Molecular Structure and Thermochemistry of Tin Dibromide Monomers and Dimers. A Computational and Electron Diffraction Study

Mária Kolonits,[†] Balázs Réffy,[†] Gábor Jancsó,[‡] and Magdolna Hargittai*,[†]

Structural Chemistry Research Group of the Hungarian Academy of Sciences at Eötvös University,
P.O. Box 32, H-1518 Budapest, Hungary, and KFKI Atomic Energy Research Institute,
P.O. Box 49, Budapest H-1525, Hungary

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The molecular structure of tin dibromide was investigated by high-level computational methods and gas-phase electron diffraction. The structural and vibrational characteristics of both $SnBr_2$ and Sn_2Br_4 were determined by computations. To reach an agreement between computed and experimental bond lengths for $SnBr_2$, very large bases and correlated methods are needed. For the dimer Sn_2Br_4, two low-energy geometries were found, one with C_s and the other with C_{2v} symmetry, the former with somewhat lower energy. Thermodynamic functions for gaseous $SnBr_2$ and Sn_2Br_4 and their dimerization reaction have been calculated on the basis of the computed structures.

Introduction

Tin dibromide has been the subject of previous investigations both from structural and thermochemical points of view, although less frequently than the chlorides and the iodides of tin. As mentioned by Hilpert et al. in their mass spectrometric study,[1] the vaporization of $SnBr_2$ has importance in the modeling of metal halide lamps, so its investigation has practical importance beside its interest for fundamental research.

The vaporization of $SnBr_2$ was studied earlier by Knowles et al.[2,3] and by Hirayama and Straw,[4] while the thermochemistry of the $SnBr_2$ dimer was studied by Hilpert et al.,[1] who identified the dimer in the vapor phase over molten tin dibromide by their mass spectrometric measurement.

The geometry of $SnBr_2$ was investigated by electron diffraction (ED) several times in the past. Apart from the very early studies in the 1940s and 1950s by Lister and Sutton[5] and Akishin et al.,[6] where only the bond lengths could be determined, Spiridonov and co-workers studied $SnBr_2$ in a series of papers as one of their test cases in their development of the joint electron diffraction and vibrational analysis of simple molecules.[7−10] The composition of the vapor was not considered in either case.

Vibrational spectroscopic studies of $SnBr_2$ include the gas-phase Raman spectroscopic study by Beattie and Perry[11] and the matrix isolation Raman spectroscopic study by Ozin and Vander Voet.[12] In neither case were dimers detected in their spectra, although the presence of “weak aggregate lines” was observed in the spectrum in ref 12, albeit not assigned.

Finally, there have been only three computational studies of monomeric $SnBr_2$,[13−15] two of which present data on both the ground state and the first excited electron state molecules.[13,15] No computational studies have yet been performed on the dimer of tin dibromide.

In this work we present the results of the ED study of tin dibromide together with high-level quantum chemical computations and thermodynamic calculations for both the monomeric and the dimeric species. The reason for our study is manifold. First, the earlier ED study by Spiridonov et al.[7−10] does not mention the possibility of having dimeric molecules in the vapor and does not present any experimental data; thus, there is no way to judge the quality of their results. Second, a recent study by Levy et al. showed that the dimer of $SnCl_2$ has a rather strange structure,[16] and this made us curious about what the geometry of Sn_2Br_4 might be. There have not been any previous studies of the geometry and vibrational characteristics of Sn_2Br_4. Finally, since the thermodynamical calculations by Hilpert et al.[1] for the dimer were based on a supposed geometry that is far from the one we found to be the minimum-energy structure, we decided to repeat these calculations with the new structure and with our computed vibrational frequencies because molecular structures and symmetries might seriously influence the outcome of thermodynamic calculations.

Experimental Section

The ED patterns of the $SnBr_2$ (Sigma-Aldrich) sample were recorded in our modified EG-100A apparatus[17] with a high-temperature nozzle system.[18] The nozzle material was stainless steel. To avoid thermal decomposition, the lowest possible temperature and gas pressure were employed at a nozzle temperature of 617 K.

