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1,1,2,2-TETRABROMODISILANE: GAS-PHASE MOLECULAR STRUCTURE AND CONFORMATIONAL COMPOSITION AS DETERMINED BY ELECTRON DIFFRACTION

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(Received 17 April 1986)

ABSTRACT

The molecular structure of 1,1,2,2-tetrabromodisilane has been investigated using gas-phase electron diffraction data obtained at 110°C. At this temperature the molecules exist as a mixture of about equal parts ($X = 0.5 \pm 0.2$) of the two conformers with the H—Si—Si—H torsion angle equal to 180° (*anti*) or 60° (*gauche*). Assuming that the two conformers differ in their geometries only in the torsion angle ϕ , some of the important distance (r_a) and angle (\angle_a) parameters are: $r(\text{Si—Si}) = 2.349(19)$ Å, $r(\text{Si—Br}) = 2.205(5)$ Å, $r(\text{Si—H}) = 1.485$ Å (assumed), $\angle \text{Br—Si—Br} = 110.1(1.6)^\circ$, $\angle \text{Si—Si—Br} = 107.1(1.2)^\circ$, $\angle \text{Si—Si—H} = 108.6^\circ$ (assumed). The error limits are 2σ . The observed conformational composition ($X_{\text{anti}} = 0.5(0.2)$) corresponds to an energy difference between the conformers of $\Delta E = E(\text{gauche}) - E(\text{anti}) = 0.5 \pm 0.6$ kcal mol⁻¹, assuming $\Delta S = R \ln 2$.

INTRODUCTION

Gas phase 1,1,2,2-tetrabromodisilane, Br₂HSi—SiHBr₂, (TBDS), may exist as *anti* (A) or *gauche* (G) conformers or as a mixture of these forms as described in Fig. 1. The *anti* form has two long and two short conformationally dependent Br...Br distances, while the *gauche* has one long and three short Br...Br distances. Gas phase electron diffraction should therefore be able to determine the conformational composition of TBDS. No experimental information about the structure or conformation of TBDS has been published, but molecular-mechanics calculations have given results for structure, conformational energies, rotational barrier heights and torsional force constants [1]. This investigation of TBDS is part of a study of the structure and conformation of molecules with X...X, X...H and H...H interactions, where X is halogen. Molecular-mechanics calculations for halogenated ethanes [2, 3], disilanes [1] and methyl silanes [4] have been published. For TBDS

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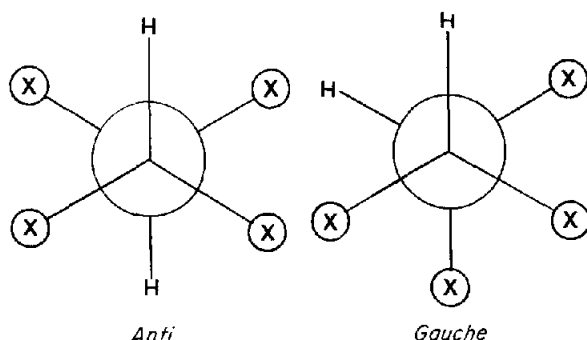


Fig. 1. Newman projections of conformations in $\text{Br}_2\text{HSi-SiHBr}_2$. The torsion angle ϕ is the dihedral angle H-Si-Si-H . The values of ϕ are 180° for *anti* and 60° for *gauche*.

a value of $\Delta E = E(\text{anti}) - E(\text{gauche}) = 0.6 \text{ kcal mol}^{-1}$ has been obtained. Thus, both conformers are expected to be present in the gas phase at 110°C in quantities detectable by electron diffraction.

EXPERIMENTAL AND DATA REDUCTION

The sample of TBDS was prepared by first dissolving 10 g $\text{Ph}_2\text{HSi-SiHPh}_2$ in 100 ml dry benzene. A small amount of AlBr_3 was added and a moderate stream of dry HBr was passed through the solution. The reaction mixture immediately warmed up, and the process was continued until the solution had cooled to room temperature. $(\text{HBr}_2\text{Si})_2$ was separated by distillation (b.p. $63^\circ\text{C}/5 \text{ Torr}$). The yield was 7 g (68%).

