Electron Diffraction Determination of the Molecular Structures of Difluoro(dimethyl)germane and Trifluoro(methyl)germane in the Vapour Phase

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The molecular structures of the title compounds in the gas phase have been determined by electron diffraction. The analyses were based on the r_g interatomic distances. For Me_2GeF_2 principal parameters are: r_g (Ge–C) 1.928 ± 0.003 Å, r_g (Ge–F) 1.739 ± 0.002 Å; F–Ge–F 105.4 ± 2.0°, F–Ge–C 107.3 ± 0.7°, and C–Ge–C 121.0 ± 3.5°. For $MeGeF_3$ principal parameters are: r_g (Ge–F) 1.714 ± 0.002, r_g (Ge–C) 1.904 ± 0.009 Å; F–Ge–F 105.5 ± 0.9°, and F–Ge–C 113.2 ± 0.6° (uncertainties estimated to include both systematic and random errors). Observed variations in r(Ge–F) and r(Ge–C) are correlated with estimated bond polarities.

NUMEROUS studies [1-9] have been reported for the vibrational spectra of halogeno(methyl)germanes of the type Me_nGeX_{4-n} (X = Cl, Br, or I; n = 1—3). Recently the series was completed by a vibrational study of the fluorides.[10] In the latter study, the force constants suggested that both Ge–C and Ge–F bonds became stiffer and perhaps significantly shorter along the series Me_3GeF, Me_2GeF_2, and $MeGeF_3$.

In the present paper the results of a vapour-phase electron-diffraction investigation of Me_2GeF_2 and $MeGeF_3$ are reported.

EXPERIMENTAL

The samples of Me_2GeF_2 and $MeGeF_3$ were prepared and purified as previously described.[10] No known impurities were visible in the vapour-phase i.r. spectra and the samples were considered >99% pure.

Sectored electron-diffraction patterns for both compounds

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were recorded on the Windsor camera [11] on 4 × 5 in Kodak Electron Image Plates, under the experimental conditions given in Table 1. The s scale [$s = (4\pi/\lambda)\sin(\theta/2)$, where λ is the electron wavelength, and the diffraction angle $\theta = \tan^{-1}$ (radius/camera length)] was calibrated with CS_2 patterns recorded during each experiment, using the known CS_2 geometrical parameters.[12]

Optical densities were recorded on the microphotometer previously described [11] and corrected to relative intensities by $I = D(1 + 0.1D)$. The experimental total intensity was then obtained as:

$$I_0(s) = s^4 I(s)/\phi(s) \qquad (1)$$

where $\phi(s)$ was the sector function obtained by calibration against argon scattering, and $I(s)$ was the relative intensity. The $I_0(s)$ data for long and short camera nozzle positions have been deposited at the National Lending Library as Supplementary Publication No. SUP 21623 (7 pp., 1 microfiche).*

TABLE 1

Experimental conditions

	Sample [a] temp./°C	Camera length/mm	Exposure time/s	Optical density	No. of plates	Range of [b] s values/Å^{-1}
Me_2GeF_2	−12	296.91	20	0.3—0.7	2	3—17
	−9	95.15	90	0.15—0.5	3	13—38
$MeGeF_3$	−15	295.89	10	0.22—0.5	3	3—17
	−15	95.14	60	0.25—0.40	2	13—38

Background pressure 1—2 × 10^{-5} torr; nozzle temperature 21 °C; nozzle orifice 0.5 mm; beam current 1 × 10^{-7} A; high voltage 58 kV stabilised to >1 × 10^{-4}.

[a] Temp. adjusted to provide static vapour pressure 5—10 Torr. [b] $q = (10/\pi)s = (40/\lambda)\sin(\theta/2)$.

