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The Molecular Structures of the Methyl Derivatives of Silicon, Germanium, Tin, Lead, Nitrogen, Sulfur and Mercury and the Covalent Radii of the Non-Metallic Elements

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Introduction

The electron diffraction investigation of the fluorides and chlorides of carbon, silicon, germanium, tin, phosphorus and arsenic[2] showed the bond distances in most of these compounds to be shorter than the corresponding sums of the covalent radii.[3] Corrections applied to the accepted values for the radii would have removed some of the discrepancies but it was impossible to set up a single set of radii which gave agreement with all of the observed distances. It was suggested that the observed shortening could be explained on the basis of two effects: (1) an extra ionic character of the bonds which is not found in the compounds from which the table of radii was obtained and (2) the contribution of a partial double bond character due to the resonance of the molecule among several structures which have some double bonds. Since structures containing double bonds are not possible in the methyl derivatives of the elements concerned the study of the methyl compounds was proposed as a means of distinguishing between the two effects and also of testing the covalent radii. The tetramethyls of silicon, germanium, tin and lead, trimethyl nitrogen, and the dimethyls of sulfur and mercury have now been investigated by the electron diffraction method. The apparatus and the method of interpreting have recently been described in detail.[4] All of the compounds were photographed with electrons having a wave length of 0.0611 Å. with a camera distance of 10.43 cm.

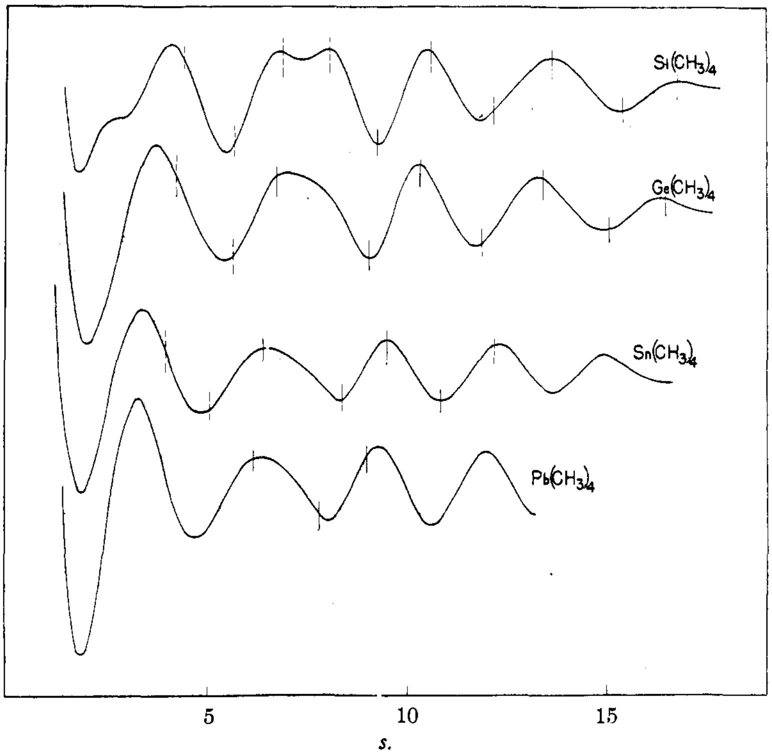

Fig. 1.—Theoretical electron diffraction curves for the tetramethyls. The observed maxima and minima are marked by the vertical lines. For $Pb(CH_3)_4$ a 3.14% shift in the *s* scale of the curve leads to agreement with the three observed points.

Tetramethyls.—Samples of the tetramethyls of silicon, germanium and tin were obtained from Dr. Warren C. Johnson of the University of Chicago and of lead tetramethyl from Mr. T. A. Boyd of the General Motors Research Laboratories.

Theoretical intensity curves for these compounds are reproduced in Fig. 1. For these curves the atomic scattering factors have been set equal to the respective atomic numbers. They are based on a molecular model in which the central atom is surrounded by four carbon atoms at the corners of a regular tetrahedron with three hydrogen atoms attached at tetrahedral angles to each carbon atom. In case of silicon and germanium tetramethyls an approximation to the free rotation of the methyl groups was made by averaging curves whose models differed in having successive

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[1] Fellow of the Commonwealth Foundation.

[2] L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934); L. O. Brockway, *ibid.*, **57**, 958 (1935).

[3] L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[4] L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

60° rotations in the orientation of the methyl groups. The use of a smaller interval in the methyl group rotation angle would have led to the same averaged curve since this effect was tested in the case of tetramethylmethane.