The ED experiments were performed using 60 kV electrons at two camera ranges, 50 and 19 cm, respectively, using Kodak electron image plates. Three and five photoplates were selected for analysis at the 50 and 19 cm camera ranges, respectively. The data intervals at the 50 and 19 cm experiments are $s = 2{-}14$ Å^{-1} (with data steps of 0.125 Å^{-1}) and $s = 9{-}28.5$ Å^{-1} (with data steps of 0.25 Å^{-1}), respectively. The electron scattering factors were taken from the literature.[19] The molecular intensities and the radial distribution curves of $SnBr_2$ are plotted in Figures 1 and 2, respectively. Listings of the total electron diffraction intensities are deposited as Supporting Information.

Quantum Chemical Calculations

No geometrical information is available on the dimer of tin dibromide; therefore, our first aim was to calculate the structure

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* Corresponding author. E-mail: hargitta@chem.elte.hu.
[†] Eötvös University.
[‡] KFKI.

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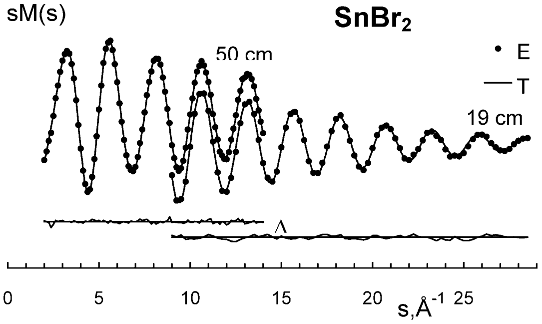

Figure 1. Experimental (E) and calculated (T) molecular intensities and their differences (Δ) for the model containing 1.4(5)% dimeric molecules of C_s symmetry.

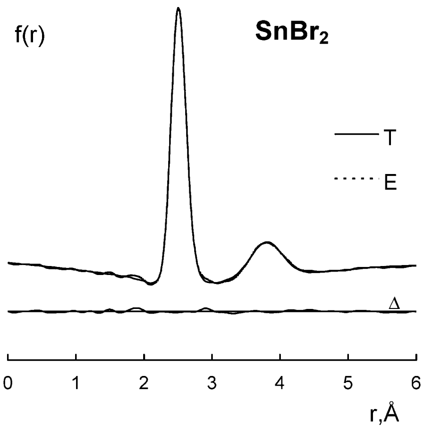

Figure 2. Experimental (E) and calculated (T) radial distributions and their differences (Δ) for the model containing 1.4(5)% dimeric molecules of C_s symmetry.

TABLE 1: Computed Geometrical Parameters of Monomeric $SnBr_2$

basis	method	r_e, Å	α, deg	ref
Sn/Basis 2, Br/cc-pVDZ	MP2	2.501	99.1	this work
Sn/Basis 2, Br/cc-pVTZ	MP2	2.513	98.6	this work
Sn/Basis 2, Br/cc-pVQZ	MP2	2.516	98.2	this work
Sn/Basis 2, Br/Basis 2	MP2	2.518	98.1	this work
Sn/Basis 1, Br/sdd	MP2	2.519	99.2	this work
Sn/Basis 1, Br/cc-pVDZ	MP2	2.522	99.7	this work
	CCSD(T)	2.527	100.0	this work
Sn/Basis 1, Br/aug-cc-pVDZ	MP2	2.531	99.1	this work
	CCSD(T)	2.536	99.5	this work
Sn/Basis 1, Br/cc-pVTZ	MP2	2.529	98.6	this work
Sn/Basis 1, Br/aug-cc-pVTZ	MP2	2.529	98.3	this work
Sn/Basis 1, Br/Basis 1	MP2	2.534	99.2	this work
	CCSD(T)	2.539	99.5	this work, 15
Sn/3s3p1d vbs, Br/4s4p1d vbs	MRSDCI	2.535	99.7	13
	CASSCF	2.552	100.3	13
	B3LYP	2.567	100.0	14
Sn/4s4p1d vbs, Br/3s3p1d vbs	CCSD(T)	2.552	100.2	15

TABLE 2: Calculated and Experimental Vibrational Frequencies of Monomeric $SnBr_2$

	computed (MP2)				exptl
	Sn/Basis 1 Br/sdd	Sn/Basis1 Br/aug-cc-pVDZ	Sn/Basis 1 Br/Basis 1	Sn/Basis 2 Br/cc-pVDZ	
ν_1, cm^{-1}	240.4	245.0	234.1	257.3	244[a,12]
ν_2, cm^{-1}	87.6	80.5	75.8	87.5	82[a,12] 80[b,11]
ν_3, cm^{-1}	231.9	237.3	228.1	250.7	231[a,12]

[a] Matrix isolation (Ar) Raman spectroscopy. [b] Gas-phase Raman spectroscopy.

and vibrational frequencies of Sn_2Br_4. To be able to check the dimer presence at the ED experimental conditions in the vapor, we also needed the differences of geometrical parameters of the monomer and the dimer to aid the ED analysis. For this purpose we had to carry out computations at the same level and basis sets for both molecular species. Besides this purpose, we also wanted to carry out high-level computations for the monomer to get better computed structures than found in the literature.