TABLE 2

Correlation matrix for least-squares parameters of Me_2GeF_2; distances (Å), angles (°)

	r(Ge–F)	Z–Ge–F	r(Ge–C)	Z–Ge–C	r(C–H)	Ge–C–H	τ(H–C–Ge–F)	l(Ge–F)	l(Ge–C)	l(C–H)	l(F · · · F)	l(F · · · C)	l(Ge · · · H
	1.739	52.7	1.928	119.5	1.12	110.8	60.	0.047	0.054	0.059	0.085	0.101	0.096
σ [a]	0.002	1.0	0.003	2.4	0.1	1.8	Fixed	0.002	0.003	0.009	0.033	0.015	0.018
	1.0												
	0.02	1.0											
	0.48	−0.04	1.0										
	−0.06	0.61	−0.13	1.0									
	0.11	−0.01	0.18	−0.01	1.0								
	−0.08	0.52	−0.23	0.40	−0.39	1.0							
	−0.01	0.13	0.02	0.01	−0.02	0.02	1.0						
	0.04	0.17	0.00	0.12	−0.40	0.44	0.00	1.0					
	−0.11	0.02	0.02	−0.01	−0.13	0.05	0.03	0.26	1.0				
	0.01	−0.02	0.09	−0.00	0.13	−0.07	0.01	0.03	−0.03	1.0			
	0.00	0.11	0.05	−0.25	−0.02	−0.03	0.10	0.00	0.01	−0.00	1.0		
	0.02	0.22	0.08	−0.18	−0.04	−0.07	0.17	−0.00	0.04	−0.00	0.69	1.0	
	−0.07	−0.04	0.08	−0.05	0.01	−0.01	0.03	−0.01	0.10	−0.01	0.51	0.16	1.0

[a] σ is estimated uncertainty of parameter; see text.

Analysis.—The experimental molecular intensity was obtained in the form:

$$sI_m^x(s) = s^5 I_a(s)[I_0(s)/B_0(s) - 1] \qquad (2)$$

where $I_a(s)$ is the theoretical atomic scattering. The background, $B_0(s)$, was hand-drawn and then adjusted smoothly at intermediate stages in the analysis. The theoretical expression for $sI_m(s)$ was calculated with the complex scattering factors [13] and included an asymmetry correction [14] for the bonded distances only. The structures were parameterised in terms of the r_g interatomic distances by means of the Cartesian co-ordinates.[15]

The theoretical molecular intensity, $sI_m(s)$, was adjusted simultaneously to the data from both camera lengths by the method of least squares.[16] A unit-weight matrix was employed and the parameter uncertainties were estimated as:

$$\sigma_i = 3[\boldsymbol{V}'\boldsymbol{W}\boldsymbol{V}(\boldsymbol{B}^{-1})_{ii}/(n - m)]^{1/2} \qquad (3)$$

The factor of three was believed adequate to account for the effect of non-optimum weighting,[17] and systematic errors.[12,18]

(*a*) *Difluoro(dimethyl)germane*. The geometric parameters selected for Me_2GeF_2 were r(C–H), Ge–C–H, r(Ge–F) r(Ge–C), Z–Ge–F, and Z–Ge–C. The last two angles were those made by the Ge–F and Ge–C bonds with the positive z axis. An additional torsional parameter τ(H–C–Ge–F) provided for rotation of the methyl groups relative to the eclipsed configuration. Root-mean-square amplitudes were: l(Ge–F), l(Ge–C), l(C–H), l(F · · · F), l(C · · · C); l(F · · · H) = l(C · · · H) = l(H · · · H). The latter grouped amplitudes were fixed at 0.1 Å because the weakness of the scattering from interatomic distances involving hydrogen made these parameters insensitive to the least-squares

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

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TABLE 3

Structural parameters for Me_2GeF_2 [a]

		Root–mean-square amplitude
r(Ge–F)	1.739 ± 0.002 [b]	0.046 ± 0.002
r(Ge–C)	1.928 ± 0.003	0.054 ± 0.003
r(C–H)	1.12 ± 0.01	0.06 ± 0.01
F–Ge–F	105.4 ± 2.0	
F–Ge–C	107.3 ± 0.7	
C–Ge–C	121.0 ± 3.5	
Ge–C–H	111.5 ± 1.5	
H–C–H	107.3 ± 1.5	
r(F · · · F)	2.77 ± 0.03	0.09 ± 0.03
r(C · · · F)	2.956 ± 0.009	0.10 ± 0.02
r(C · · · C)	3.35 ± 0.05	0.128 [c]
r(Ge · · · H)	2.55 ± 0.02	0.10 ± 0.02
r(H · · · H)	1.80 ± 0.03	0.1 [c]
l(C · · · H) = l(F · · · H) = l(H · · · H)		
K (long) [d]	1.23 ± 0.02	
K(short) [d]	1.74 ± 0.05	
R [e]	0.07	