The photographs show the general features of the respective curve in Fig. 1. The positions of the maxima and minima which were measured are marked by the vertical lines. In silicon tetramethyl the second maximum was observed to be a double ring. The components of this doublet were not very well resolved and visual measurements of their diameters showed wide fluctuations. Measurements of the first maximum and second minimum showed the usual displacement toward larger diameters because of their proximity to the dense central spot on the photograph. These four points, marked by dashed vertical lines in Fig. 1, were not used in the determination of the size of the molecule as given in Table I. In this table are listed the visually observed s values (equal to $4\pi(\sin\theta/2)/\lambda$), the calculated s values based on the assumed distances Si–C = 1.94 Å. and C–H = 1.06 Å., and the experimental Si–C distances. The average value taken from the more reliable ring measurements is Si–C = 1.93 ± 0.03 Å. The radial distribution function[5] was calculated with the use of the estimated intensities given in the third column of Table I. In Fig. 2 the radial distribution functions are shown for the various compounds. In each case the principal maximum corresponds to the bond distance between the central atom and the carbon atoms, and the vertical line indicates the value found for this distance by the usual method of comparing theoretical intensity curves with the photographs. The maximum for silicon tetramethyl occurs at 1.94 Å. in good agreement with the foregoing result of the usual method of interpretation, 1.93 Å.

Table I

Silicon Tetramethyl

Max.	Min.	I	s, obsd.	s, calcd. for Si–C = 1.94 Å.	Si–C, Å.
1		10	4.39	4.05	(1.790)
	2		5.66	5.45	(1.868)
2		12	(6.87)	6.84	
2a			(8.02)	7.95	
	3		9.21	9.25	1.946
3		6	10.58	10.44	1.913
	4		12.16	11.78	1.880
4		2	13.60	13.66	1.950
	5		15.36	15.30	1.932
5		1	16.72	16.83	1.952
				Average	1.929

Radial distribution function result; 1.94 Å. Final value: Si–C = 1.93 ± 0.03 Å.

Table II

Germanium Tetramethyl

Max.	Min.	I	s, obsd.	s, calcd. for Ge–C = 1.99 Å.	Ge–C, Å.
1		9	4.21	3.73	(1.763)
	2		5.63	5.40	(1.909)
2		12	6.70	7.06	(2.097)
	3		9.01	9.03	1.994
3		6	10.32	10.26	1.980
	4		11.86	11.68	1.960
4		3	13.38	13.27	1.974
	5		15.04	14.92	1.975
5		1	16.43	16.31	1.976
				Average	1.977

Radial distribution function result: 2.00 Å. Final value: Ge–C = 1.98 ± 0.03 Å.

The results for germanium tetramethyl are given in Table II. The model from which the theoretical intensity curve was calculated is the tetrahedral model described above with Ge–C = 1.99 Å. and C–H = 1.06 Å. The photographs show five maxima of which the second is distinguished by the gradual decrease of intensity on its outer edge. This characteristic is also shown by the theoretical curve in Fig. 1. The first maximum and second minimum again lead to interatomic distance values which are smaller than the average. The second maximum shows the anticipated St. John effect and the corresponding interatomic distance value is too large. The average from the remaining three minima and three maxima is 1.977 Å. with a mean deviation of only 0.007 Å. The radial distribution function shown in Fig. 2 has a maximum corresponding to the Ge–C distance at 2.00 Å. The most probable value for this distance is 1.98 ± 0.03 Å.

Table III

Tin Tetramethyl

Max.	Min.	I	s, obsd.	s, calcd. for Sn–C = 2.17 Å.	Sn–C, Å.
1		6	3.95	3.37	(1.85)
	2		5.06	4.88	(2.095)
2		10	6.38	6.49	2.208
	3		8.37	8.32	2.158
3		6	9.46	9.48	2.174
	4		10.82	10.85	2.176
4		3	12.14	12.28	2.196
				Average	2.182

Radial distribution function result: 2.16 Å. Final value: Sn–C = 2.18 ± 0.03 Å.

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(5) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

The tin tetramethyl photographs show four maxima. The theoretical intensity curve was calculated with an assumed Sn–C distance of 2.17 Å. and a C–H distance of 1.06 Å. The comparison of observed and calculated *s* values for three maxima and two minima leads to an average value of Sn–C of 2.18 ± 0.03 (Table III). The value 2.16 Å. given by the radial distribution function is in satisfactory agreement.

