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The Molecular Structures of the Bromomethanes

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The investigation of the molecular structures of the halogen substituted methanes has been undertaken in these Laboratories as a means of testing the constancy of chemical bond lengths and of determining the bond radii and the variations in bond angles in unsymmetrical molecules. The results of the investigations on the fluoro-, chloro- and fluorochloromethanes already have been reported.[1] Using the experimental procedure which has been described in detail elsewhere,[2] we have applied the electron diffraction method of studying molecular structures to the bromomethanes, obtaining the results which are reported in this paper.

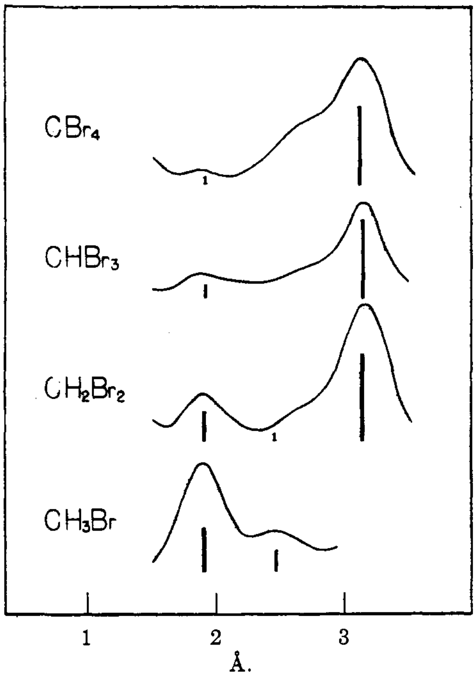

Fig. 1.—Radial distribution curves for the bromomethanes. The tall peaks near 3 Å. represent the Br–Br distances; those near 2 Å. the C–Br distances.

The electron wave length was 0.0611 Å. and the camera distance was near 10.5 cm. The diameters of the maxima and minima appearing in the photographs were measured visually, and the corresponding S_0 values (equal to $4\pi(\sin \theta/2)/\lambda$), where θ is the angle of scattering and λ is the electron wave length, are tabulated below for each substance. These were combined with the visually estimated intensities (shown under the column heading I) to give the observed radial distribution of scattering matter shown by the curves in Fig. 1. The "calculated S" values are taken from the theoretical scattering curves in Figs. 2 and 3.

Carbon Tetrabromide.—Photographs of carbon tetrabromide vapor were taken with a sample of the Eastman preparation heated to 115 to 130°. The pattern contains seven extraordinarily sharp, evenly-spaced rings. The radial distribution function (Fig. 1) shows a sharp peak at 3.13 Å., corresponding to the Br–Br separation, together with smaller, less reliable peaks at shorter distances. The theoretical scattering curve (Fig. 2) based on a regular tetrahedral arrangement of four bromine atoms around a central carbon atom with an assumed C–Br distance of 1.91 Å. shows excellent agreement with the photographs. The quantitative comparison in Table I and the radial distribution curve lead to final values of C–Br = 1.91 ± 0.02 Å. and Br–Br = 3.12 ± 0.03 Å.

TABLE I
CARBON TETRABROMIDE

Max.	Min.	I	S_0	$S_{calcd.}$	$S_{calcd.}/S_0$
1		12	2.662	2.49	(0.936)
	2		3.615	3.48	(.973)
2		15	4.528	4.49	.992
	3		5.597	5.51	.984
3		12	6.525	6.58	1.008
	4		7.514	7.56	1.006
4		10	8.464	8.51	1.005
	5		9.507	9.51	1.000
5		12	10.51	10.59	1.007
	6		11.56	11.62	1.005
6		5	12.49	12.58	1.007
	7		13.56	13.56	1.000
7		4	14.49	14.54	1.003
				Mean	1.002
				Br–Br	3.12 Å.
				C–Br	1.91 Å.

In an earlier investigation, Wierl[3] obtained a

(1) L. E. Sutton and L. O. Brockway, THIS JOURNAL, **57**, 473 (1935); L. O. Brockway, *J. Phys. Chem.*, **41**, 185, 747 (1937).
(2) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).
(3) R. Wierl, *Ann. Physik*, **8**, 521 (1931).