[a] r_g structure; distance (Å), angles (°), mean amplitudes (Å). [b] Estimated uncertainties, see text. [c] Value fixed and not refined. [d] Index of resolution; $K = \langle |I_{\rm m}(s)|/|I_{\rm m}^{x}(s)| \rangle$. [e] Crystallographic R factor (see ref. 16).

analysis. The value of l(C · · · C) was calculated by the method of Stolevik *et al.*,[19] with the previously reported force field.[8]

The refined value of τ(H–C–Ge–F) depended on the starting point (eclipsed, staggered, semi-staggered), and the solutions obtained differed in the refined values of Z–Ge–F and Z–Ge–C. Since none of these solutions was favoured, the value of τ(H–C–Ge–F) was fixed at 60° (staggered) in the final refinement. The estimated uncertainties in Z–Ge–F and Z–Ge–C were made large enough to take into account the small dependence on τ(H–C–Ge–F), by taking a factor of four times the least-squares estimates.

The refined parameters and correlation matrix are given in Table 2. The molecular structure, calculated from the analytical parameters, is given in Table 3. The dependent parameter uncertainties were calculated using the error matrix with the factor 3 included as in equation (3).

The molecular intensity and the radial distribution [19] are given in Figures 1 and 2 respectively.

(*b*) *Trifluoro(methyl)germane*. The independent geometric parameters selected for $MeGeF_3$ were r(Ge–F), r(Ge–C), r(C–H), Ge–C–H, and F–Ge–C. A staggered configuration of the methyl group about the Ge–C bond was assumed. The root-mean-square amplitudes were l(Ge–F), l(Ge–C), l(C · · · F), l(F · · · F), l(Ge · · · H), and l(F · · · H) = l(H · · · H) = 0.1 Å (see foregoing discussion). Refined parameters and correlation matrix are given in Table 4. The complete molecular structure is given in Table 5.

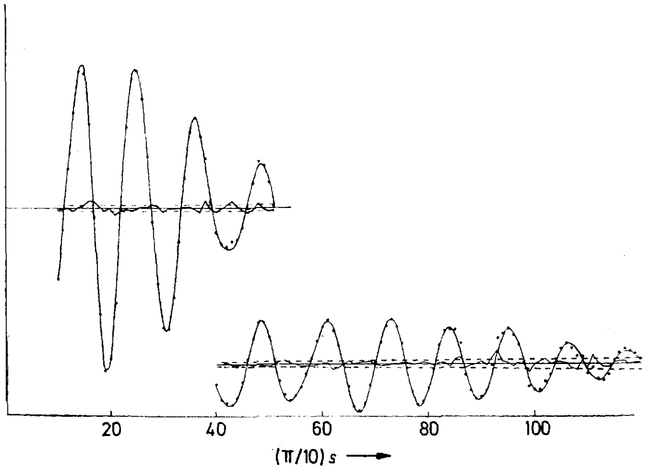

FIGURE 1 Molecular intensity of Me_2GeF_2. Experimental (dots) and theoretical (solid curve) $sI_{\rm m}(s)$ curves and difference curve calculated from refined structural parameters

