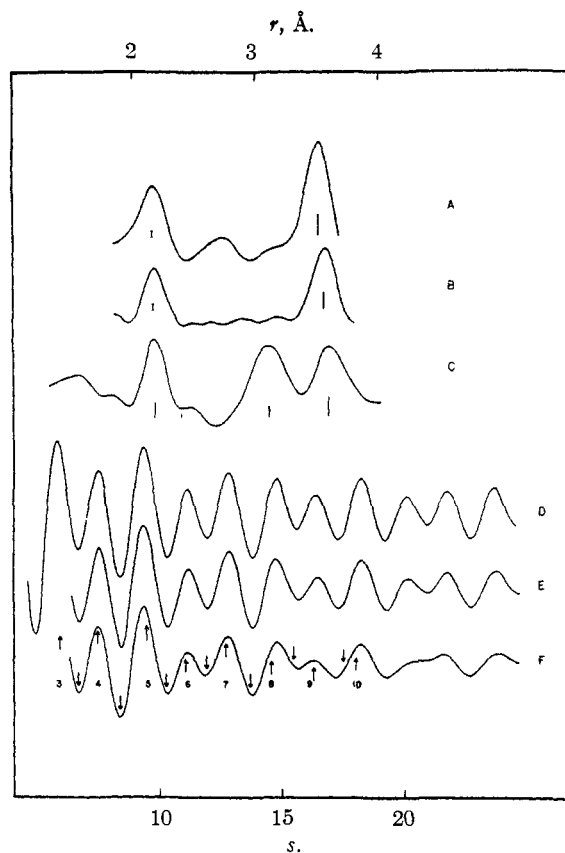


Fig. 1.—Radial distribution functions: simplified theoretical intensity curves for SiBr_4 .

of 0.9 per cent. This gives 3.50 Å. for the Br-Br distance. The radial distribution function (Fig. 1) gives

$$l_{\text{Si-Br}} = 2.16 \text{ Å.}, l_{\text{Br-Br}} = 3.51 \text{ Å.}$$

Since the Br-Br distance is the more reliable, we base our value of l on it. The estimated best values are

$$\begin{aligned} l_{\text{Br-Br}} &= 3.51 \pm 0.03 \text{ Å.} \\ l_{\text{Si-Br}} &= 2.15 \pm 0.02 \text{ Å.} \\ a &= 0.002 \end{aligned}$$

Tribromosilane.—Thirty features were measured, of which twenty were used for the quantitative comparison with the theoretical curves. The photographs were better than those for silicon tetrabromide. The values assumed for the Br-Si-Br angle ϕ were 113° (curve A), 111° (B), $109.28'$ (C), and 107° (D). The Si-Br distance was set at 2.15 Å. in the calculations. The curves in Fig. 2 are divided into three groups—curves A, B, C, D, with $a = 0, A', B', C'$ and D' with $a = 0.001$ and A'', B'', C'', D'' with $a = 0.003$.

In this molecule, as in silicon tetrabromide, it may be seen that the effect of changing the tem-