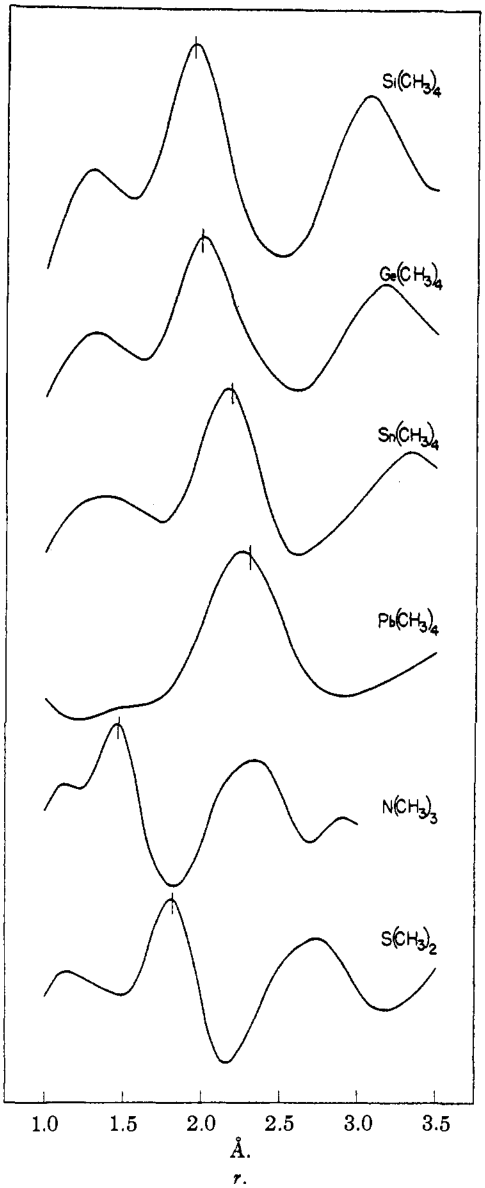

Fig. 2.—Radial distribution functions for the methyl compounds. In each case the maximum corresponding to the bond distance between the central and the carbon atoms is marked at the value for this distance as determined by the method illustrated in Fig. 1.

Good photographs of lead tetramethyl were not obtained. The heavy background on the negatives made it possible to distinguish only three rings, and of these the first was so uncertain that measurements of its diameter gave widely scattered values. Fairly consistent measurements were made on the second and third maxima and third minimum as reported in Table IV. The theoretical curve shown in Fig. 1 is based on an assumed Pb–C distance of 2.23 Å. while the experimental value is 2.30 Å. A change in the scale of the theoretical curve of 3.14% leads to excellent agreement between theory and experiment. The three term radial distribution function shows the Pb–C maximum at 2.26. Because of the relatively poor quality of the photographs, an unusually large estimate of the probable error is made; the best value for the Pb–C distance is 2.29 ± 0.05 Å.

TABLE IV

LEAD TETRAMETHYL

Max.	Min.	*I*	*s*, obsd.	*s*, calcd. for Pb–C = 2.23 Å.	Pb–C, Å.
1		12	(3.5)	3.26	
	2		(4.6)	4.69	
2		10	6.15	6.32	2.291
	3		7.76	8.05	2.312
3		5	8.98	9.28	2.306
				Average	2.303

Radial distribution function result: 2.26 Å. Final value: Pb–C = 2.29 ± 0.05 Å.

Comparison of the photographs of the four compounds shows the effect of the increasing size and scattering power of the central atom. The maxima occur at successively smaller angles due to the increase in the size of the molecule. This is shown in Fig. 1 by the shift toward smaller angles of the maxima on successive curves. The increase of the scattering power of the central atom is shown in the curves by the approach to a simple $(\sin x)/x$ curve; this is due to the preponderant effect of a single term in the formula for the theoretical intensity. Especially notable is the change in the appearance of the second maximum from a resolved doublet in $Si(CH_3)_4$ to an asymmetric single maximum in $Ge(CH_3)_4$ to a symmetric maximum in $Pb(CH_3)_4$.

It will be noted that the number of rings observed on the photographs of this series of compounds decreased with increasing scattering power of the central atom. This is due to the disproportionate increase of the background of atomic scattering relative to the molecular scattering