Diffraction photographs were recorded on Kodak Electron Image plates in the Oslo electron diffraction apparatus [5]. Voltage/distance calibrations were based on recordings with benzene as a standard [6] using the same conditions as those used for the sample. Optical densities were measured by a Joyce-Loebl MK 111 C microdensitometer. Six photographic plates from the long camera (48.489 cm) and five from the short camera (20.489 cm) distances were selected for analysis. The data were reduced in the usual way [7–9], and a calculated background [10] was subtracted from the data for each plate to yield experimental molecular intensity data in the form $sI_m(s)$. Data from the long and short camera distances were obtained over the ranges $2.00 \leq s \leq 18.00$ and $7.00 \leq s \leq 32.00 \text{ \AA}^{-1}$, respectively, at intervals $\Delta s = 0.25 \text{ \AA}^{-1}$. Plots of the average experimental intensity curves from the two camera distances are shown in Fig. 2; the individual curves and backgrounds are available as supplementary materials [11]. The scattering amplitudes and phase shifts [9] were calculated analytically by a program written by Yates [12] using Hartree–Fock–Slater potentials [13] for Si and Br, and a molecular bonded potential for H [14].

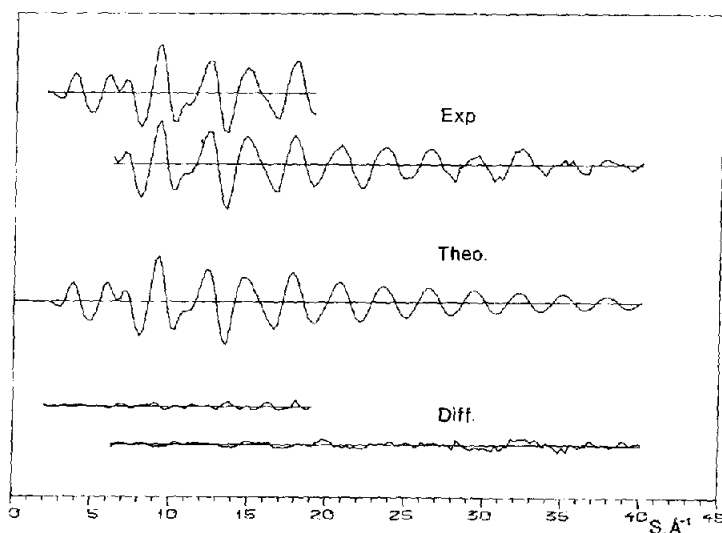


Fig. 2. 1,1,2,2-Tetrabromodisilane: experimental (Exp.) and theoretical (Theo.) intensity curves and Diff. = Exp. — Theo.

CALCULATIONS OF VIBRATIONAL QUANTITIES

A normal-coordinate analysis [15] was carried out and vibrational amplitudes (I), perpendicular amplitude corrections (K) and centrifugal distortion constants (δr) [16] were calculated using the force field from ref. 1. Three different values for the torsional force constant were tried. From the MM-calculations [1] the values 0.100 and 0.093 mdyn Å rad⁻² were obtained for the *gauche* and *anti* conformers, respectively. The torsional frequencies calculated from the different force constants are given in Table 1. In Table 2 the vibrational parameters calculated from the force field in ref. 1 with $F_\phi = 0.15$ mdyn Å rad⁻² for both conformers are shown. Also shown in Table 2 are the interatomic distances for the final model.

TABLE 1

Torsional frequencies (cm⁻¹) and torsional force constant F_ϕ (mdyn Å rad⁻²) for Br₂HSi—SiHBr₂

F_ϕ	ω (<i>anti</i>)	ω (<i>gauche</i>)
0.05	17	17
0.10 ^a	24	23 ^b
0.15	28	28

^aObtained by molecular-mechanics calculations [1]. ^bUsing F_ϕ (*gauche*) = 0.093 gave 22 cm⁻¹.

TABLE 2

BrHSi—SiHBr₂: r.m.s. vibrational amplitudes (l), perpendicular vibrational correction terms (K), centrifugal distortion parameters (δr) and internuclear distances (r_a) in ångströms calculated from the normal-coordinate analysis; K^* and l^* are framework values

X = Br	r_a	$l \times 10^4$	$l^* \times 10^4$	$K \times 10^4$	$K^* \times 10^4$	$\delta r \times 10^4$
Common for both conformers						
Si—Si	2.349	579	579	49	46	9
Si—X	2.205	548	548	191	93	6
Si—H	1.485	878	878	255	207	0
X1...X1	3.603	1333	1333	241	68	13
X1...H1	3.071	1431	1424	283	154	-8
X1...Si2	3.658	1461	1459	109	45	33
H1...Si2	3.143	1522	1522	148	113	-6
<i>anti</i> -conformer						
X1...X2	5.539	1440	1440	20	20	46
X1...X2	4.216	3051	2355	137	36	55
X1...H2	3.901	2693	2454	170	85	32
H1...H2	4.302	1753	1753	152	152	-5
<i>gauche</i> -conformer						
X1...X2	4.193	3010	2329	96	34	122
X1...X2	5.537	1452	1451	44	19	38
X1...H2	3.918	2702	2519	216	88	-10
X1...X2	4.160	3072	2543	108	40	108
X1...H2	4.908	1638	1625	89	88	32
H1...H2	3.558	2460	2317	24	15	-11

