Molecular Structures of Dimethylgermyl Dibromide and Methylgermyl Tribromide determined by Vapour-phase Electron Diffraction

By **John E. Drake, Raymond T. Hemmings, J. Lawrence Hencher,* Francis M. Mustoe,** and **Quang Shen,*** Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada

The molecular structures of $GeBr_2Me_2$ and $GeBrMe_3$ have been determined by vapour-phase electron diffraction. The geometrical parameters based on the r_g interatomic distances are as follows: for $GeBr_2Me_2$: r(C–H) = 1.12 (assumed), r(Ge–C) = 1.91 ± 0.01, and r(Ge–Br) = 2.303 ± 0.002 Å, angle BrGeBr = 104 ± 1, CGeBr = 107 ± 3, CGeC = 124 ± 7, and GeCH = 105 ± 6°; for $GeBr_3Me$: r(C–H) = 1.12 (assumed), r(Ge–C) = 1.89 ± 0.03, and r(Ge–Br) = 2.276 ± 0.002 Å, angle BrGeBr = 107.1 ± 0.4, CGeBr = 111.6 ± 0.3, and GeCH = 109.5°. The quoted uncertainties have been estimated to include both systematic and random errors. In neither case could the analysis determine the rotational positions of the methyl groups because the scattering components due to distances involving hydrogen are too weak.

IN a previous paper the molecular structures of $GeMe_2F_2$ and $GeMeF_3$ were reported.[1] As part of a continuing investigation of the molecular structures of the halogenomethylgermanes [$GeMe_nX_{4-n}$ (X = F, Cl, Br, or I)], structures for $GeBr_2Me_2$ and $GeBr_3Me$ are presented here. It is hoped that these structural studies will help to elucidate the effects of multiple-halogen substitution and different halogen substitution on the bonding in the methylgermanes.

EXPERIMENTAL

The samples of $GeBr_2Me_2$ and $GeBr_3Me$ were prepared by the reactions of $GeMe_2Cl_2$ and $GeMeCl_3$ respectively with excess of HBr.[2] The samples were purified by vacuum fractionation. The purities of the samples were checked by vibrational and ^1H n.m.r. spectra. The spectra were in agreement with those previously published,[3-5] and showed no absorption peaks attributable to impurities.

Electron-diffraction photographs of the samples were made with the University of Windsor apparatus[6] using

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[1] J. E. Drake, R. T. Hemmings, J. L. Hencher, F. J. Mustoe, and Q. Shen, *J.C.S. Dalton*, 1976, **394**.

[2] R. T. Hemmings, Ph.D. Thesis, University of Windsor, 1973.

[3] D. F. Van de Vondel, G. P. Vander Velen, and G. Van Hooydonk, *J. Organometallic Chem.*, 1970, **23**, 431.

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4 × 5 in Kodak electron-image plates. Detailed experimental conditions are summarized in Table 1. In the same experiments, carbon disulphide patterns were recorded for the scale-factor calibration.[7] The procedures adopted in extracting the experimental molecular intensity, $sI_m(s)$, and the subsequent least-squares refinement of the structural parameters and root-mean-square amplitudes were described

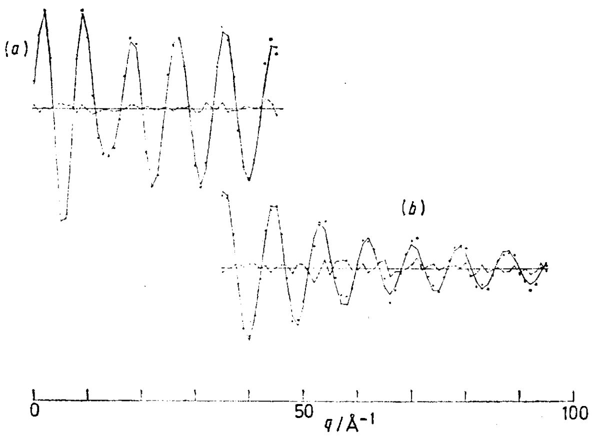

FIGURE 1 Molecular intensity curves, $sI_m(s)$, for $GeBr_2Me_2$ [$q = (10/\pi)s$]: (a), long camera intensity; (b), short camera intensity. (●), Experimental points; (——), calculated curve; (— — —), difference between experimental and calculated values