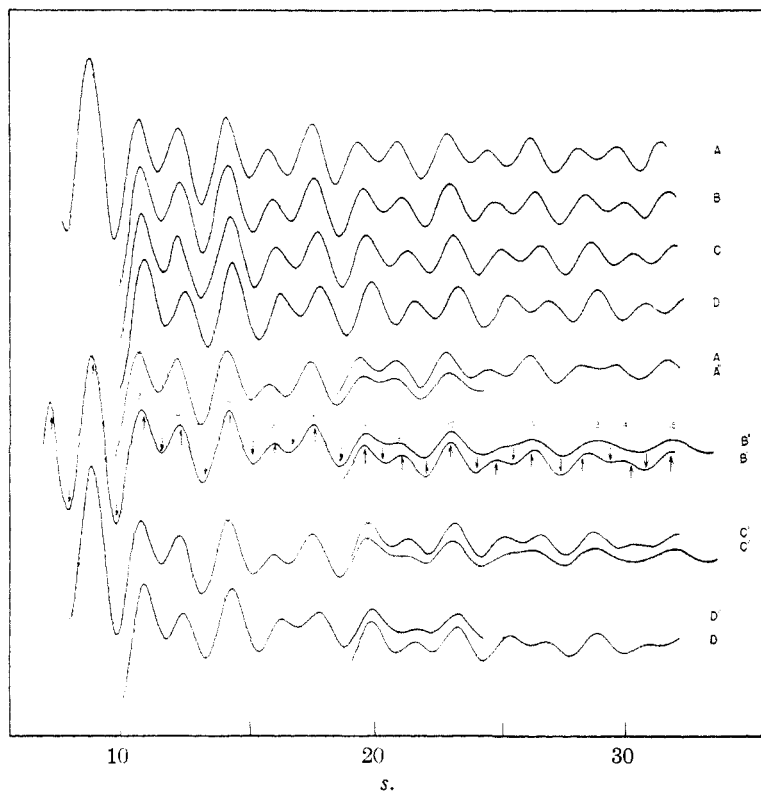


Fig. 2.—Simplified theoretical intensity curves for SiHBr_3 .

perature factor is quite distinct from the effect of changing the model. This is not true in general; for example, in difluorodibromosilane it is difficult to decide on a model because the application of the temperature factor produces changes in the curves that cannot be distinguished from changes brought about by varying the structural parameters slightly.

The singly primed curves show the best agreement with the photographs with respect to the effect of the temperature factor, in that the doubly primed group loses too much detail beyond $s = 20$, and the unprimed group shows many features too sharply. This indicates that $a = 0.001$ is approximately correct. The singly primed curves are not shown below $s = 14$ because small differences in the temperature factor have virtually no effect in this region. The curve C' represents the appearance of the photographs quite adequately.

The curves D, D' and D'' for $\vartheta = 107^\circ$ can be eliminated because they show minimum 9 deeper than 10, maximum 11 higher than 12, and minimum 6 deeper than 8. These difficulties persist for all values of a .

The curves A, for $\vartheta = 113^\circ$, are unsatisfactory because they show minima 6 and 7 with the same

depth, maximum 6 too low compared with 7, maxima 8 and 9 too nearly equal, and minimum 12 too deep compared with 11 and 13.

The curves C for $\vartheta = 109^\circ 28'$, and B for $\vartheta = 111^\circ$ are almost identical. The only respect in which curves C disagree with the photographs is that they show minimum 8 slightly shallower than 6.

Table II gives $s_{\text{obs.}}/s_{\text{calcd.}}$ for models B and C. In both cases, the Br-Br distance agrees well with the radial distribution value of 3.55 Å., but the tetrahedral model gives a long value for the Si-Br distance—2.18 Å. compared with the radial distribution value of 2.16 Å. The peaks of the radial distribution curve lead to the value $110^{1/2}^\circ$ for ϑ . For this reason, as well as the slight qualitative superiority of C, we choose our final model closer to C than B, but assign limits of error which

include both. The best values are

$$\begin{aligned} l_{\text{Si-Br}} &= 2.16 \pm 0.03 \text{ \AA.} \\ \angle \text{Br-Si-Br} &= 110^{1/2} \pm 1^{1/2}^\circ \\ l_{\text{Br-Br}} &= 3.55 \pm 0.02 \text{ \AA.} \\ a_{\text{Br-Br}} &= 0.001 \end{aligned}$$

Difluorodibromosilane.—The photographs showed eleven measurable rings. The pattern is well represented by curve J (Fig. 3) except for peaks 3-4 and 9. The exact nature of these features is doubtful. The maximum labeled 3-4 is quite broad and appeared at first glance to be rather more flat-topped than the figure indicates. For this reason two terms, numbers 3 and 4, were put into the radial distribution function to represent the extra width. The appearance of the ninth maximum and adjacent minima was also uncertain; hence s values for these features were not used in the quantitative comparison.