ANALYSIS

An experimental radial distribution (RD) curve (Fig. 3) was calculated in the usual way [7] by Fourier transformation of the function $sI_m(s)Z_{\text{Si}}Z_{\text{Br}}A_{\text{Si}}^{-1}A_{\text{Br}}^{-1}\exp(-Bs^2)$ with $B = 0.002 \text{ \AA}^2$. Theoretical RD-curves were calculated for the *gauche* and *anti* conformers and for a model with a mixture of the two forms. The conformationally important parts of these curves are shown in Fig. 4 together with the experimental RD-curve. From Fig. 4 it was obvious that TBDS had to be a mixture of conformers.

Refinements of the structure were carried out by the least-squares method [17] based on intensity curves by adjusting one theoretical curve to the two average experimental curves (one each from the long and short camera distances) using a unit weight matrix. Assuming that the two forms of TBDS have the same geometry apart from the torsion angle, the structure of TBDS can be defined by 8 geometrical parameters, three bond distances ($r(\text{Si—Si})$, $r(\text{Si—Br})$ and $r(\text{Si—H})$), three valence angles ($\angle\text{Si—Si—Br}$, $\angle\text{Br—Si—Br}$ and $\angle\text{Si—Si—H}$) and ϕ_A and ϕ_G , the H—Si—Si—H torsion angles for the two conformers. Most of the vibrational amplitudes were kept constant at the calculated values; only $l(\text{Si—Si})/l(\text{Si—Br})$ and $l(\text{Si}\cdots\text{Br})/l(\text{Br}_1\cdots\text{Br}_1)$ were

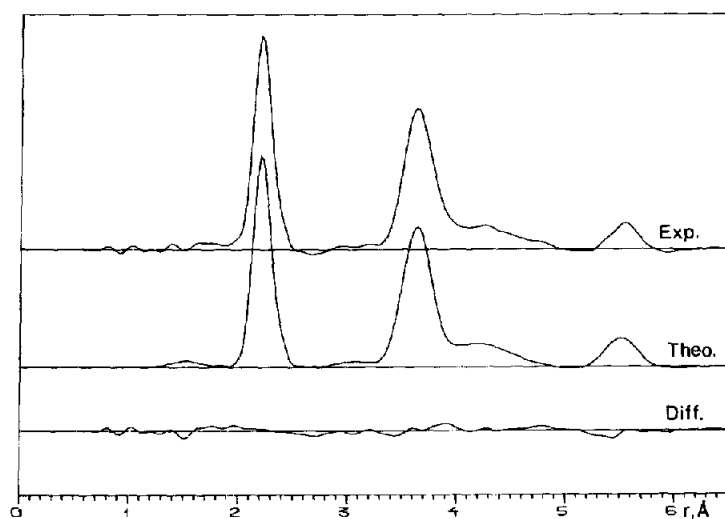


Fig. 3. 1,1,2,2-Tetrabromodisilane: experimental (Exp.) and theoretical (Theo.) radial distribution curves, and Diff. = Exp. — Theo. The artificial damping constant was equal to 0.002 \AA^2 .

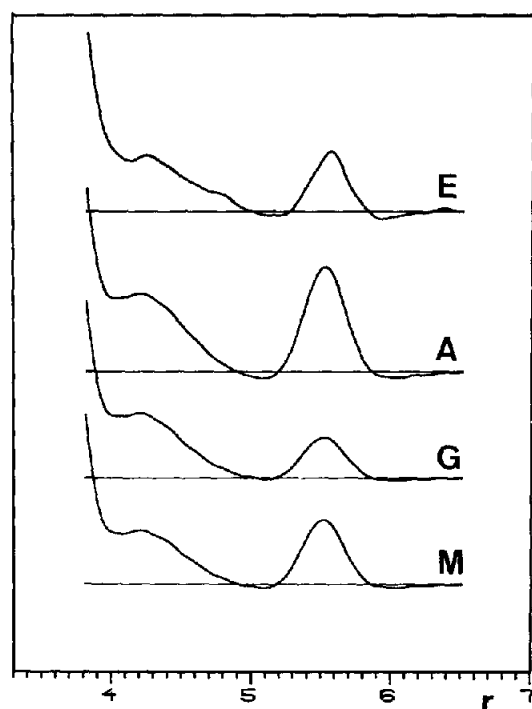


Fig. 4. 1,1,2,2-Tetrabromodisilane: radial distribution curves with artificial damping constant equal to 0.002 \AA^2 . The curves are: experimental (E), theoretical for *anti* (A), theoretical for *gauche* (G) and theoretical for a mixture of 53% *anti* and 47% *gauche* (M).