Full geometry optimizations were carried out first for the monomer using density functional (B3LYP,[20] B3PW91[21]), second-order Møller−Plesset (MP2), and CCSD(T) level computations with the Gaussian 98 program package.[22] A multielectron adjusted quasi-relativistic effective core potential (ECP) covering 46 electrons ([Kr]$4d^{10}$) was used for Sn[23] with two different associated basis sets, a triple-ζ (14s10p2d1f)/[3s3p2d1f] "Basis 1" and a quadruple-ζ (14s10p3d2fg)/[4s4p3d2fg] "Basis 2".[24] For bromine, correlation-consistent double- and triple-ζ all-electron basis sets (cc-pVDZ and cc-pVTZ with and without diffuse functions)[25] and a quasi-relativistic effective core potential developed by the Stuttgart group, covering 28 electrons ([Ar]$3d^{10}$)[23] and three associated basis sets, a simple (4s5p)/[2s3p] type[26] ("sdd") and two larger ones of the type used for Sn (Basis 1 and Basis 2),[24] were tried.

We found that it was impossible to get proper MO symmetries with the larger basis set (Basis 2) on the Sn and the Br atoms using the Gaussian 98 program package. Eventually, we repeated these calculations with the Gaussian 03 program[27] and that solved this problem. Therefore, all the Basis 2 calculations were carried out with the Gaussian 03 program package. The density functional calculations consistently gave larger bond lengths and larger bond angles than the MP2 calculations. The difference was about 0.02−0.03 Å and about 1−3° for the B3LYP functional and somewhat less, about 0.01−0.02 Å and 0.5−1.0°, for the B3PW91 functional. Since the experimental geometry of the monomer agreed better with the MP2 results (vide infra), we concentrated on those.

We were interested in what basis set we need in order to get the same Sn−Br bond length for the monomer as the estimated equilibrium bond length from electron diffraction. Therefore, we carried out several trial calculations for the monomer with different basis set combinations. Some of the results are collected in Table 1, together with the literature data. A perfect agreement with the estimated electron diffraction equilibrium distance was achieved by using Basis 2 on Sn and a Huzinaga type cc-pVDZ basis on Br, with the bond angle also within the uncertainty of the experimental value. The computed frequencies for the monomer, together with the experimental values, are shown in Table 2.

Geometry optimizations of the dimer were carried out with initial structures of C_s and C_{2v} symmetry. Several basis set combinations were tried from among those used for the monomer calculation. Two low-energy structures were found, one with C_s and the other with C_{2v} symmetry, independently of the basis sets. Frequency calculations for the dimer could be carried out only for the smaller basis sets. They indicated that both the C_s and the C_{2v} structures are minima with no imaginary frequencies, with the C_s structure being the global minimum. The geometrical parameters of the two dimer structures are given in Table 3, while the frequencies are given in Table 4. Since earlier calculations of the Sn_2Cl_4 molecule[16] showed the same type of minimum-energy structures as found here—and no other minima—we did not carry out further searches for other