Fourteen theoretical curves (Fig. 3) were calculated for symmetrical (C_{2v}) tetrahedral models with $l_{\text{Si-Br}} = 2.16$ Å., $l_{\text{F-Br}}$ ranging from 3.01 to 3.11 Å. and $l_{\text{Br-Br}}$ from 3.49-3.61 Å. as suggested by the radial distribution function peaks (Fig. 1c) at 2.15, 3.07 and 3.56 Å. Because the appearance of the theoretical curves is insensitive to variations in the Si-F distance, and the radial distribu-

TABLE II

Max.	Min.	I_n	C_n	s_0	s_C^a	s_C/s_0	s_B^b	s_B/s_0
	1	- 3	- 1	1.64				
1		4	2	2.35				
	2	- 6	- 3	3.06				
2		10	7	3.97				
	3	-10	- 9	4.92				
3		6	6	5.97	5.91	(0.990)	5.93	(0.993)
	4	- 4	- 5	6.68	6.78	1.015	6.70	1.003
4		4	5	7.42	7.52	1.013	7.58	0.999
	5	- 9	-12	8.45	8.38	0.992	8.31	.983
5		10	14	9.37	9.47	1.011	9.36	.999
	6	- 7	-10	10.31	10.45	1.014	10.38	1.007
6		4	6	11.18	11.33	1.013	11.18	1.000
	7	- 3	- 5	11.88	11.92	1.003	11.72	0.987
7		7	10	12.77	12.85	1.006	12.75	.998
	8	-10	-15	13.83	13.89	1.004	13.79	.997
8		10	14	14.80	14.92	1.008	14.83	1.002
	9	- 7	- 3	15.58	15.86	1.026	15.55	0.998
9		2	3	16.25	16.51	1.016	16.31	1.004
	10	-10	-13	17.24	17.31	1.004	17.15	0.995
10		10	12	18.19	18.38	1.011	18.23	1.002
	11	- 8	- 9	19.25	19.42	1.009	19.22	0.998
11		4	4	20.00	20.39	1.020	20.09	1.005
	12	- 1	- 1	20.70	21.04	1.017	20.69	1.000
12		6	5	21.43	21.84	1.019	21.63	1.009
	13	- 9	- 7	22.59	22.85	1.012	22.69	1.005
13		5	4	23.44	23.87	1.019	23.75	1.013
	14	- 1	- 1	24.05	24.89	(1.035)	24.61	(1.023)
14		6	4	24.57	25.65	(1.043)	25.08	(1.021)
	15	-10	- 6	25.55	26.21	(1.027)	25.98	(1.017)
15		7	3	27.01	27.25	(1.008)	(27.19)	(1.007)
					Average		1.012	1.000
					Av. dev.		0.006	0.005
					l_{Si-Br}		2.175	2.15
					l_{Br-Br}		3.55	3.54

^a Br-Si-Br = 109°28'. ^b Br-Si-Br = 111°.

tion function does not show a corresponding, well resolved peak, the value 1.545 Å. was assumed, in agreement with the Si-F distance found in silicon tetrafluoride.⁶ This assumption may be partially justified by analogy with CF₂Cl₂ and CF₄,⁷ in both of which the C-F distance is the same. It should be borne in mind that the reported values of the Br-Si-F and F-Si-F angles are also essentially assumed values inasmuch as they depend on the assumed Si-F distance.

The models investigated were systematized by locating them on a two-dimensional map of l_{F-Br} against l_{Br-Br} . All models lying outside a closed curve corresponding to the assigned limits of error are unacceptable, and, in general, become progressively worse as their distance from the selected points increases in any direction. Since it was impossible, as discussed above, to determine

the temperature factor experimentally, the value $a_{Br-Br} = 0.001$, which is approximately equal to that obtained for the Br-Br vibration in SiBr₄ and SiHBr₃, was adopted here for both a_{Br-Br} and a_{Br-F} . a_{Si-F} , a_{F-F} , and a_{Si-Br} were all arbitrarily set at zero.

The curves disagreed with the photographs as follows: (a) Curves A, B and D show minimum 7 too deep, relative to minima 6 and 8. Curve D also reverses the relative depths of minima 3 and 5, and makes maximum 3 too high compared with 5. (b) In curves K and N, minimum 5 is deeper than 6, contrary to the appearance of the photographs. K also shows the fifth maximum higher than the second. C and G are also unsatisfactory in the latter respect. (c) L and H give maximum 3 too high relative to 5, and minimum 3 deeper than 5.

None of the group E, F, I, J or M is definitely unacceptable, hence the assigned limit of error

(6) L. O. Brockway, *J. Phys. Chem.*, **41**, 747 (1937).

(7) L. O. Brockway and F. T. Wall, *THIS JOURNAL*, **56**, 2372 (1934).