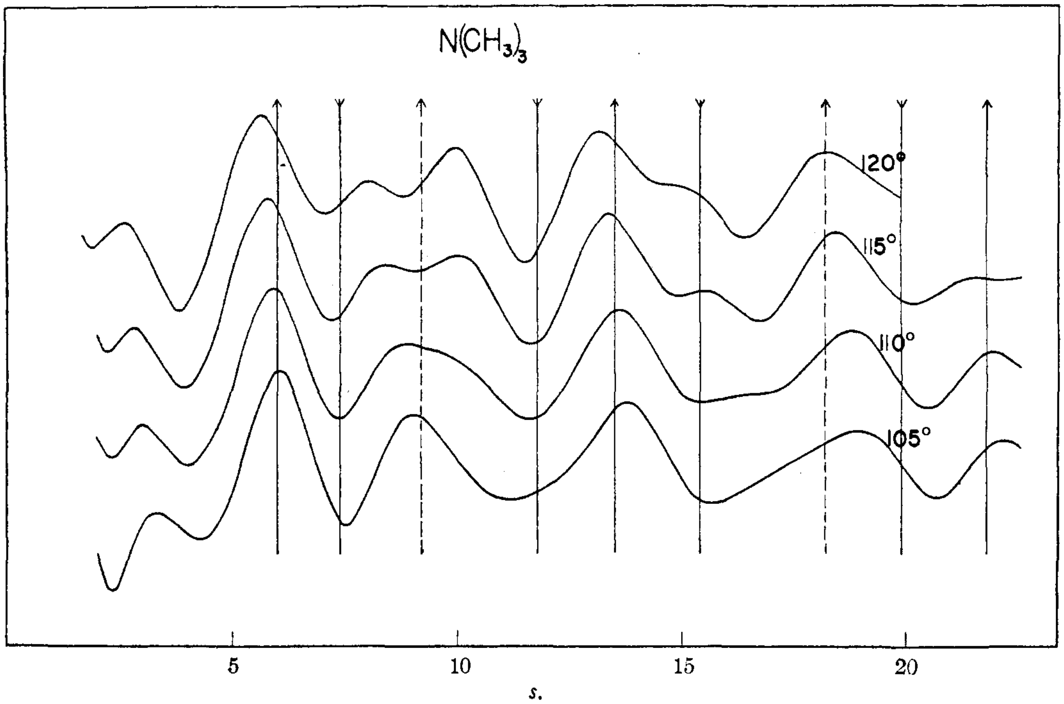

Fig. 3.—Theoretical electron diffraction curves for nitrogen trimethyl. The observed points marked by the dashed lines are not reliable for quantitative comparisons.

(*i. e.*, the part of the scattering in which the interference effects appear). Since the apparent intensity of the diffraction maxima is approximately proportional to the ratio of the molecular to the atomic scattering,[6] the relative increase of atomic scattering in a series of molecules in which one atom progressively scatters much more strongly than the others causes the maxima to become weaker and a smaller number of them to appear in the diffraction patterns of the successive molecules. On microphotometer records the fluctuations due to the interference effects become less pronounced and the intensity curve approaches that for monatomic scattering. Thus it happens that increased scattering power of a molecule results in less pronounced interference effects and poorer photographs for structure determination if the increase of scattering power occurs in only one of the atoms of the molecule.

Nitrogen Trimethyl.—The photographs of nitrogen trimethyl were obtained with the use of the Eastman product redistilled.

Theoretical intensity curves were calculated for pyramidal models having the nitrogen atom at the apex and with C–N–C bond angles of 120, 115, 110 and 105°. All terms except the H–H terms were included. Free rotation of the methyl groups was assumed and for each curve shown in Fig. 3 the scattering was averaged from a set of models which differ in having 30° intervals in the orientation of the methyl groups. The C–N distance assumed for the curves was 1.47 Å.

The measured positions of the maxima and minima are shown by the vertical lines in Fig. 3. The 120° model is eliminated since the corresponding curve shows two maxima in the region from 8 to 10 on the s scale where only one maximum is observed; also it shows a well-marked shelf near $s = 15$ at the position of an observed minimum. For the same reasons the 115° model is also unsatisfactory. The third ring on the photographs is broad with no well-defined maximum point and this appearance agrees better with the 110° curve than with any other. The fourth maximum is sharp whereas the fifth is indistinct on the inner edge in agreement with its appearance in the 105° curve. The general qualitative features correspond to an angle of 108 ± 4° for the C–N–C bonds.

The quantitative comparison for the 110 and 105° models is given in Table V. The wide deviations in the measurements of the third and fifth maxima make them unreliable and they are not included in the average value for the N–C distance. The five term radial distribution function

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(6) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 870 (1934).

TABLE V

NITROGEN TRIMETHYL

Max.	Min.	I	s, obsd.	s, calcd. for N–C = 1.47 Å.		N–C	
				110°	105°	110°	105°
1			Not measured	3.04	3.35		
2		10	6.00	5.92	6.07	1.450 Å.	1.487 Å.
	3		7.39	7.36	7.53	1.464	1.497
3		7	(9.20)	8.88	9.06		
	4		11.78	11.60	11.21	1.448	1.400
4		5	13.51	13.63	13.78	1.481	1.498
	5		15.43	15.45	15.67	1.477	1.492
5		3	(18.34)	18.88	18.93		
6		1	21.80	21.93	22.19	1.479	1.496
					Average	1.466	1.478
					Mean deviation	0.011	0.026

Radial distribution function result: 1.46 Å. Final values: N–C = 1.47 ± 0.02 Å., angle C–N–C = 108 ± 4°.