TABLE 3: Computed Geometrical Parameters (MP2) of Sn_2Br_4

Sn basis Br basis	Basis 1 sdd	Basis 1 Basis 1	Basis 1 cc-pVDZ	Basis 2 cc-pVDZ	Basis 2 Basis 2
Sn_2Br_4 of C_s Symmetry[a]					
$r(Sn_2-Br_3)$, Å	2.765	2.758	2.762	2.729	2.809
$r(Sn_1-Br_3)$, Å	2.809	2.817	2.821	2.783	2.842
$r(Sn_2-Br_6)$, Å	2.550	2.570	2.556	2.538	2.573
$r(Sn_1-Br_5)$, Å	2.525	2.543	2.527	2.513	2.555
$\angle Br_3-Sn_1-Br_4$, deg	84.8	84.6	84.9	84.8	85.4
$\angle Br_3-Sn_2-Br_4$, deg	83.3	82.4	82.8	82.8	84.2
$\angle Sn_1-X-Sn_2$,[b] deg	136.5	132.9	133.1	132.7	143.1
$\angle X-Sn_1-Br_5$,[b] deg	96.6	92.5	93.1	95.7	98.5
$\angle X-Sn_2-Br_6$,[b] deg	94.4	95.3	96.2	93.0	96.4
Sn_2Br_4 of C_{2v} Symmetry[c]					
$r(Sn_1-Br_3)$, Å	2.791	2.792	2.796	2.759	2.830
$r(Sn_1-Br_5)$, Å	2.516	2.528	2.515	2.500	2.547
$\angle Br_3-Sn_1-Br_4$, deg	85.3	85.7	85.7	86.0	85.6
$\angle Sn_1-X-Sn_2$,[b] deg	177.7	167.7	167.0	172.2	167.3
$\angle X-Sn_1-Br_5$,[b] deg	97.6	96.8	97.5	97.0	99.7
ΔE, kJ mol^{-1} [d]	6.0	9.14	9.0	10.4	4.3

[a] Ground state. The molecular model is shown in Figure 3a. [b] X is the midpoint of the $Br_3\cdots Br_4$ distance. [c] The molecular model is shown in Figure 3b. [d] Energy difference between the C_{2v} structure and the C_s symmetry structure.

TABLE 4: Vibrational Frequencies of the Two Models of the Sn_2Br_4 Dimer from MP2 Sn/Basis 1, Br/sdd Computation

Sn_2Br_4, model **A** (C_s symmetry)		Sn_2Br_4 model **B** (C_{2v} symmetry)	
symmetry	frequency, cm^{-1}	symmetry	frequency, cm^{-1}
A'	235.8	A_1	241.4
A'	226.3	A_1	167.9
A'	178.1	A_1	100.1
A'	158.8	A_1	66.5
A'	96.6	A_1	11.4
A'	89.9	A_2	104.4
A'	56.3	A_2	49.6
A'	26.1	B_1	159.4
A''	168.1	B_1	69.4
A''	101.5	B_2	235.9
A''	71.2	B_2	163.6
A''	49.6	B_2	65.6

TABLE 5: Geometrical Parameters of $SnBr_2$ from Electron Diffraction[a,b]

	refining the dimer content	100% monomer
$r_g(Sn-Br)$	2.515 ± 0.005	2.517 ± 0.005
$r_e^M(Sn-Br)$	2.500 ± 0.005	2.502 ± 0.005
$r_e(Sn-Br)$		2.499 ± 0.005
$l(Sn-Br)$	0.077 ± 0.002	0.077 ± 0.002
$\kappa(Sn-Br)$	$3.0 \times 10^{-5} \pm 4.3 \times 10^{-6}$	$3.4 \times 10^{-5} \pm 4.2 \times 10^{-6}$
$r_g(Br\cdots Br)$	3.803 ± 0.015	3.812 ± 0.013
$l(Br\cdots Br)$	0.225 ± 0.012	0.212 ± 0.009
$\angle_a(Br-Sn-Br)$	97.9 ± 0.4	98.2 ± 0.4
$\angle_e(Br-Sn-Br)$		98.3 ± 0.9
monomer %	98.6 ± 0.5	100
R (%)	4.8	5.1

[a] Bond lengths (r_g) and vibrational amplitudes (l) in Å, angles in degrees, and asymmetry parameters (κ) in Å^3. Error limits are estimated total errors, including systematic errors, and the effect of constraints used in the refinement: $\sigma_t = (2\sigma_{LS}{}^2 + (cp)^2 + \Delta^2)^{1/2}$, where σ_{LS} is the standard deviation of the least squares refinement, p is the parameter, c is 0.002 for distances and 0.02 for amplitudes, and Δ is the effect of constraints. For the dimer, the minimum-energy C_s symmetry structure was taken into account, from the MP2 Sn/Basis 1, Br/sdd computation. [b] Earlier electron diffraction results: $r_g(Sn-Br) = 2.512(3)$ Å and $\angle(Br-Sn-Br) = 99.7(20)°$ from ref 7 and $r_e(Sn-Br) = 2.501(3)$ Å and $\angle_e(Br-Sn-Br) = 100.0(20)°$ from ref 9.

minimum structures for the Sn_2Br_4 dimer, considering the very costly nature of these computations.