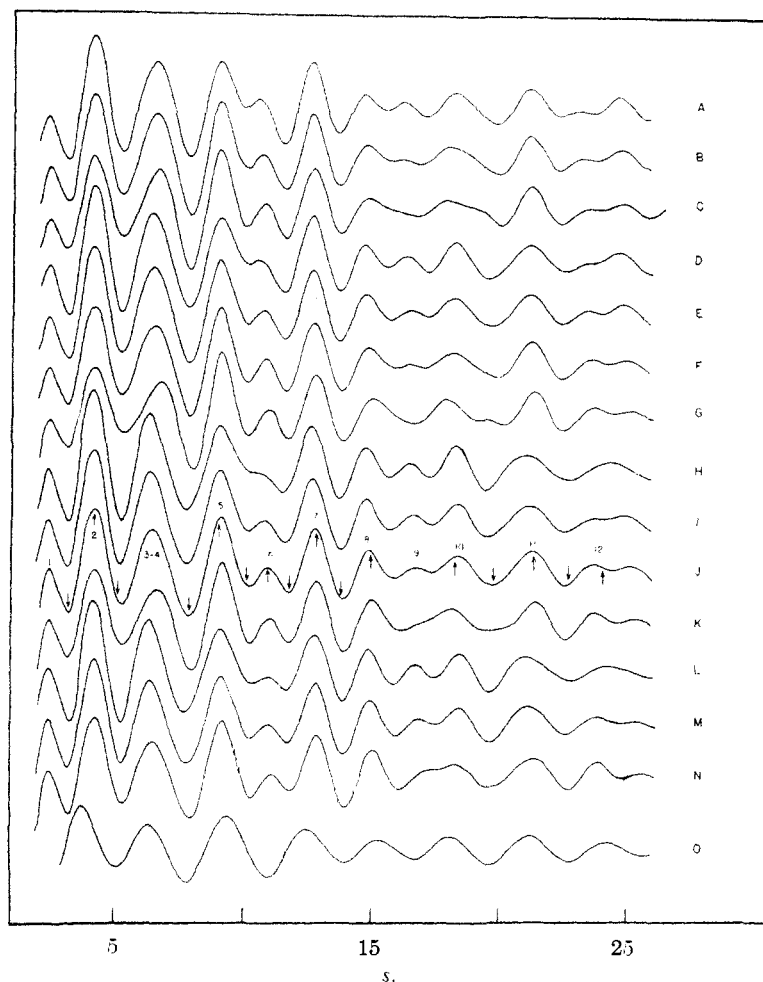


Fig. 3.—Simplified theoretical intensity functions for SiF_2Br_2 . The models are described by the following parameters:

	$l_{\text{Br}-\text{Br}}$	$l_{\text{F}-\text{Br}}$	$l_{\text{F}-\text{F}}$	$\angle \text{Br}-\text{Si}-\text{Br}$	$\angle \text{F}-\text{Si}-\text{Br}$	$\angle \text{F}-\text{Si}-\text{F}$
A	3.53	3.05	2.07	$114^\circ 10'$	$113^\circ 55'$	$93^\circ 50'$
B	3.63	3.09	2.23	$114^\circ 10'$	$112^\circ 0'$	$92^\circ 25'$
C	3.63	3.06	2.37	$114^\circ 10'$	$110^\circ 20'$	$100^\circ 10'$
D	3.59	3.12	2.13	$112^\circ 10'$	$113^\circ 55'$	$87^\circ 5'$
E	3.59	3.09	2.29	$112^\circ 10'$	$112^\circ 0'$	$95^\circ 15'$
F	3.59	3.06	2.41	$112^\circ 10'$	$110^\circ 20'$	$102^\circ 40'$
G	3.59	3.02	2.55	$112^\circ 10'$	$108^\circ 10'$	$112^\circ 5'$
H	3.55	3.12	2.19	$110^\circ 10'$	$113^\circ 55'$	$90^\circ 0'$
I	3.55	3.09	2.33	$110^\circ 10'$	$112^\circ 0'$	$97^\circ 40'$
J	3.55	3.06	2.45	$110^\circ 10'$	$110^\circ 20'$	$104^\circ 50'$
K	3.55	3.02	2.59	$110^\circ 10'$	$108^\circ 10'$	$114^\circ 0'$
L	3.51	3.09	2.37	$108^\circ 30'$	$112^\circ 0'$	$99^\circ 50'$
M	3.51	3.06	2.48	$108^\circ 30'$	$110^\circ 20'$	$106^\circ 45'$
N	3.51	3.02	2.61	$108^\circ 30'$	$108^\circ 10'$	$115^\circ 30'$