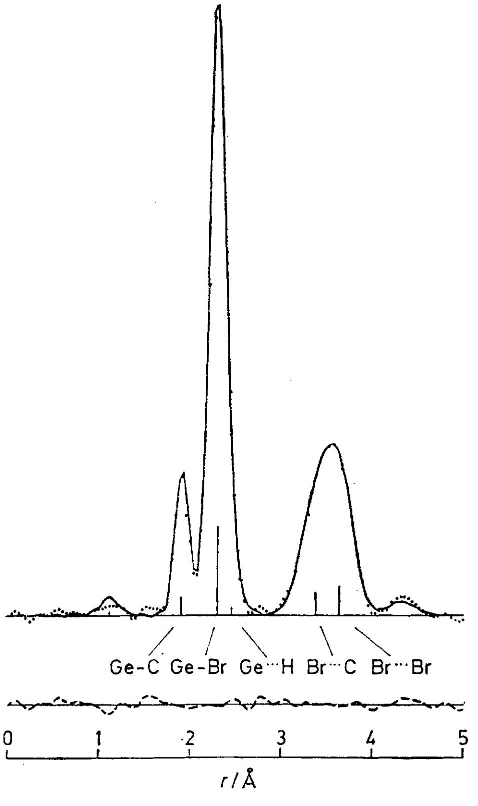

FIGURE 2 Radial distribution curves for $GeBr_2Me_2$. (●), Experimental points; (——), calculated curve; (— — —), difference between experimental and calculated values. The vertical bars indicate the distribution of important interatomic distances

TABLE 1

Experimental conditions

Compound	Camera length/ mm	Exposure time/ s	Density range/ g cm^{-3}	s Range/ Å^{-1}	Number of plates
$GeBr_2Me_2$	296.30	15—20	0.1—0.55	3—16	2
	95.21	50—60	0.2—0.47	15—33	3
$GeBr_3Me$	296.16	10—20	0.1—0.4	3—17	3
	95.45	60	0.1—0.5	15—37	3

High voltage = 58 kV, beam current ca. 1 × 10^{-7} A, ambient pressure ca. 1.5 × 10^{-5} Torr, sample pressure 9—11 Torr [1 Torr = (101 325/760) Pa], and reservoir temperature ca. 21 °C. $s = (4\pi/\lambda)s$ in $(\theta/2)$, where λ is the electron wavelength and θ is the diffraction angle.

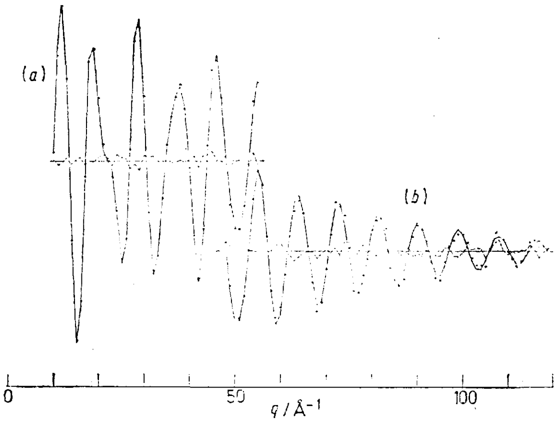

FIGURE 3 Molecular intensity curves, $sI_m(s)$, for $GeBr_3Me$. See Figure 1 for key

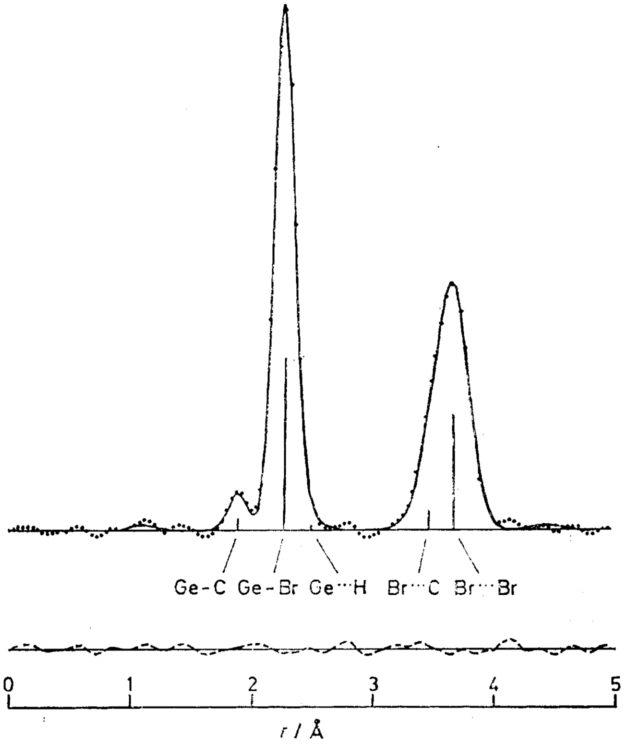

FIGURE 4 Radial distribution curve for $GeBr_3Me$. See Figure 2 for key

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[7] K. Kuchitsu, ' Molecular Vibrations and Structure Studies,' ed. S. J. Cyvin, Elsevier, Amsterdam, 1972, ch. 10.