TABLE VI

SULFUR DIMETHYL

Max.	Min.	I	s, obsd.	s, calcd. for S–C = 1.81 Å.		S–C	
				110°	100°	110°	100°
1		12	5.07	4.06	3.92	(1.450) Å.	(1.400) Å.
	2		6.36	6.02	6.25	(1.715)	(1.780)
2		20	7.71	7.85	7.85	1.844	1.844
	3		9.71	9.79	9.69	1.825	1.805
3		12	11.16	11.24	11.32	1.823	1.834
	4		12.92	12.74	12.77	1.784	1.788
4		6	14.34	14.26	14.36	1.800	1.813
	5		16.35	16.55	16.16	1.832	1.790
5		3	18.13	18.54	18.56	1.851	1.853
					Average	1.823	1.818
					Mean deviation	0.017	0.022

Radial distribution function result: 1.81 Å. Final value: S–C = 1.82 ± 0.03 Å.

using the estimated intensities given in the table is shown in Fig. 2 with its N–C maximum at 1.46 Å. This result combined with the average value from Table V leads to an N–C distance of 1.47 ± 0.02 Å.

X-Ray diffraction photographs of nitrogen trimethyl vapor were taken by Richter,[7] who considered three models having bond angles of 60, 110 and 120° and an assumed N–C distance of 1.5 Å. Of these three the second gave the best agreement with his photographs, a conclusion which is supported by the result of the present investigation.

The observed dipole moments, 0.60 *D*[8] and 0.82 *D*,[9] also require a pyramidal structure for nitrogen trimethyl.

Sulfur Dimethyl.—Sulfur dimethyl (redistilled Eastman product) gave photographs showing five good rings. Theoretical curves for two bond angles, 110 and 100°, were calculated (Fig. 4) but no significant differences appear since the interference terms which change with the bond angle are much smaller than the unchanging term associated with the sulfur–carbon distance. This distance was taken as 1.81 Å. and the C–H as 1.06 Å. The radial distribution function (Fig. 2) shows a sharp peak at 1.81 Å. The quantitative comparison of Table VI leads to a final value of 1.82 ± 0.03 Å.

The dipole moment of sulfur dimethyl is 1.40 *D*.[10] The sulfur bond angle in this compound is very probably between 100 and 110°.

Mercury Dimethyl.—Photographs of mercury dimethyl were obtained from a sample supplied by Professor D. M. Yost of this Laboratory. The maxima were not well resolved from the very heavy background of atomic scattering due to the mercury atom and the measured diameters are not very reliable. For this reason the data are not given in detail; they lead to the approximate value Hg–C = 2.20 ± 0.10 Å. A determination of the bond angle in this compound by electron diffraction experiments is not possible.

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(7) H. Richter, *Physik. Z.*, **36**, 85 (1935).

(8) O. Steiger, *Helv. Phys. Acta*, **3**, 161 (1930).

(9) P. N. Ghosh and T. P. Chatterjee, *Phys. Rev.*, **37**, 427 (1931).

(10) E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.*, 2819 (1932).

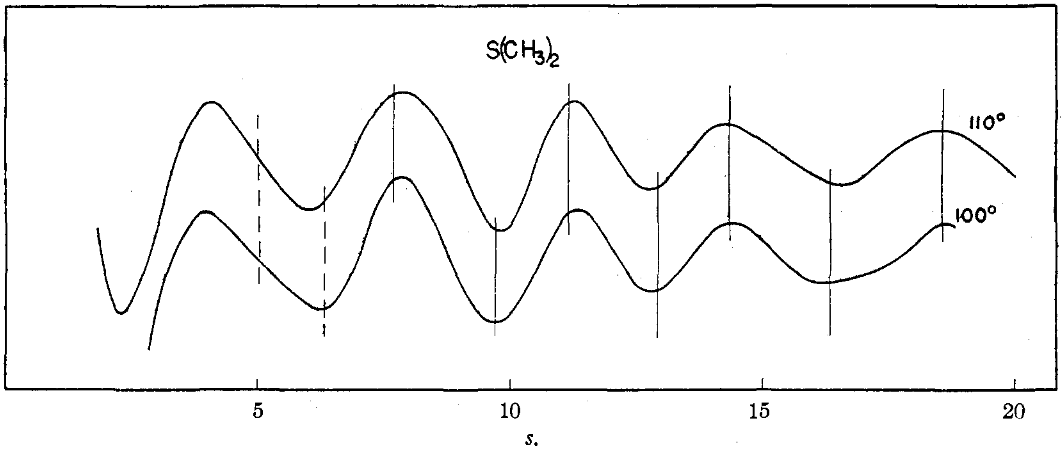

Fig. 4.—Theoretical electron diffraction curves for sulfur dimethyl.

