ELECTRON DIFFRACTION STUDY OF THE MOLECULAR STRUCTURE OF GERMANIUM DIBROMIDE

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ABSTRACT

The molecular structure of ground-state monomeric germanium dibromide ($r_g 2.337 \pm 0.013$ Å, $\angle 101.2 \pm 0.9^{\circ}$) has been determined by electron diffraction. The GeBr₂ is produced by a reaction between Ge metal and GeBr₄ vapour. Experimental data may indicate the presence of another state.

INTRODUCTION

We have recently reported the molecular structure of germanium dichloride from a combined electron diffraction/mass spectrometric investigation [1]. As a continuation of our research on the dihalides of Group IV elements [1, 2], we present here a structure determination of the unstable monomeric germanium dibromide.

EXPERIMENTAL

Parallel quadrupole mass spectrometric and electron diffraction experiments (cf. ref. 1) were performed on the product of the reaction

$Ge(solid) + GeBr_4(gas) \rightarrow 2GeBr_2(gas)$

The dibromide species was found to be predominant and in sufficient concentration for an electron scattering experiment at a temperature of the stainless steel reactor nozzle of about 620°C. Other experimental conditions and the data reduction procedure were similar to those employed in the germanium dichloride investigation [1]. A complete list of the experimental intensities is available from B.L.L.D. as Supplementary Publication No. SUP 26217 (2 pages). The molecular intensities and radial distribution curves are shown in Figs. 1 and 2.

ANALYSIS

Interpretation of the first two maxima in the radial distribution curve (Fig. 2) is straightforward for the $GeBr_2$ molecule, and the reduced parameters are plausible considering the stereochemical variations in the dihalides of Group IV elements (see ref. 1).

Model (i)

A least-squares refinement of the molecular parameters based on the molecular intensities for a model (i) consisting of ground-state monomeric GeBr₂ molecules only, yielded the data of Table 1, column (i). As can be seen in Fig. 2, however, considerable discrepancies in the radial distributions, most notably the unaccountable peak at 4.5 Å, indicate that model (i) is inadequate to represent satisfactorily the experimental data. The molecular intensities also show considerable discrepancies in the small-angle region. The good agreement with the rest of the data is partly due to the relatively large asymmetry parameter (κ) obtained for the Ge—Br bond. Another comment concerning the mean amplitudes of vibration is given later.

In order to eliminate the discrepancies two further models were examined.

Model (ii)

In this model the presence of dimeric species, $Br_t - Ge < Br_b - Ge - Br_t$, was assumed and satisfactory agreement was achieved, see Figs. 1 and 2. The

length of the terminal bond of the dimer was assumed to be the same as



Fig. 1. Molecular intensities, E = experimental, T = theoretical, calculated for model (ii). The difference curves (Δ) refer to models (i), (ii) and (iii) from top to bottom, respectively.



Fig. 2. Radial distribution curves, see Fig. 1 for notation. The distances and amplitudes referring to the three maxima on the experimental curve are also given.

that of the bond in the monomer (cf. refs. 3, 4). The following four additional geometrical parameters then described the dimer geometry: the bridge Ge—Br bond length, the intraring angle Br—Ge—Br, the ring puckering angle (BrGeBr/BrGeBr) and the angle between the terminal bond and the adjacent BrGeBr plane of the ring. The latter was negative for an equatorial orientation. The results for the monomer are given in Table 1, column (ii). The four additional parameters for the dimer refined to 2.45(1) Å, $91(3)^{\circ}$, $68(12)^{\circ}$ and $-7(12)^{\circ}$ respectively. Several of the non-bond amplitudes of vibration refined to very large values with large standard deviations, e.g. $l(Br_b \cdots Br_t) 0.22(3)$, $l(Ge \cdots Br_t) 0.5(2)$, $l(Br_t \cdots Br_t) 0.3(2)$ Å. A further model involving a dimer with a direct Ge—Ge linkage led to similar observations with even larger l values.