Electron Diffraction Analysis

On the basis of mass spectrometric evidence,[1] the presence of dimeric molecules in the vapor could not be ruled out at the ED experimental conditions. Therefore, they had to be included in the analysis. In the course of the refinement, it soon became clear that the vapor consisted mainly of monomeric molecules and the amount of dimers, if any, could not be more than just a “contamination” of a few percent. There was no hope to determine the structure of the dimer from the experiment, so we had to rely on its computed geometry. According to our usual practice, we used bond length *differences* as constraints in the analysis, rather than actual bond lengths—the latter would not be right due to the different physical meaning of computed and thermal average geometries.[28,29] While the actual bond lengths obtained from computation and experiment may be rather different, this difference mostly cancels out if we carry over the bond length differences from the computations to the experiment.

Least-squares refinements including both monomeric and dimeric molecules were carried out. The geometrical parameters of the monomer, their vibrational amplitudes, and the asymmetry parameter of the monomer bond length were always refined independently. For the dimer, several constraints were applied, such as the difference of the dimer terminal and bridging bond lengths and the difference between the dimer terminal and the monomer bond lengths. The dimer bond angles were also accepted from the computation. All these constraints were taken from the computations using Basis 1 on Sn and the basis “sdd” on Br. The energy difference between the two dimer structures was relatively small; therefore, we checked both forms in the ED analysis. Since there was no observable difference in the results concerning the monomer structure and the dimer content for the two different dimer structures, in our final calculation we accepted the minimum-energy, C_s symmetry dimer structure.

The amount of dimer we found in the vapor was about 2%, too small to yield any reliable information on its structure from experiment. It is interesting to note that the estimation of the dimer content of the vapor above liquid tin bromide at 617 K, using the equilibrium constant of the dimerization process[1] and the vapor pressure of $SnBr_2$ above the liquid,[30] yielded a value of 1.5%. The inclusion of dimers did not change the monomer parameters more than their total errors. The R-factor (goodness of fit) was also about the same in the two cases. The geometrical parameters of monomeric $SnBr_2$ from experiment are given in Table 5.

Thermodynamic Calculations

Detailed thermodynamic calculations were carried out earlier by Hilpert et al.[1] using experimentally determined molecular parameters for the monomer,[8] and assuming a planar structure of D_{2h} symmetry for the dimer as well as some changes in the geometry of the monomer on dimer formation. Since the molecular structure and symmetry of the dimer appear to be very different from those assumed in the above work, we decided to recalculate the thermodynamic functions using the geometry and vibrational frequencies of both the monomer and the two different dimers (**A** and **B**) from our ab initio calculations. We were curious to see whether changing the dimer

TABLE 6: Thermodynamic Functions of $SnBr_2$(g) and Sn_2Br_4(g)

T (K)	$-[G_m^0(T) - H_m^0(0)]/T$ (J K^{-1} mol^{-1})	$H_m^0(T) - H_m^0(0)$ (kJ mol^{-1})	$S_m^0(T)$ (J K^{-1} mol^{-1})
	$SnBr_2$(g)		
100	230.96	3.94	270.32
200	260.36	9.11	305.91
298.15	279.22	14.57	328.07
300	279.52	14.67	328.42
400	293.89	20.35	344.77
500	305.39	26.09	357.57
600	314.99	31.85	368.08
700	323.22	37.63	376.99
800	330.44	43.42	384.72
900	336.86	49.22	391.55
1000	342.64	55.02	397.66
1100	347.89	60.83	403.19
1200	352.72	66.63	408.24
	Sn_2Br_4(g) **A**		
100	294.86	7.55	370.37
200	355.04	19.49	452.49
298.15	396.02	32.04	503.47
300	396.69	32.28	504.27
400	428.49	45.31	541.76
500	454.18	58.45	571.08
600	475.73	71.65	595.14
700	494.28	84.87	615.52
800	510.57	98.11	633.21
900	525.08	111.37	648.82
1000	538.16	124.67	662.80
1100	550.08	137.91	675.45
1200	561.01	151.19	687.00
	Sn_2Br_4(g) **B**		
100	296.03	7.68	372.80
200	356.86	19.63	455.01
298.15	398.08	32.17	505.99
300	398.75	32.41	506.79
400	430.66	45.45	544.28
500	456.42	58.59	573.60
600	478.02	71.78	597.66
700	496.60	85.01	618.04
800	512.91	98.25	635.73
900	527.44	111.51	651.34
1000	540.54	124.78	665.32
1100	552.47	138.05	677.97
1200	563.42	151.33	689.52

shape, structure, and frequencies had any influence on the thermodynanic properties of the dimer and those of the dimerization process.