Discussion

The data obtained from the methyl compounds are of special interest in the study of the normal covalent radii of the elements. The single bond radii proposed by Pauling and Huggins[8] for the non-metals are as follows:

C	N	O	F
0.77	0.70	0.66	0.64
Si	P	S	Cl
1.17	1.10	1.04	0.99
Ge	As	Se	Br
1.22	1.21	1.17	1.14
Sn	Sb	Te	I
1.40	1.41	1.37	1.33

These values for the carbon and halogen groups are half of the observed interatomic distances in the elements; the intermediate values were obtained by interpolation with the aid of crystal structure data. Radius sums taken from this table are intended to represent interatomic distances for single bonds when the elements have their normal valence, *i. e.*, four for the carbon group, three for the nitrogen group, two for the oxygen group and one for the halogens. Small corrections are to be applied for other valence states.

The observed bond distances in the methyl compounds may be compared with the corresponding radius sums. In Table VII this comparison is made for the elements whose methyl derivatives are reported in this paper (except lead and mercury) in addition to oxygen and chlorine, whose methyl derivatives were previously reported,[11] and for carbon, fluorine and bromine for which the details of the structure determinations will appear in forthcoming publications. The upper number in each case is the observed bond distance and the lower is the sum of the covalent radii.

TABLE VII

BOND DISTANCES AND RADIUS SUMS IN METHYL COMPOUNDS

C–C	N–C	O–C	F–C
1.55 ± 0.02	1.47 ± 0.02	1.42 ± 0.03	1.42 ± 0.02
1.54	1.47	1.43	1.41
Si–C		S–C	Cl–C
1.93 ± 0.03		1.82 ± 0.03	1.77 ± 0.02
1.94		1.81	1.76
Ge–C			Br–C
1.98 ± 0.03			1.91 ± 0.05
1.99			1.91
Sn–C			
2.18 ± 0.03			
2.17			

The agreement between the observed distances and the radius sums for all of these compounds is excellent, the differences being less than the experimental error. This shows that with respect to the factors affecting the distance the bond type in the methyl compounds is the same as in the elements where the bonds are formed between atoms of the same element. It may be pointed out that the existence of a dipole moment can have only a very small effect on the bond distance. In the methyl halides, which have appreciable moments, the distances are the averages of the carbon–carbon distance in diamond and aliphatic hydrocarbons and of the distances in the respective halogen molecules. For the other compounds, too, the bond between unlike atoms, with which there is associated an electric moment, has just the average distance of the two bonds between like

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(11) L. E. Sutton and L. O. Brockway, THIS JOURNAL, **57**, 473 (1935).

atoms, which have zero moments. The introduction of the moment has no appreciable effect on the distance.

It is now possible to discuss the data for the halogen derivatives. In Table VIII are shown the observed bond distances and the radius sums for the fluorides and chlorides in which the carbon group elements form four bonds to halogens, the nitrogen group form three, the oxygen group two and the halogens one. The table includes the compounds on which electron diffraction measurements have been made and the data are taken from a recent survey.[4] For Cl_2 and ICl the band spectral results are reported in preference to the electron diffraction results.

TABLE VIII

BOND DISTANCES AND RADIUS SUMS IN CHLORIDES AND FLUORIDES

C–Cl 1.755 ± 0.005 1.76 0.00		O–Cl 1.68 ± 0.03 1.65 +0.03	
Si–Cl 2.00 ± 0.02 2.16 −0.16	P–Cl 2.00 ± 0.02 2.09 −0.09		Cl–Cl 1.983 ± 0.005 1.98 +0.00
Ge–Cl 2.08 ± 0.03 2.21 −0.13	As–Cl 2.16 ± 0.03 2.20 −0.04		
Sn–Cl 2.30 ± 0.03 2.39 −0.09		Te–Cl 2.36 ± 0.03 2.36 0.00	I–Cl 2.315 ± 0.005 2.32 0.00
C–F 1.36 ± 0.02 1.41 −0.05		O–F 1.41 ± 0.05 1.30 +0.11	
Si–F 1.54 ± 0.02 1.81 −0.27	P–F 1.52 ± 0.04 1.74 −0.22		
	As–F 1.72 ± 0.02 1.85 −0.13		

Five of the chlorides have bond distances which within the experimental error are equal to the corresponding radius sums. Among these is the chlorine molecule whose bond distance determines the chlorine radius. The chlorides of silicon, germanium, tin, phosphorus and arsenic, on the other hand, have distances which are appreciably shorter than the radius sums. It was suggested in a previous paper[2] that two effects might contribute to this shortening. The first is related to the extra ionic character of the bonds due to the differences in the electronegativities of the atoms involved. The covalent radii quoted above were obtained from bonds between atoms of the same element having the same electronegativity; and the bonds in question between atoms with different electronegativities might well be expected to show an extra ionic character which would strengthen and shorten the bonds. The results on the methyl compounds, however, show that this explanation is not valid. Although the differences in electronegativity are more extreme in some of these compounds than in the chlorides, no deviations from additivity of the covalent radii are observed.