Model (iii)

This model incorporates the presence of an excited state of the GeBr₂ molecules, in addition to the ground state. Satisfactory agreement was again achieved (cf. Figs. 1 and 2). The parameters for the ground-state molecule are given in Table 1, column (iii). The two sets of values differ in the assumption of the asymmetry parameters (κ) for the Ge—Br bond. The refinement in which κ was set at about $al^4/6$ (a = 2 Å⁻¹) was considered to be the more acceptable. In this case the parameters for the excited state refined to the following values: r(Ge-Br) 2.370(10) Å, l(Ge-Br) 0.136(9) Å, $\angle Br-Ge-Br 141.2(1.9)^\circ$, $l(Br\cdots Br) 0.166(16)$ Å.

The least-squares refinements based on the electron diffraction data were complemented by spectroscopic calculations of the mean vibrational ampli-

TABLE 1

Parameters	Model (i) (one state only)	Model (ii) (monomer + dimer)	Model (iii) (ground + excited states)	
$r_{a}(Ge-Br)(A)$	2.341(1)	2.324(2)	2.322(3)	2.334(2)
l(Ge-Br)(A)	0.093(1)	0.085(1)	0.084 ^b	$0.084(1)^{c}$
κ (Ge-Br) (Å ³)	3.6(8) × 10 ⁻⁵	0ª	0 ^a	1.7×10^{-5} d
$r_{a}(\text{Br}\cdots\text{Br})$ (Å)	3.608(9)	3.614(11)	3.609(6)	3.608(6)
$l(Br \cdots Br)(A)$	0.220(7)	0.190(8)	0.186(5)	0.185(5)
LBr-Ge-Br (°)	100.8(4)	102.1	102.0(3)	101.2(2)
Main component (%)	100d	91(1)	77(2)	77(2)
R factor (%)	8.87	5.72	5.69	5.65

Molecular parameters with estimated standard deviations in parentheses for ground-state germanium dibromide from various refinements

^aAssumed. When allowed to vary it refined to a nearly zero negative value.

^b Assumed at the calculated value from those spectroscopic calculations in which $l(Br \cdots Br)$ was identical with the experimental value; in this refinement l(Ge-Br) for the second species has been allowed to vary.

^cFrom repeated refinement in which both l(Ge-Br) values have been allowed to vary with almost zero shift.

^d Assumed.

tudes for the GeBr₂ molecule utilizing the frequencies and force constants of a far-IR investigation of matrix isolated species by Isabel et al. [5]. The superiority of models (ii) and (iii) over model (i) is also indicated by the better consistency of their l values with the calculated data, as shown in Fig. 3. The l value pair obtained for model (i) not only deviates from the line representing the calculations but corresponds to a higher temperature



Fig. 3. Bond versus non-bond mean amplitudes of vibration for the ground-state monomeric germanium dibromide molecule. Points denote values calculated from spectroscopic data, crosses denote those obtained from the structure analyses based on models (i), (ii), and (iii), respectively. The experimental nozzle temperature was 893 K.

than that of experiment. Thus the l values of model (i) may indicate that a broader peak is used to approximate a superposition of two maxima from two slightly different internuclear distances.

DISCUSSION

The molecular geometry and mean vibrational amplitudes of groundstate GeBr₂ have been reliably determined. Note that the longer Ge—Br distance determined for model (i) together with the relatively large κ value compensated for the lack of a contribution from a second bond. On the other hand, ignoring the asymmetry parameter may introduce serious error in the bond length. It is to be emphasized that the parameters determined for the monomer were invariant to the choice of the second component in the mixture.

The results for the ground-state geometry of GeBr_2 are given in Table 2. These data are consistent with the geometrical variations observed in the carbene-analogue molecules AX_2 (A = C, Si, Ge, Sn, Pb; X = F, Cl, Br) investigated to date. The relevant data are collected in Table 3. Parameters for hitherto unstudied compounds are also estimated. The stereochemical aspects of the geometrical variations have been discussed previously [1].