previously.[6,8] The calculated curve employed complex scattering factors [9] and a correction for inelastic scattering.[10] A diagonal unit-weight matrix was assumed. Uncertainties were estimated as three times the least-squares values in order to encompass both systematic and random errors. The $sI_m(s)$ curves for $GeBr_2Me_2$ and $GeBr_3Me$ are presented in Figures 1 and 3 respectively. The radial-distribution curves are given in Figures 2 and 4. Tables of the reduced intensities and the background are available as Supplementary Publication No. SUP 21711 (6 pp.).*

TABLE 2

Correlation matrix for $GeBr_2Me_2$ [a]

	r(Ge–Br)	$\frac{1}{2}$(BrGeBr) 52	r(Ge–C)	ZGeC 118	l(Ge–Br)	l(Ge–C)	l(Br · · · Br)
σ [b]	0.0008	0.364	0.004	1.635	0.0007	0.005	0.0015
	1.000						
	−0.134	1.000					
	−0.125	0.008	1.000				
	0.032	−0.225	−0.185	1.000			
	0.006	0.073	0.097	0.095	1.000		
	0.031	0.033	0.022	0.021	−0.068	1.000	
	0.093	−0.401	0.001	0.498	0.013	−0.005	1.000

[a] Distances in Å and angles in °. [b] Standard deviation from least-squares refinement.

TABLE 3

Correlation matrix for $GeBr_3Me$ [a]

	r(Ge–C)	r(Ge–Br)	BrGeC	l(Ge–C)	l(Ge–Br)	l(Br · · · Br)
σ [b]	0.0110	0.0006	0.1026	0.0127	0.0005	0.0010
	1.000					
	−0.088	1.000				
	−0.156	0.310	1.000			
	0.129	0.033	−0.013	1.000		
	−0.002	0.122	0.020	−0.124	1.000	
	0.277	0.013	0.012	0.070	0.047	1.000

[a] Distances in Å and angles in °. [b] Standard deviation from least-squares refinement.

RESULTS

$GeBr_2Me_2$.—The molecule was assumed to have C_{2v} symmetry with the $C_2(z)$ axis bisecting the CGeC and BrGeBr angles. The geometry was described by the parameters r(GeC), r(GeBr), the angles $\frac{1}{2}$(BrGeBr), ZGeC [$\pi - \frac{1}{2}$(CGeC)], and GeCH, r(CH), and τ(HCGeBr) (the torsional angle relative to the staggered configuration about the GeC bond). The least-squares analysis was not sensitive to the distances involving hydrogen atoms because they contributed very little to the total scattering; thus it was necessary to fix the following parameters in the analysis: r(CH) = 1.12 Å; GeCH = 109.5°; τ(HCGeBr) = 0°; l(CH) = 0.084 Å; l(Ge · · · H) = 0.11 Å; and l(Br · · · H) = l(C · · · H) = l(H · · · H) = 0.1 Å (l denotes a root-mean-square amplitude).

Both r(GeC) and r(GeBr) were resolved in the radial distribution (Figure 2), so that the addition of any two of r(C · · · C), r(C · · Br), and r(Br · · · Br) would define the C_2GeBr_2 skeletal angles. Unfortunately the latter distances all lay beneath the peak at 3.5 Å and could not be resolved unless l(C · · · C), l(C · · · Br), and l(Br · · · Br) were determined independently. This difficulty was overcome by grouping the latter amplitudes and refining them as one parameter. In principle, this constraint solved the problem, but the weakness of the GeC scattering relative to GeBr, Br · · · Br, and C · · · Br caused all the parameters except r(GeBr) to have unusually large uncertainties. The correlation matrix for the least-squares parameters is in Table 2.

$GeBr_3Me$.—Both the $CGeBr_3$ and the methyl group were assumed to have local C_{3v} symmetry and the methyl group was assumed to be staggered with respect to $GeBr_3$. The geometric parameters were r(CH), r(GeC), and r(GeBr), and the angles CGeBr and GeCH. Again the constraint l(Br · · · Br) = l(C · · · Br) = l(C · · · C) was required in order to resolve the corresponding interatomic distances.