refined as two groups. For both conformers a dynamic model was used where each conformer was represented by nine distinct forms with different torsion angles, each weighted according to a Gaussian potential function. The r.m.s. amplitudes $\langle(\Delta\phi)^2\rangle$ for the torsional vibration (τ_{anti} and τ_{gauche}) were introduced as parameters in the dynamic model; framework values were used for the vibrational amplitude corrections (see Table 2).

Because of the very low scattering power of H compared with that of Si and Br, $r(\text{Si-H})$ and $\angle\text{Si-SiH}$ could not be determined very well in the least squares refinements and these parameters were therefore given reasonable values and kept constant in the final refinement. The *gauche* torsion angle was correlated both with τ_G , the *gauche* r.m.s. torsional amplitude and with the percentage *gauche* present. The best fit between experimental and theoretical RD-curves was obtained with $\phi_G = 60^\circ$ and $\tau_G = 15^\circ$ and the parameters were kept constant at these values. Different values were also tried for τ_A , the *anti* torsional amplitude, but the best fit was obtained when the two amplitudes had about the same value. This is in agreement with the MM-calculations where the torsional force constant for the two conformers had almost the same value ($F_\phi = 0.093$ and 0.10 m dyn Å rad⁻²). In the final refinement four geometrical parameters, two amplitude parameters and the conformational composition were determined simultaneously. The results for the independent parameters are given in Table 3; Table 4 shows the correlation matrix for the refined parameters.

DISCUSSION

The geometrical parameters obtained for TBDS are not unusual when compared with the results obtained for similar molecules. One of the two

TABLE 3

$\text{Br}_2\text{HSi-SiHBr}_2$: final results from least squares refinements^a

Parameter		Parameter	
$r(\text{Si-Si})$	2.349(19)	ϕ_{anti}	[180.0]
$r(\text{Si-Br})$	2.205(5)	ϕ_{gauche}	[60.0]
$r(\text{Si-H})$	[1.485]	τ_{anti}	[15.0]
$\angle\text{Br-Si-Br}$	110.1(1.6)	τ_{gauche}	[15.0]
$\angle\text{Si-Si-Br}$	107.1(1.2)	X_{anti}^b	0.5(0.2)
$\angle\text{Si-Si-H}$	[108.6]	$l(\text{Si-Si})^c$	0.046(4)
		$l(\text{Si-Br})^c$	0.043(4)
		$l(\text{Br}_1 \cdots \text{Br}_1)^d$	0.131(4)
		$l(\text{Si} \cdots \text{Br})^d$	0.106(6)

^aError-limits are 2σ ; quantities in square brackets were kept constant in the final refinement; ϕ is the H-Si-Si-H torsion angle; τ is the r.m.s. torsional amplitude and X is the mole fraction. ^bSee text for discussion of error limit. ^cRefined as a group. ^dRefined as a group.

TABLE 4

Correlation matrix ($\times 100$) for the parameters of 1,1,2,2-tetrabromodisilane

	σ^a	r_1	r_2	L_1	L_2	l_1	l_2	X
$r(\text{Si}-\text{Br})$	0.0008	100	57	-20	-46	27	5	-6
$r(\text{Si}-\text{Si})$	0.0061		100	-26	-61	58	8	-12
$\angle \text{BrSiBr}$	0.54			100	-41	-16	69	2
$\angle \text{SiSiBr}$	0.62				100	-34	-58	7
$l(\text{Si}-\text{Si})$	0.0014					100	22	-16
$l(\text{Br} \cdots \text{Br})$	0.0028						100	-5
X_{anti}	0.17							100

^a Standard deviations from least squares refinement.

vibrational amplitude parameters ($l(\text{Si}-\text{Si})/l(\text{Si}-\text{Br})$) refined to a value significantly smaller than the one calculated from the normal coordinate analysis. If these vibrational amplitudes were kept constant at the calculated values, a much larger R -factor was obtained (0.171 versus 0.146) and the fit between experimental and theoretical RD-curves was also bad. A very large value of 2.379(28) Å was obtained for $r(\text{Si}-\text{Si})$ using calculated values for $l(\text{Si}-\text{Si})$ and $l(\text{Si}-\text{Br})$. In our final refinement we therefore allowed these amplitudes to refine even though the results for the amplitudes are unreasonably small.