TABLE 4

Correlation matrix for least-squares parameters of $MeGeF_3$

	r(Ge–C)	r(GeF)	F–Ge–C	r(C–H)	Ge–C–H	l(Ge–C)	l(C–H)	l(Ge–F)	l(C · · · F)	l(F · · · F)	l(Ge · · · H)
	1.904	1.714	113.2	1.09	116.0	0.051	0.042	0.053	0.093	0.091	0.099
σ [a]	0.009	0.002	0.9	0.03	5.0	0.009	0.027	0.002	0.018	0.018	0.090
	1.0										
	0.51	1.0									
	−0.15	−0.04	1.0								
	−0.04	0.07	0.00	1.0							
	−0.02	−0.02	0.26	−0.28	1.0						
	−0.05	−0.08	0.04	0.02	0.003	1.0					
	−0.00	−0.01	−0.00	0.09	−0.03	−0.05	1.0				
	0.14	0.13	−0.04	0.04	−0.03	0.33	0.01	1.0			
	−0.08	−0.07	0.22	0.03	−0.01	−0.01	−0.02	0.01	1.0		
	0.04	0.06	0.59	0.01	0.64	0.01	0.00	−0.01	0.05	1.0	
	−0.11	−0.09	0.78	−0.01	0.45	0.09	−0.01	−0.06	−0.01	0.75	1.0

[a] Estimated uncertainty.

The molecular intensity and radial distribution curve are given in Figures 3 and 4 respectively.

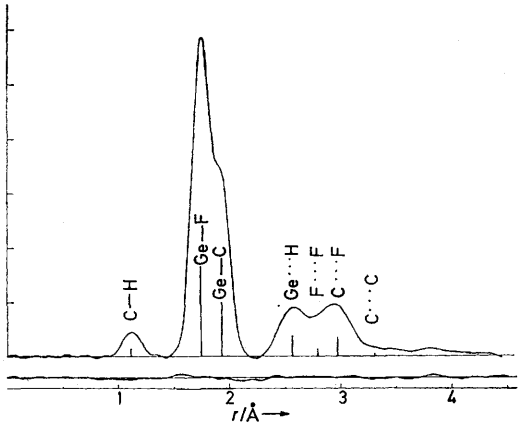

FIGURE 2 Radial distribution of Me_2GeF_2

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DISCUSSION

A comparison of the molecular structures of Me_2GeF_2 and $MeGeF_3$, summarized in Tables 3 and 5 respectively, reveals that both the Ge–F and Ge–C bonds are shorter in the tri- than in the di-fluoride and that the angles decrease in the order C–Ge–C < C–Ge–F [F(3)] < C–Ge–F [F(2)] < F–Ge–F [F(3)] ≈ F–Ge–F [F(2)]. All these trends are related to the polarities of the bonds and should be consistent with either the hybrid atomic orbital [HAO] [20] or the valence-shell electron-pair repulsion [VSEPR] [21,22] models.

TABLE 5

Structural parameters for $MeGeF_3$ [a]

		Root–mean-squares amplitude
r(Ge–F)	1.714 ± 0.002 [b]	0.053 ± 0.002
r(Ge–C)	1.904 ± 0.009	0.051 ± 0.009
r(C–H)	1.09 ± 0.03	0.04 ± 0.03
F–Ge–C	113.2 ± 0.6	
F–Ge–F	105.5 ± 0.9	
Ge–C–H	116.0 ± 5.4	
H–C–H	102.3 ± 6.5	
r(C · · · F)	3.02 ± 0.02	0.09 ± 0.02
r (F · · · F)	2.73 ± 0.02	0.09 ± 0.02
r(Ge · · · H)	2.58 ± 0.06	0.10 ± 0.09
r(H · · · H)	1.7 ± 0.1	0.10 [c]
l(F · · · H) = l(C · · · H) = l(H · · · H) [c]		
K (long) [d]	1.02 ± 0.1	
K (short) [d]	0.86 ± 0.2	
R [d]	0.07	

[a] r_g structure; distances and amplitudes (Å), angles (°). [b] Estimated uncertainties, see text. [c] Value fixed and not refined. [d] See Table 3 footnotes.