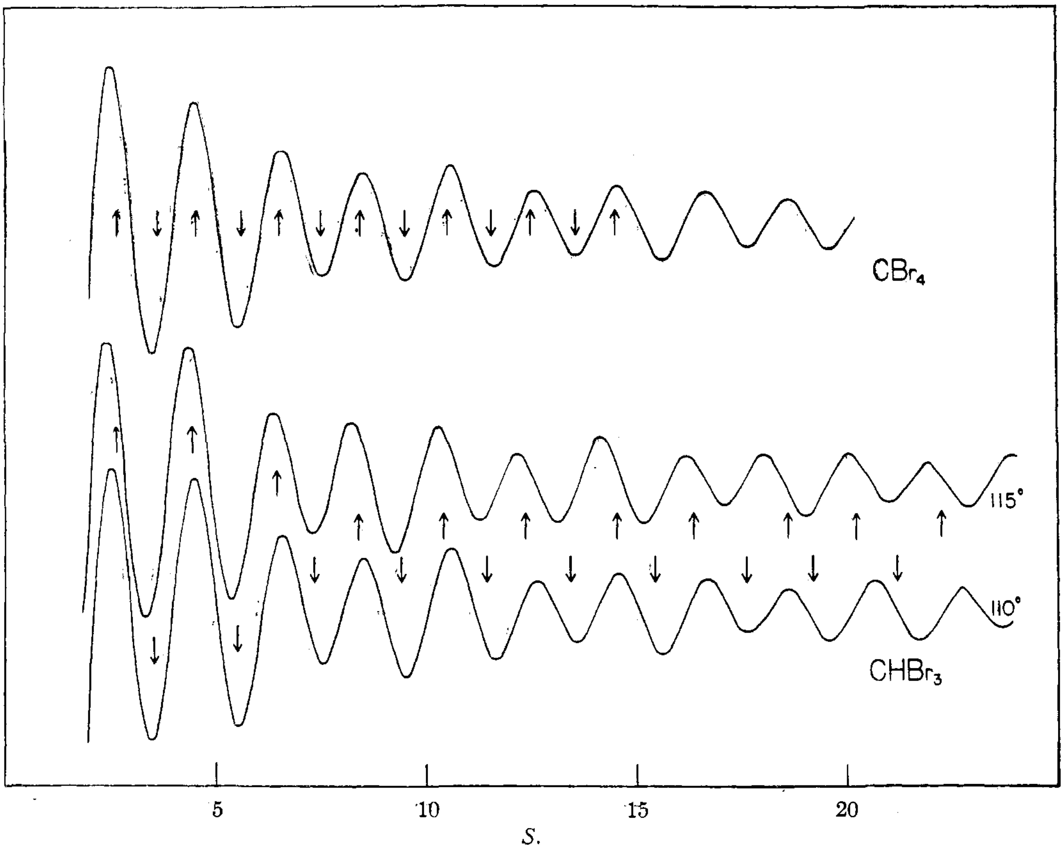

Fig. 2.—Theoretical scattering curves for carbon tetrabromide and tribromomethane.

value of 2.05 Å. for the C–Br distance from photographs showing only three maxima. More recently de Laszlo[4] reported in a brief note a distance of 1.93 Å.

Tribromomethane.—The vapor of tribromomethane (Eastman) was photographed at a temperature of 75 to 100°. Eleven rings are observed on the photographs, whose pattern resembles that of carbon tetrabromide in general appearance. The radial distribution curve (Fig. 1) has a sharp peak due to the Br–Br interaction at 3.14 Å. and a smaller one due to the C–Br interaction at about 1.88 Å. Theoretical scattering curves were calculated for three models each having an assumed C–Br distance of 1.91 Å. and with Br–C–Br angles of 110, 112, and 115°, respectively. Because of the small scattering power of the carbon atom relative to the three bromine atoms the curves are determined chiefly by the positions of the bromine atoms; accordingly the three curves are indistinguishable except for the change in scale corresponding to the change in the assumed Br–Br separation. On comparison with the observed maxima and

(4) H. de Laszlo, *Nature*, **135**, 474 (1935).

TABLE II

TRIBROMOMETHANE

Max.	Min.	I	S_0	$S_{calcd.}$	$S_{calcd.}/S_0$
1		8	2.693	2.48	(0.921)
	2		3.563	3.39	(.952)
2		12	4.480	4.40	.983
	3		5.570	5.46	.981
3		8	6.519	6.48	.994
	4		7.419	7.41	.998
4		7	8.459	8.36	.989
	5		9.477	9.38	.990
5		9	10.48	10.43	.995
	6		11.53	11.44	.992
6		6	12.45	12.38	.994
	7		13.51	13.31	.986
7		6	14.41	14.31	.994
	8		15.53	15.37	.990
8		3	16.45	16.40	.996
	9		17.45	17.35	.995
9		3	18.32	18.28	.997
	10		19.32	19.29	.998
10		1	20.34	20.32	.998
	11		21.33	21.33	1.000
11		1	22.36	22.30	0.997
				Mean	0.993
				Br–Br	3.15 Å.