One of the most important parts of this investigation was to determine the conformational composition in TBDS. However, as Fig. 4 shows, the RD-curves for the *gauche* and *anti* forms are not very different, and an accurate value for X_A , the mole fraction for the *anti* conformer, could not be determined. The least squares refinement gave as a result $X_A = 0.5 \pm 0.5$. From Fig. 4 it can be seen, however, that this error-limit must be too large. The RD-curves clearly show that both conformers must be present in approximately equal amounts.

From the separate $\text{Br} \cdots \text{Br}$ peak at about 5.5 Å an estimate of the conformational composition can be made independently of the least squares refinement. Figure 5 shows this $\text{Br} \cdots \text{Br}$ peak in RD-curves calculated without including intensity data for $0 < s < 1.75$, where we have no experimental intensity data available. The areas of the peak in the experimental curve and in the two theoretical curves for $X_A = 1.0$ and $X_A = 0.0$ were estimated, and from these results (2.39 ± 0.1 for the experimental curve, 3.41 ± 0.1 for the theoretical curve with $X_A = 1.0$ and 1.78 ± 0.1 for $X_A = 0.0$) a value of 0.4 ± 0.2 was obtained for X_A . Within error limits the estimates $X_A = 0.4 \pm 0.2$ and $X_A = 0.5 \pm 0.5$ are equal. However, the error limit obtained by the least-squares refinement is more than twice the value obtained from area analysis in the RD-curves. It is our opinion that the least-squares value for the error limit of X_A is too large in this case. Figure 4 shows that X_A can be neither 1.0 nor 0.0. Our final estimate for the conformational composition is therefore $X_A = 0.5 \pm 0.2$ and this is also the value we have reported in Table 3.

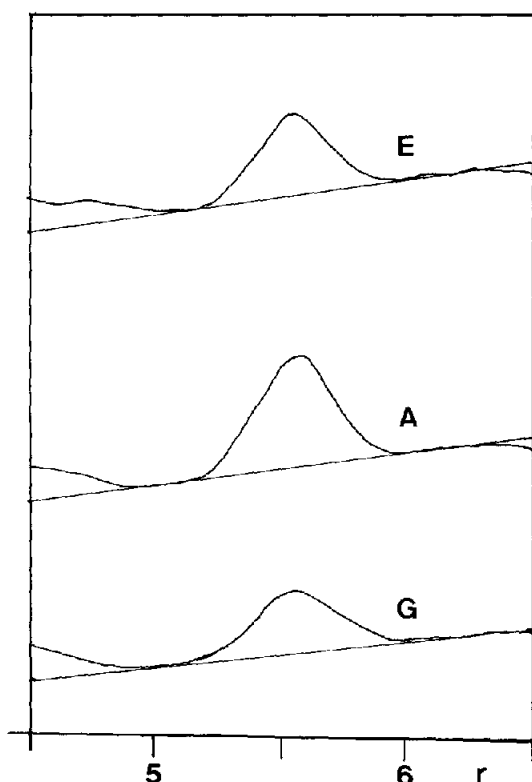


Fig. 5. 1,1,2,2-Tetrabromodisilane: radial distribution (RD) curves with artificial damping constant equal to 0.002 \AA^2 . The unobserved inner part of the intensity curve was not included in the calculation of these RD curves. The curves are experimental (E), theoretical for *anti* (A) and theoretical for *gauche* (G).

If we assume that the only contribution to $\Delta S = S(\textit{gauche}) - S(\textit{anti})$, coming from the fact that there are two *gauche* forms and only one *anti* form, $X_A = 0.5 \pm 0.2$ corresponds to an energy difference, ΔE , between the *gauche* and *anti* conformers of $\Delta E = 0.5 \pm 0.6 \text{ kcal mol}^{-1}$. The value obtained from MM-calculations was $\Delta E = -0.6 \text{ kcal mol}^{-1}$ [1]. The two values do not agree.

ACKNOWLEDGEMENTS

We are grateful to siving. Ragnhild Seip, cand. scient. R. Blom and Ms. S. Gundersen for help with recording the experimental data. Financial support from the Norwegian Research Council for Science and the Humanities is acknowledged.

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