Thermodynamic functions for the gaseous monomers and dimers were calculated in the rigid rotator harmonic oscillator approximation by using the equations given in ref 30. The molecular symmetries, geometrical parameters, and vibrational frequencies for all three molecular species were taken from the MP2 computation with Basis 1 on Sn and basis sdd on Br (see Tables 1−4). The symmetry numbers were 2 for $SnBr_2$ and the **B** structure of Sn_2Br_4 and 1 for Sn_2Br_4 structure **A**. The thermodynamic functions for the monomer and the two dimer structures (**A** and **B**) are listed for different temperatures in Table 6.

In the case of the monomer, there is a fairly good agreement between the calculated values of the Gibbs energy function ($-[G_m^0(T) - H_m^0(0)]/T$) and those given in Table 6 of the review paper by Brewer et al.,[31] as well as those calculated by Hilpert et al.[1] For example, at 298.15 K the corresponding values are 279.22, 280.03, and 274.69 J K^{-1} mol^{-1}, respectively; the differences are within the uncertainties of the measurements and calculations. The enthalpy increments ($H_m^0(298.15) - H_m^0(0)$) are also in good agreement with each other (14.57, 14.31, and 14.60 kJ mol^{-1}). The small differences in the Gibbs energy function (and in entropy) can be accounted for by the differences in the molecular geometries and vibrational frequencies used in the calculations. As far as the thermodynamic functions of the Sn_2Br_4 dimer are concerned, the enthalpy and entropy values calculated by Hilpert et al.[1] for their assumed dimer structure are lower (e.g., at 298.15 K by about 2%) than those obtained for the dimer structures of the present work.

The Gibbs energy functions and the enthalpy increments of $SnBr_2$(g) and Sn_2Br_4(g) can be used in the calculation of the enthalpy of dimerization:

$$2SnBr_2 \rightarrow Sn_2Br_4$$

The enthalpy change of the dimerization reaction at 298 K ($\Delta_r H_m^0(298.15)$) can be obtained by the third-law method[30] from the experimentally determined equilibrium constant of the dimerization (K_p) using the equation

$$\Delta_r H_m^0(298.15) = -T\{R \ln K_p + \Delta_r[G_m^0(T) - H_m^0(298.15)]/T\}$$

where K_p is the equilibrium constant and Δ_r on the right-hand side of the equation denotes the change of the Gibbs energy function in the dimerization process. The equilibrium constants for the dimerization were taken from Table 5 of the paper by Hilpert et al.,[1] who studied the vapor-phase equilibria over $SnBr_2$ by Knudsen effusion mass spectrometry in the temperature range of 423−573 K. Our calculations were carried out by using the values of the thermodynamic functions for the monomer and dimers **A** and **B**. The average values for the enthalpy change of the dimerization ($\Delta_r H_m^0(298.15)$) were found to be -105.5 ± 0.3 and -104.0 ± 0.4 kJ mol^{-1}, for dimers **A** and **B**, respectively. These values are in excellent agreement with that obtained by Hilpert et al.[1] (106.7 ± 5.0 kJ mol^{-1}).

The second-law evaluation method[30] is based on the temperature dependence of the equilibrium constant of the dimerization. The logarithm of K_p is a linear function of $1/T$ (see Figure 2 of ref 1), and from the slope of the straight line an average value of -103.8 ± 2.9 kJ mol^{-1} was obtained for $\Delta_r H_m^0(500)$.[1] From this value, by using the enthalpy increments given in Table 6, one obtains for $\Delta_r H_m^0(298.15)$ the same value of -107.2 ± 3 kJ mol^{-1} for both dimers **A** and **B**, which is in good agreement with the calculated value reported by Hilpert et al. (-106.9 ± 5.3 kJ mol^{-1}).[1] The agreement between the enthalpy of dimerization values calculated by second- and third-law evaluation methods, on one hand, and between the present values and those obtained by Hilpert et al.,[1] on the other, is remarkably good.