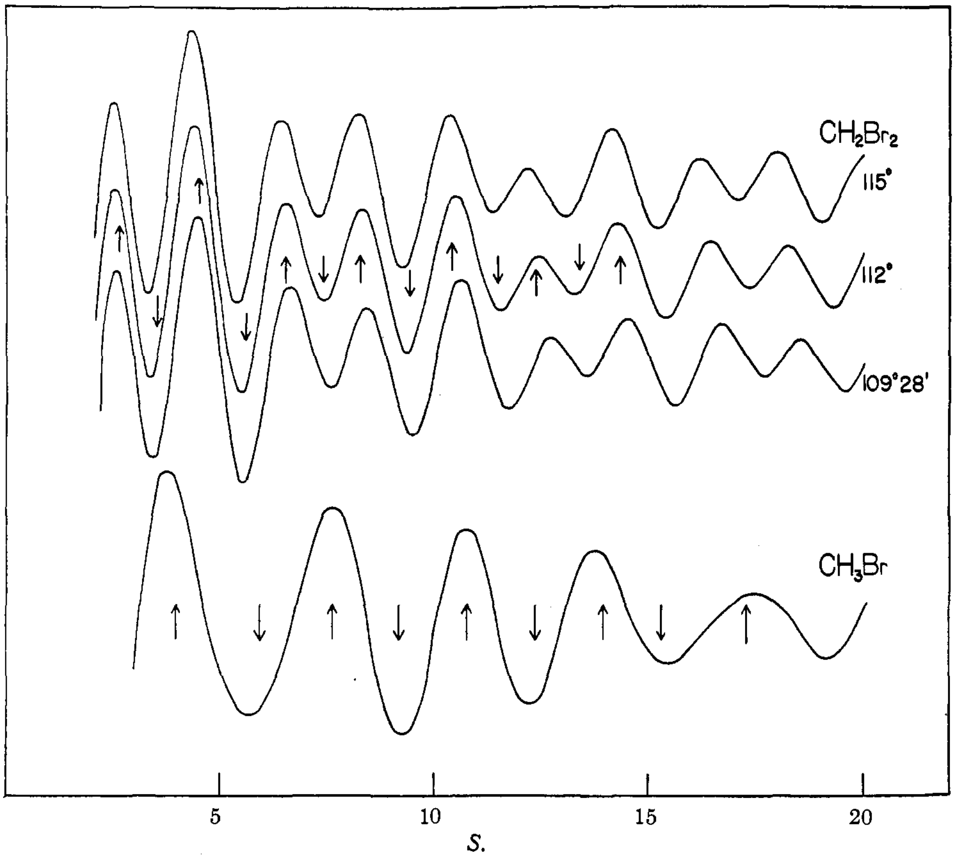

Fig. 3.—Theoretical scattering curves for dibromomethane and bromomethane.

minima (Table II) each of these curves leads to the value Br–Br = 3.15 Å.

Although the carbon–bromine distance cannot be determined directly in this molecule it is very probable that it has the same value as in carbon tetrabromide. This assumption is supported by the observed equality of the bond distances in trichloro- and tetrachloromethane and in trifluoro- and tetrafluoromethane. We accept as the final values: C–Br = 1.91 Å., Br–Br = 3.15 ± 0.03 Å. and ∠Br–C–Br = 111 ± 2°.

Wierl[5] found with the aid of photographs showing three maxima the values C–Br = 2.03 and ∠Br–C–Br = 111°. Dornte[6] obtained the values C–Br = 2.05 and ∠Br–C–Br = 115° from five maxima.

Dibromomethane.—Photographs of dibromomethane (Eastman) were obtained on which seven well-defined maxima are observed. Of these the second is much stronger than the first, while the fifth and the seventh are each a little stronger than the fourth and sixth maxima, respectively. The radial distribution curve (Fig. 1) shows a strong reliable peak at 3.16 Å., the Br–Br distance.