As regards the remainder of the results obtained for model (ii), the plausibility of the dimeric structures is questionable at best. For example, the extremely puckered ring brings the two germanium atoms much closer

TABLE 2

	Ge-Br	Br···Br	Br-Ge-Br
Ground state			
$r_g(A)$	2.337 ± 0.013	3.617 ± 0.011	
l(A)	0.084 ± 0.002	0.185 ± 0.008	
κ(Å ³)	1.7×10^{-5} b	0 _р	
∠(°)			101.2 ± 0.9
Supposed excit	ted state		
$r_{g}(A)$	2.378 ± 0.045	4.477 ± 0.026	
l(A)	0.136 ± 0.013	0.166 ± 0.023	
κ(Å ³)	4.4×10^{-5} b	0 ^ь	
۷(°)			141 ± 6

Molecular parameters with estimated total errors^a for germanium dibromide, determined from electron diffraction (620°C)

^aHere $r_g \approx r_a + l^2/r_a$ and the error limits were estimated by the formula $[q\sigma^2 + (\beta p)^2 + \gamma^2]^{1/2}$ where q = 2 takes into account the effect of neglecting correlation between measurements, σ is the standard deviation in the least-squares refinement, $\beta = 0.002$ corresponds to the estimated 0.2% experimental scale error, p is the parameter and γ is the difference between results using different assumptions for κ (Ge–Br), viz. $\kappa = 0$ and $\kappa = al^4/6$, where a = 2 Å⁻¹. For l values $\beta = 0.02$ was used. ^b Assumed.

TABLE 3

Α		X = F	X = Cl	X = Br
c	r(Å) ∠(°) Ref.	1.304 104.8 6	1.758 108	1.907 109
Si	r(A) ∠(°) Ref.	1.590 100.8 7	2.044 104	219.4 105
Ge	r(Å) ८(°) Ref.	1.732 97.2 8	2.186 100.3 1	2.337 101.2 Present work
Sn	r(Å) ∠(°) Ref.	1.893 96	2.346 99 9	2.497 100.5
РЬ	r(Å) ∠(°) Ref.	1.989 95	2.444 98.3 2	2.594 100

Bond lengths and angles in carbene-analogue AX_2 molecules from experimental determinations and as estimated by analogy (in italics)

(2.86 Å) than twice the (1,3) non-bond radius of germanium (1.58 Å [10]). Noteworthy also are the very large l values for some of the non-bond distances. These may indicate the lack of contribution from corresponding atomic pairs. Although not conclusive evidence, the mass spectra showed no indication of the dimers.

Several theoretical studies have dealt with the singlet/triplet separation of carbene-analogue molecules and their geometries [11-15]. Primarily, it is the 101° bond angle of GeBr₂ that can be taken as geometrical evidence for a singlet ground state (${}^{1}A_{1}$). A possibility for interpreting the additional experimental evidence for another species is the consideration of an excited state. According to the calculations for analogous molecules cited above, the bond angle is expected to increase considerably in the ${}^{3}B_{1}$ and ${}^{1}B_{1}$ excited states. The bonds generally shorten in going from the singlet to the triplet state although this tendency appears to be ambiguous. The lowest-lying excited state is a triplet for germilene and its analogues, and the next lowest-lying excited state has been shown to be a singlet [13]. It is interesting to observe in the calculations an increase in both the bond angles and the bond lengths of the latter relative to the triplet state [13].

As regards the electron diffraction results, even if the presence of an excited state is assumed, the geometrical parameters tentatively determined for it (Table 2) do not readily indicate which state (singlet or triplet) they should be assigned to. The data could, furthermore, correspond to a mixture

of two excited states in addition to the ground state. Provided that the excitation is thermally induced, the 77/23 ratio determined at the reactor nozzle temperature corresponds to singlet/triplet $({}^{1}A_{1}/{}^{3}B_{1})$ and singlet/singlet $({}^{1}A_{1}/{}^{1}B_{1})$ separations of 4 and 2 kcal mol⁻¹ respectively. These energy differences are much smaller than those calculated for other germilene analogues [13, 14]. An alternative explanation may be that the excited state is formed during the reaction. Then, of course, no energy differences may be estimated from the present data.

The mean amplitudes of vibration determined for the supposedly excited state seem reasonable. The larger l(Ge-Br) value (i.e. larger than that for the ground state) is consistent with a looser, more flexible bond. On the other hand, the smaller $l(Br\cdots Br)$ value accords with the considerably larger Br-Ge-Br bond angle at which the same displacements change the interatomic distance less than they would at smaller angles.

The electron diffraction data give only an indication of the presence of other species in addition to the unambiguously determined ground-state $GeBr_2$ molecule. To identify reliably these species further experimental and/or theoretical evidence is required. It is also true, however, that when/if these species are identified, the present results will provide useful information on their molecular structure.

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