The alternative explanation for the shortening is that the bonds may have some double bond character. If one of the structures contributing to the normal state of the molecule has two atoms joined by a single bond and one of the atoms has an unshared pair of electrons while the other has an unoccupied orbital, then another structure in which a double electron pair bond is formed between two atoms may contribute to the normal state of the molecule. If this occurs the bond distance will be shorter than the single bond distance by an amount depending on the relative contributions of the various resonating structures. The maximum shortening will be ten per cent. since the ratio of double to single bond distance is 90%.

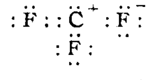
Shortening due to double bond character will not be expected when the formulation of the structure having the double bond would violate the octet rule for an atom of the first row of the periodic table. In one of these atoms the four orbitals of the L shell are filled by the four electron pairs and the higher lying levels of the M shell are not available for bond-formation. In the later rows of the periodic table, however, four electron pairs occupy the *s* and *p* orbitals with *d* orbitals of the same shell available for the formation of additional bonds.

In examining the data for the chlorine compounds we see that carbon tetrachloride could not show a double bond effect, and no shortening is observed. In chlorine monoxide the fact that no shortening occurs shows that chlorine has little or no tendency to hold five pairs. The 8% shortening observed in silicon tetrachloride indicates a considerable double bond effect. If it is the only cause of the shortening, the bonds in silicon tetrachloride have 40% double bond character according to the relation between interatomic distance and single bond–double bond resonance.[12] This requires a considerable contribution to be made by structures having two and three double bonds to silicon.

All of the shortenings observed in the chlorine compounds are compatible with the explanation on the basis of double bond character. In the methyl compounds double bonded structures are not possible because there are no unshared electrons, and no shortening is observed. Another example of shortening due to double bond character has been observed in the case of nickel carbonyl.[13]

The deviations from additivity shown in Table VIII become less in passing to the right or down through the periodic arrangement of the elements. In the second row this is inevitable since the distance in the molecule Cl_2 furnishes the standard for comparison. We have in reality measured the excess of the effect over that in Cl_2 itself. It is probable, however, that Cl_2 has very little double bond character inasmuch as the distance in carbon tetrachloride would be larger than the sum of the radii if the chlorine radius were affected by double bond character in Cl_2. The zero deviation observed for ICl also lends some significance to the apparent trend in the tendency toward double bond formation.

The bond distances of the fluorides require additional explanation. It will be noted that the C–F distance in methyl fluoride is 1.42 Å. and in carbon tetrafluoride 1.36 Å. This difference is beyond the range of experimental error. The shortening below the sum of the radii for the second compound is not due merely to ionic effects since it would also appear in some degree in the first. Professor Pauling has suggested that in addition to the single bonded structure the CF_4 molecule resonates among structures having an F^- ion bonded electrostatically to a CF_3^+ ion in which one double and two single covalent bonds are formed.



$$\begin{array}{c} :\ddot{F}: \\ :\ddot{F}::\overset{+}{C}\ :\ddot{F}:^{-} \\ :\underset{\cdot\cdot}{F}: \end{array}$$

The quantum mechanical principle of resonance among structures having equal energies would require the four bonds to be equivalent and they would show an equal shortening. The effect could not take place in methyl fluoride and thus the difference between the two compounds is accounted for. If this explanation is correct, the effect should be observed whenever two or more fluorine atoms are attached to the same carbon or even when a fluorine and one or more chlorine atoms are bonded to carbon. It is known that the halogen derivatives of methane containing two or more halogen atoms of which fluorine is one have different chemical properties from the others. This fact is undoubtedly associated with the variations in the bond distances. A report of the electron diffraction investigation of the mixed fluorine and chlorine derivatives of methane will be published soon.

The described effect should be especially important in the fluorides on account of the pronounced electronegativity of fluorine. That the explanation is not entirely satisfactory is indicated by the magnitude of the deviations observed in silicon tetrafluoride and phosphorus trifluoride. The shortenings here are 15 and 13%, respectively, although the maximum difference observed between single and double bonds is 10%. The contribution of structures involving triple bonds is probably small in view of the slight tendency for elements of the second row to form triple bonds. If the large shortening can be explained by the combined extreme ionic-double bond character described above, then the shortening in the fluoromethanes should be greater.