Theoretical curves (Fig. 3) were calculated for four models. The C–Br distance was taken as 1.91 Å., the C–H distance 1.05 Å., the H–C–H angle 109°28′ and the Br–C–Br angle 109°28′, 112, 115, and 118°, respectively. As the angle is increased the model becomes unsatisfactory because the fourth maximum becomes too strong, rising above the third and fifth, and the sixth maximum becomes too weak in comparison with the fifth and seventh. For these reasons it is improbable that the angle is greater than 112°. On the other hand, the sixth and seventh maxima in the curve for the 109°28′ model are not so well set off from each other as they are in the photographs. The most probable value of the Br–C–Br angle is accordingly 112 ± 2°.

The S values for the 112° model are shown in Table III; comparison of these with the S_0 values gives a Br–Br distance of 3.17 ± 0.02 Å., in agreement with the position of the strong peak in the radial distribution curve. The C–Br distance is 1.91 ± 0.02 Å.

(5) R. Wierl, *Ann. Physik*, **13**, 453 (1932).
(6) R. W. Dornte, *J. Chem. Phys.*, **1**, 630 (1933).

TABLE III

DIBROMOMETHANE

Max.	Min.	I	S_0	$S_{calcd.}$ 112°	$S_{calcd.}/S_0$
1		5	2.641	2.50	(0.947)
	2		3.538	3.34	(.944)
2		10	4.507	4.37	(.970)
	3		5.597	5.47	(.977)
3		8	6.517	6.51	.999
	4		7.399	7.40	1.000
4		6	8.275	8.29	1.002
	5		9.407	9.34	0.993
5		7	10.40	10.47	1.007
	6		11.47	11.53	1.005
6		2	12.37	12.44	1.005
	7		13.38	13.23	0.989
7		3	14.32	14.25	.995
				Mean	0.999
				Br–Br	3.17 Å.
				C–Br	1.91 Å.

Dornte[6] reported C–Br = 2.05 Å. and ∠ Br–C–Br = 125°. The discrepancy between this result and ours is probably due in part to the smaller number of maxima which he observed.

Bromomethane.—Bromomethane was prepared from methanol and hydrobromic acid and was fractionated at 0°. The photographs show five rather diffuse rings. The poor definition in the pattern is due to the presence in the molecule of one atom whose scattering power is much larger than that of all the other atoms.

The radial distribution curve shows one peak at 1.90 Å. The theoretical curve calculated for a methyl group with tetrahedral angles and C–H distances of 1.05 Å. and for a C–Br distance of 1.91 Å. gives on comparison with the photographs (Table IV) an observed distance C–Br = 1.91 ± 0.06 Å. The large estimated probable error is assigned because of the difficulty of making precise measurements on the photographs. Dornte[6] reported C–Br = 2.06 Å.

TABLE IV

BROMOMETHANE

Max.	Min.	I	S_0	$S_{calcd.}$	$S_{calcd.}/S_0$
1		12	3.997	3.76	(0.942)
	2		5.942	5.67	(.954)
2		12	7.626	7.64	1.002
	3		9.186	9.20	1.000
3		10	10.77	10.74	0.998
	4		12.35	12.16	1.005
		4	13.94	13.74	0.986
4	5		15.30	15.44	1.010
5		2	17.28	17.60	1.018
				Mean	0.999
				C–Br	1.91 Å.

Discussion

The results for the bromomethanes are collected in Table V with assumed values given in parentheses.

TABLE V

Substance	C–Br, Å.	Br–Br, Å.	∠ Br–C–Br
CBr_4	1.91 ± 0.02	3.12 ± 0.03	(109°28′)
$CHBr_3$	(1.91)	3.15 ± 0.03	111 ± 2°
CH_2Br_2	1.91 ± 0.02	3.17 ± 0.03	112 ± 2°
CH_3Br	1.91 ± 0.06		

The observed C–Br bond distances are for all the substances equal to the sum of the single bond covalent radii[7] for carbon and bromine, 1.91 Å. The Br–C–Br bond angles show only small increases in tri- and dibromomethane above the tetrahedral angle which occurs in the symmetrical tetrabromide. This increase is of the same order as that found in the chloromethanes. The increased repulsion between the halogen atoms which might be expected in comparing the bromine and the chlorine compounds evidently is offset by the greater separation between the bromine atoms due to the larger bond distances; the bond angle is not appreciably affected when bromine is substituted for chlorine.

Summary

The molecular structures of the bromomethanes have been investigated by means of electron diffraction. The C–Br distance in each compound is 1.91 Å.; the Br–C–Br angle is 109°28′ in carbon tetrabromide, 111° in tribromomethane and 112° in dibromomethane.

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(7) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).