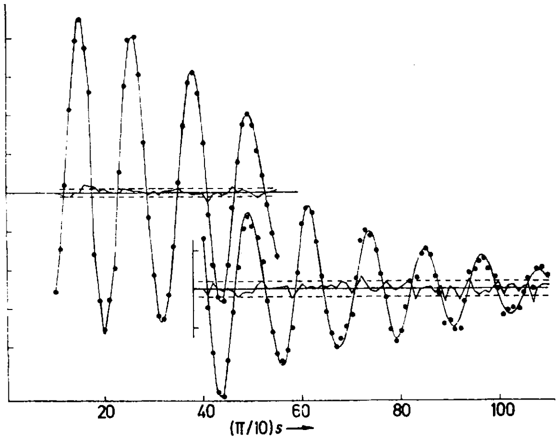

FIGURE 3 Molecular intensity of $MeGeF_3$. Experimental (dots), theoretical (solid curve), and difference curves calculated from refined structural parameters

In order to examine more fully the effects of bond polarity on the bonds and angles in Me_2GeF_2 and $MeGeF_3$, the formal charges on the atoms were calculated by Huheey's method.[23] In this approach, the charge is distributed among the atoms so that the electronegativities are equal in the valance state. The assumed valence states were p for fluorine, sp^3 for Ge, and sp^3 for Me, which was treated as a group. The absolute differences in charge, $|\delta_F - \delta_{Ge}|$ and $|\delta_{Me} - \delta_{Ge}|$, were deemed to reflect the bond polarities of the Ge–F and Ge–C bonds.

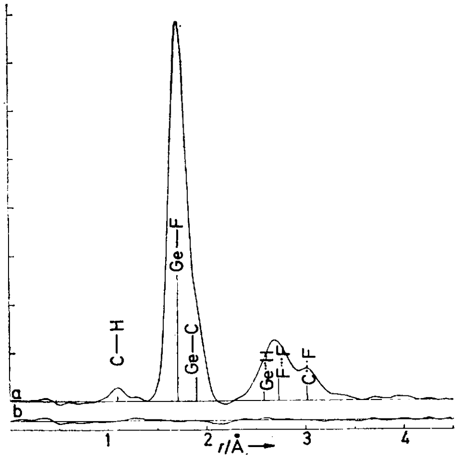

FIGURE 4 Radial distribution of $MeGeF_3$

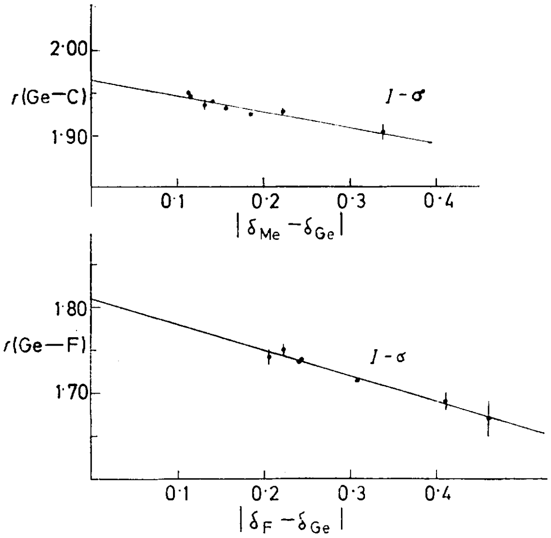

FIGURE 5 Correlation of bond length and bond polarity for Ge–C (upper) and Ge–F (lower) bonds. r(Ge–C) 1.966—0.187-$|\delta_{Me}-\delta_{Ge}|$ and r(Ge–F) 1.810—0.300 $|\delta_F-\delta_{Ge}|$

The calculated formal charges for Me_2GeF_2, $MeGeF_3$, and several related molecules [24-32] are presented in Table 6.

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The correlation between bond polarity and bond length is evident from Table 6, and is shown in Figure 5 as r(Ge–C) *vs.* $|\delta_{\mathrm{Me}} - \delta_{\mathrm{Ge}}|$ and r(Ge–F) *vs.* $|\delta_{\mathrm{F}} - \delta_{\mathrm{Ge}}|$. The relationship appears to be linear, within the uncertainties quoted for the bond lengths; however, the slope and intercept should not be interpreted quantitatively considering the crudeness of the bond polarity estimate. We have found similar correlations for the Si–F and C–F bonds.