$l_{\text{Si}-\text{Br}} = 2.16 \text{ \AA.}$, $l_{\text{Si}-\text{F}} = 1.547 \text{ \AA.}$ for all models.

allows the range of parameters covered by these models. The values of $s_{\text{calcd.}}/s_{\text{obs.}}$, which vary little from one curve to another, are given in Table III for curve J.

Curve O, which includes only Si-Br and Si-F

interactions, shows the effect of an infinite temperature effect on the Br-Br and Br-F vibrations.

The selected best values are

$$\begin{aligned}
 l_{\text{Si}-\text{Br}} &= 2.16 \pm 0.02 \text{ \AA.} \\
 l_{\text{Si}-\text{F}} &= 1.55 \text{ \AA. (assumed)} \\
 \angle \text{Br}-\text{Si}-\text{Br} &= 110^\circ 50' \pm 3^\circ \\
 l_{\text{Br}-\text{Br}} &= 3.56 \pm 0.05 \text{ \AA.} \\
 \angle \text{Br}-\text{Si}-\text{F} &= 111^\circ 20' \pm 3^\circ \\
 l_{\text{F}-\text{Br}} &= 3.08 \pm 0.04 \text{ \AA.} \\
 \angle \text{F}-\text{Si}-\text{F} &= 99^\circ \pm 10^\circ \\
 l_{\text{F}-\text{F}} &= 2.35 \pm 0.15 \text{ \AA.}
 \end{aligned}$$

Previous Work.—Wouters, De Hemptinne and Capron⁸ have used the electron diffraction method to determine the structure of SiHBr_3 . They obtain the results

$$\begin{aligned}
 l_{\text{Si}-\text{Br}} &= 2.19 \pm 0.05 \text{ \AA.} \\
 l_{\text{Br}-\text{Br}} &= 3.63 \text{ \AA.} \\
 \angle \text{Br}-\text{Si}-\text{Br} &= 110^\circ
 \end{aligned}$$

These values for the Br-Br distance and the Si-Br distance are significantly higher than ours although the bond angle values agree well. We believe the present determination to be the more reliable because Wouters and co-workers measured only the first five maxima, whereas we measured fifteen maxima and fifteen minima. It has been our experience that

determinations based on a few measurements extending to only relatively small values of s are likely to be inaccurate, particularly if the minima are neglected. Moreover, it may be significant that the above authors have reported several other interatomic distances which appear to be too high by about their assigned experimental error. Their determination of the size of the SiHCl_3 ⁹ molecule gives a result 2 to 3% higher than that obtained by Brockway³ and by Pirenne.¹⁰ For SiBrCl_3 ^{9b} De Hemptinne and Wouters again report 2.19 Å. for the Si-Br distance, and give 2.05 Å.

(8) Wouters, De Hemptinne and Capron, *Ann. soc. sci. Bruxelles*, **574**, 25 (1937).

(9) (a) De Hemptinne and Wouters, *Nature*, **138**, 884 (1936); (b) **139**, 928 (1937).

(10) Pirenne, *J. Chem. Phys.*, **7**, 144 (1939).