As in the chlorides, the shortening for fluorides becomes less toward the right and in lower rows of the periodic system. In fluorine monoxide the bond distance is larger than the sum of the radii. No explanation of this anomaly is apparent.

Because of the agreement found for methyl compounds we believe that the covalent radii given in Pauling and Huggins' table are reliable and applicable even to bonds with considerable ionic character. The radii are also useful for predicting distances in compounds in which deviations from additivity occur due to resonance of the molecule among several electronic structures. The results for the chlorine compounds indicate the circumstances under which such deviations may be expected.

We express our indebtedness to Professor Linus Pauling for valuable discussions on the interpretation of the data on internuclear distances.

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(12) L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935).

(13) L. O. Brockway and P. C. Cross, *J. Chem. Phys.*, **3**, 828 (1935).

Summary

By electron diffraction investigation of the gases the structures of certain methyl compounds have been determined. Four tetramethyls with tetrahedral symmetry have the following bond distances: Si–C = 1.93 ± 0.03 Å., Ge–C = 1.98 ± 0.03 Å., Sn–C = 2.18 ± 0.03 Å., Pb–C = 2.29 ± 0.05 Å. Nitrogen trimethyl has a bond angle of 108 ± 4° with N–C = 1.47 ± 0.02 Å. In sulfur dimethyl and mercury dimethyl the interatomic distances are S–C = 1.82 ± 0.03 Å. and Hg–C = 2.20 ± 0.10 Å., respectively. These distances agree with the sums of covalent radii given by Pauling and Huggins.

In a discussion of previous data for the chlorides it is shown that relative electronegativities (or the existence of electric moments in the bonds) are not responsible for the shortening observed in some of the chlorides. This effect is instead probably due to the contribution of structures having double electron pair bonds. Further investigation is required to explain the observed deviations in the chlorides.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF H. S. NEWCOMB COLLEGE, TULANE UNIVERSITY]

Diazotization of Weakly Basic and Insoluble Amines. The Use of Pyridine, Quinoline and Isoquinoline as Solvents for the Amines

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A series of experiments in this Laboratory on the diazotization of 4-aminobiphenyl with the use of pyridine as a solvent for the amine[2] led the authors to an investigation of the use of pyridine as a solvent for other weakly basic and insoluble amines. The success of this work led to experimentation on the use of quinoline and isoquinoline as solvents.

The use of pyridine as a solvent for the difficultly diazotizable amines has been described by Krishna and Bhatia,[3] who reported the successful diazotization of tribromoaniline, 2,6-dichloro-4-nitroaniline, dibromo-*p*-aminobenzoic acid and dibromo-*p*-aminobenzaldehyde.

The experimental work described in this paper substantiates the conclusion so often expressed that the diazotization proceeds only with the substituted ammonium salt and never with the free amine.[4,5] As groups which decrease the basicity of the amine replace the hydrogen atoms in the benzene ring, the concentration of the ammonium salt in the aqueous solution is correspondingly decreased. In order to prevent this hydrolytic action, Schoutissen[5] found that it was necessary to use a large excess of strong mineral acid or a solvent which reduces the dissociating effect of water. With the use of pyridine, quinoline and isoquinoline as solvents for the weakly basic and insoluble amines, it is possible to introduce the amine into the diazotizing mixture, namely, sulfuric acid and sodium nitrite, so that the amine is evenly distributed throughout the mixture in a very finely divided condition. The amine solution is added slowly to the cold nitrosylsulfuric acid. The solvent seems to hold the amine in solution until the sulfate is formed, which in turn reacts with the nitrous acid that is liberated by the action of the solvent on the nitrosylsulfuric acid. It is to be noted, however, that even though all other quantities and factors are the same, complete diazotization of the amine is not obtained in a reasonable length of time unless the amine is entirely dissolved in the liquid that is being used as the solvent.

The excess of mineral acid that is necessary depends upon the solubility of the amine and the nature, number and position of the groups that are present in the benzene ring. A study of the acid concentrations used in the diazotization of the substituted amines, showed that when a relatively small volume of organic solvent was used, the more dilute acid solution is satisfactory except for 4,6-dibromo-2-nitroaniline and picramide. If, however, a much larger volume of solvent is necessary to dissolve the amine, then the stronger acid solution must be

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[1] The material of this paper is from the thesis of Gertrude Van Zandt, presented in partial fulfilment of the requirements for the degree of M.S. at Tulane University, June, 1935.

[2] Carolyn Samuel, Master's Thesis, Tulane University, June, 1934.

[3] Proc. 15th Indian Sci. Cong., 152 (1928).

[4] Witt, *Ber.*, **42**, 2953 (1909).

[5] Schoutissen, THIS JOURNAL, **55**, 4531 (1933).