TABLE 4

Molecular structures of $GeBr_2Me_2$ and $GeBr_3Me$ [a]

	$GeBr_2Me_2$		$GeBr_3Me$	
		l_{ij}		l_{ij}
C–H	1.120 [b]	0.08	1.120	0.078
Ge–C	1.911(12)	0.055	1.889(32)	0.061(4)
Ge–Br	2.303(2)	0.063(2)	2.276(2)	0.061(1)
BrGeBr	104(2) [c]		107.1(4) [c]	
CGeBr	107(3) [c]		111.6(3)	
CGeC	124(7) [c]			
GeCH	109.5 [b]		109.5 [b]	
τ(BrGeCH) [d]	0		0	
C · · · C	3.37(15)	0.11		
C · · · Br	3.39(6) [c]	0.13 } (2)	3.45(2) [c]	0.12 } (3)
Br · · · Br	3.64(5) [c]	0.13 }	3.663 [c]	0.12 }
Ge · · · H	2.46(15) [c]	0.11	2.49(3) [c]	0.09
R [e]	9.3		7.7	

[a] Structure based on r_g distances. Distances and amplitudes in Å. Angles in °. Values in parentheses are estimated errors and values in braces were refined as a group. [b] Uncertainties are not quoted for fixed parameters. [c] Dependent parameter values calculated from the refined parameters. The refined angle parameters (ZGeC) and $\frac{1}{2}$(BrGeBr) are given in Table 3. [d] Methyl groups were assumed to be staggered with respect to $CGeBr_3$ and $GeBr_3$. [e] $R = 100\{\Sigma[sI_m(s)_{exp} - sI_m(s)_{calc}]^2/\Sigma[sI_m(s)_{exp}]^2\}^{\frac{1}{2}}$.

The correlation matrix for the least-squares parameters is given in Table 3.

The complete structures of $GeBr_2Me_2$ and $GeBr_3Me$, based on r_g interatomic distances, are presented in Table 4.

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

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[9] L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, 1971, **55**, 3055.

[10] C. Tavard, D. Nicolas, and M. Rouault, *J. Chim. phys.*, 1967, **64**, 540.

DISCUSSION

A comparison of the structures of $GeBrMe_3$,[11] $GeBr_2Me_2$, and $GeBr_3Me$ reveals similar trends to those observed for the corresponding fluorides.[1] The GeBr and GeC bond lengths both decrease with increased bromine substitution. The angles decrease in the order CGeC (124 ± 7, $GeBr_2Me_2$; 112.4 ± 0.1, $GeBrMe_3$), CGeBr(111.6 ± 0.3, $GeBr_3Me$; 107 ± 3, $GeBr_2Me_2$; 106.3 ± 0.1, $GeBrMe_3$), and BrGeBr (107.1 ± 0.4, $GeBr_3Me$; 104 ± 2, $GeBr_2Me_2$). The XGeX angle in $GeBr_3Me$ (107.3°) is greater than in $GeMeF_3$ (105.5°) as predicted using polarity arguments.[12] However, the corresponding angles in the dihalides are approximately equal (105°) within the uncertainty limits. The Ge–Br bonds in $GeBr_3Me$ are shorter than in $GeBr_2Me_2$ by 0.025 Å, which is very close to the difference between the GeF bonds in $GeMeF_3$ and $GeMe_2F_2$ (0.027 Å).

The atomic charges, δ, were calculated by the method previously described[1] and used to estimate the GeBr bond polarities, $|\delta_{Br} - \delta_{Ge}|$. A plot of r(GeBr) against $|\delta_{Br} - \delta_{Ge}|$ is presented in Figure 5, for the methylgermyl bromides [$GeBr_4$ (2.272 ± 0.001),[13] $GeBrH_3$ (2.2970 ± 0.0002),[14] and $GeBr_2H_2$ (2.277 ± 0.003 Å)[15]]. Although the correlation with bond polarity is clear, the relation is apparently not linear.

Recent X-ray photoelectron studies in this laboratory have indicated a strong correlation between electron binding energy and estimated charges for Ge and Cl atoms in $GeCl_4$ and the methylgermyl chlorides. Since atomic radius also depends on effective nuclear charge, it may be possible to correlate our bond lengths with the p.e. data that are currently being gathered by us.

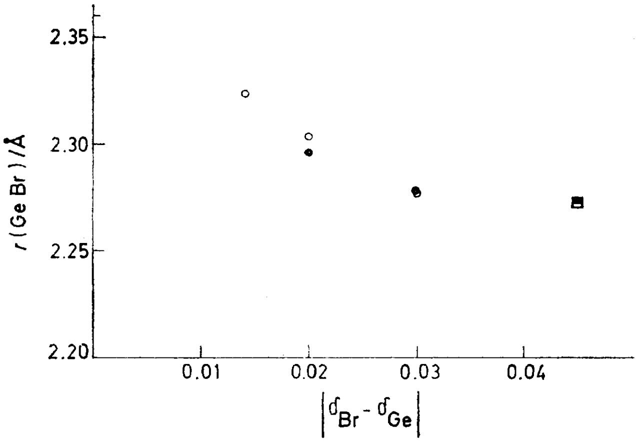

FIGURE 5 Plot of Ge–Br bond length against bond polarity for germyl bromides (●), methylgermyl bromides (○), and tetrabromogermane (□)

[5/1732 *Received, 9th September*, 1975]

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