TABLE III

Max.	Min.	I_n	C_n	s_0	s_J	s_J/s_0	12	10	6	23.96	23.61	(0.969)
										Average		1.002
										Av. dev.		0.003
										l_{Si-Br}		2.16
1	1	-5	-4	1.61						^a See text for discussion.		
		6	4	2.49	2.45	(0.984)				for the Si-Cl distance, a value 2% higher than that (2.01 Å.) which has been reported for the Si-Cl bond in other molecules. ¹¹		
2	2	-8	-6	3.20	3.22	1.005				Summary		
		10	9	4.21	4.18	0.993				The molecular structures of SiBr ₄ , SiHBr ₃ and SiF ₂ Br ₂ have been studied by the electron diffraction method. In all of these molecules the Si-Br distance is 2.16 ± 0.03 Å., and the valence angles are but little distorted from the tetrahedral value. The relative temperature factors have been estimated for SiBr ₄ and SiHBr ₄ from the appearance of the electron diffraction photographs.		
3	3	-7	-8	5.14	5.28	1.027				(11) Lister and Sutton [<i>Trans. Faraday Soc.</i> , 37 , 393 (1941)] report from an electron diffraction study that the Si-Br distance in silicon tetrabromide is 2.14 ± 0.02 Å., in substantial agreement with our value.		
4	4	5	7	6.23	6.47 ^a	(0.972)				PASADENA, CALIFORNIA RECEIVED SEPTEMBER 13, 1941		
5	5	-11	-17	7.89	7.87	.997						
6	6	10	16	9.03	9.07	1.003						
7	7	-5	-8	10.10	10.19	1.010						
8	8	3	4	10.91	10.90	0.999						
9	9	-7	-11	11.74	11.75	1.000						
10	10	10	16	12.78	12.75	0.998						
11	11	-10	-16	13.74	13.84	1.008						
12	12	6	9	14.90	14.86	0.999						
		9	-2	15.33	15.74	(1.027)						
		2	3	16.72	16.71	(1.000)						
		10	-6	17.12	17.27	(1.009)						
		10	10	18.18	18.13	0.997						
		11	-8	19.67	19.62	.997						
		8	7	21.25	21.24	1.000						
		12	-10	22.71	22.61	0.996						

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY SCHOOL OF MEDICINE, ST. LOUIS, MISSOURI]

Preparation of Tetrahydroxyquinone and Rhodizonic Acid Salts from the Product of the Oxidation of Inositol with Nitric Acid*

BY PAUL W. PREISLER AND LOUIS BERGER

Some confusion exists in the literature concerning the identification of the salts of rhodizonic acid (dihydroxy-diquinone) and of tetrahydroxyquinone. The quantitative analytical procedures usually employed for this purpose do not distinguish with certainty between substances of such close elementary composition, especially when they are hydrated or cannot be properly dried.¹ These materials have now been conclusively identified by application of electrometric oxidation-reduction potential measurements.

Modification of the methods for the preparation of these substances from the products of the oxidation of inositol (cyclohexanehexol) by nitric acid have been devised and crystalline materials of high purity have been prepared. The quantities of rhodizonate or of tetrahydroxyquinone salt

have been found to be affected by the rate of the addition and the basic properties of the salt added to the oxidized inositol, and by the degree of agitation with air or oxygen of the mixture so formed. When potassium acetate is used, pure potassium rhodizonate is obtained, whereas with potassium carbonate mixtures with tetrahydroxyquinone, salts usually result.

Salts of rhodizonic acid and of tetrahydroxyquinone are utilized as indicators in the volumetric determination of sulfates with barium salt solution.² A comparison of the properties of the pure substances indicates that the color changes when used as indicators are probably due to salts of rhodizonic acid rather than of tetrahydroxyquinone.

Preparation of Oxidation Products of Inositol.—To ensure uniform reproducible results the procedure is given in

* Presented before the American Chemical Society at St. Louis, Mo., April, 1941.

(1) E. Bartow and W. W. Walker, *Ind. Eng. Chem.*, **30**, 300 (1938); O. Gelormini and N. E. Artz, *This Journal*, **52**, 2483 (1930); F. A. Hoglan and E. Bartow, *ibid.*, **62**, 2397 (1940); B. Homolka, *Ber.*, **54**, 1393 (1921); M. Maquenne, *Compt. rend.*, **104**, 297 (1887); R. Nietzki and T. Benckiser, *Ber.*, **18**, 499 (1885).

(2) G. Gutzeit, *Helv. Chim. Acta*, **12**, 725 (1929); W. A. Peabody and R. S. Fisher, *Ind. Eng. Chem., Anal. Ed.*, **10**, 651 (1938); W. C. Schroeder, *Ind. Eng. Chem., Anal. Ed.*, **5**, 403 (1933); **8**, 127 (1936); **9**, 69 (1937); **10**, 206 (1938); R. Strebing and L. Zombory, *Z. anal. Chem.*, **79**, 1 (1929).