TABLE 6

Bond lengths and polarities

	δ_{Ge}	$\delta_{\mathrm{CH_3}}$	δ_{F}	$\lvert\delta_{\mathrm{CH_3}} - \delta_{\mathrm{Ge}}\rvert$	r(Ge–C)	$\lvert\delta_{\mathrm{F}} - \delta_{\mathrm{Ge}}\rvert$	r(Ge–F)
GeF_4 [a]	0.368		−0.092			0.460	1.67(2)
$MeGeF_3$ [b]	0.117	0.455	−0.191	0.338	1.904(9)	0.308	1.714(2)
Me_2GeF_2 [b]	0.008	0.230	−0.234	0.222	1.928(3)	0.243	1.739(2)
Me_3GeF [c]	−0.053	0.103	−0.258	0.156	1.932(3)	0.205	1.742(9)
MeH_2GeF [d]	−0.025	0.160	−0.247	0.185	1.925(2)	0.222	1.751(5)
$GeClF_3$ [e]	0.29		−0.12			0.410	1.69(1)
H_3GeF [f]	0.01		−0.23			0.240	1.74(1)
Me_3GeBr [g]	−0.076	0.055		0.131	1.936(6)		
Me_3GeCl [h]	−0.067	0.074		0.141	1.940(1)		
Me_4Ge [c]	−0.092	0.023		0.115	1.946(2)		
Me_3GeH [i]	−0.092	0.024		0.116	1.947(6)		
Me_2GeH_2 [j]	−0.090	0.023		0.113	1.950(3)		
$MeGeH_3$ [k]	−0.090	0.025		0.115	1.9453(5)		

[a] Ref. 24. [b] Present work. [c] Our preliminary results. [d] Ref. 25. [e] Ref. 26. [f] Ref. 27. [g] Ref. 28. [h] Ref. 29. [i] Ref. 30. [j] Ref. 31. [k] Ref. 32.

VSEPR Model.—In the absence of bond polarity, the germanium atom would be neutral, each of its orbitals would contain one electron, and the configuration would be tetrahedral. However, in $MeGeF_3$ the charges 0.455 on Me and −0.191 on F imply that the corresponding Ge orbitals contain 1.455 and 0.809 electrons, respectively. In Me_2GeF_2 the corresponding orbitals would contain 1.23 (Me) and 0.77 (F) electrons. The C–Ge–C angle is the largest because the electron density is concentrated in the germanium orbitals to carbon. The F–Ge–F angles are smallest because in both Ge–F bonds there is an electron-density deficit around germanium. Since this electron density in Ge–F is almost the same in both Me_2GeF_2 and $MeGeF_3$, the large difference in C–Ge–F presumably results from the difference in the electron densities in the Ge–C bonds.

Hybrid Atomic Orbital Model.—When an electron-donating ligand such as a methyl group, Me, is attached to germanium, the amount of *s* character in the HAO is increased in order to accommodate the excess charge. The cumulative effect of increasing the number of Me ligands is to leave less *s* character in the other bonds. In Me_2GeF_2, the Ge–F bonds have less HAO *s* character than those in $MeGeF_3$ and are consequently longer. The excess *s* character in the Ge–C bonds is smaller in Me_2GeF_2 than in $MeGeF_3$ because it is divided between two Me ligands. Thus the Ge–C bond length is longer in the di- than in the tri-fluoride.

The C–Ge–C angle is largest because both Ge–C bonds have excess of *s* character. The C–Ge–F angle in $MeGeF_3$ is larger than in Me_2GeF_2 because the germanium orbital contributing to the Ge–C bond has the greater *s* character. The amount of *s* character in the bonds to fluorine is least, and the F–Ge–F angles are smallest in both molecules.

Both models qualitatively predict the structural trends correctly. The parallel between the arguments based on *s* character and excess of electron density is to be expected because of the relationship between *s* character and charge capacity. However, an apparent contradiction exists between the descriptions of the bond lengths in that the bond-length–bond-polarity correlation indicates variations in the bond length even though the valence state of Ge was fixed at sp^3 in all calculations. Even when Ge was given the extreme valence state sp^2p, the GeF relationship (assuming sp^2 to fluorine) was still linear. The HAO model has been criticised previously because of its neglect of electronegativity.[33] The present results tend to indicate that bond polarity is a greater factor than rehybridization in determining bond length.

[5/1033 *Received*, 29*th May*, 1975]

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