Results and Discussion

The shape of monomeric $SnBr_2$ is bent, as expected, due to the lone electron pair on its central atom.[32] The thermal average bond length, r_g, and the bond angle from ED agree well with the previous ED results (see Table 5). We have also estimated the experimental equilibrium distance in two different ways. One of them is by the Morse-type correction, $r_e^M = r_g - (3al^2)/2$ (a is the Morse constant and l is the mean-square vibrational amplitude),[33] $r_e^M = 2.502 \pm 0.005$ Å, and the other by an anharmonic joint electron diffraction−vibrational spectroscopic analysis.[34] The result of the latter is 2.499 ± 0.005 Å; the two values very well agree with each other and with the one calculated by Spiridonov et al. by another type of anharmonic correction (2.501(3) Å).[9]

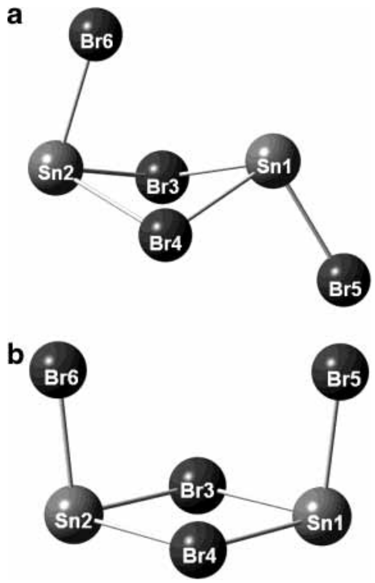

Figure 3. Molecular models of Sn_2Br_4. (a) Model with C_s symmetry corresponding to the global minimum. (b) Model with C_{2v} symmetry (also stable).

When we compare experimental and computed bond lengths, the computed parameters have to be compared with the estimated experimental equilibrium bond length. Our new computed geometrical parameters for the monomer agree with the experimental ones much better than any of the previous computed values, also shown in Table 1, although for a good agreement a rather large, quadruple-ζ basis is needed for the tin atom (see Table 1). One might argue that this large basis on tin with the relatively modest double-ζ basis on the bromine atoms produces a somewhat uneven distribution. However, as Table 1 shows, gradually increasing the basis size on bromine causes a gradual lengthening of the Sn−Br distance, thus worsening the agreement with the experimental bond length. The same effect can be observed with Basis 1 on tin. The proper description of the central atom seems to be more important in describing the geometry of the molecule than that of the ligands.

The experimental equilibrium bond angle is 98.3 ± 0.9°. The calculated bond angles are in the range of 98−100°, which is a reasonable agreement. Using better basis sets on bromine causes a gradual, albeit small, decrease of the bond angle. Comparison of the calculated frequencies of the monomer molecule with the experimental values[11,12] shows that the best agreement is reached by using the Sn/Basis 1 and Br/sdd sets of basis functions. Interestingly, the basis set that gives the best agreement for the geometry overemphasizes the frequencies. Anharmonicity of the vibrations, not accounted for by the computations, might be the reason.

We determined the geometry of dimeric tin dibromide, Sn_2Br_4, by quantum chemical calculations for the first time. The lowest energy structure has C_s symmetry and is shown in Figure 3a; the structure is in agreement with the larger space requirement of the lone electron pairs on the tin atoms. Another structure, about 4−10 kJ/mol higher in energy than this one, has C_{2v} symmetry and is shown in Figure 3b. According to the frequency analysis, this latter is also a minimum structure and, considering the high temperature of our ED experiment, it may even appear in the vapor phase if we consider that the thermal energy at 617 K is comparable to the energy differences of these two forms. Of course, this also depends on what the energy barrier is between these two dimeric forms. The two structures found for the dimer are in agreement with the ones calculated for the Sn_2Cl_4 dimer earlier,[16] so this type of arrangement seems to be general for the dimers of tin dihalides. The same comment as given for the monomer molecule about the sizes of basis sets on the tin and the bromine atoms, respectively, applies for the dimer as well. It has to be emphasized that the shape and relative stabilities of the dimeric molecules are irrespective of the applied basis sets; therefore, they can be considered well determined.

The dimer structures **A** and **B** of the present work yielded, within the error limit, the same thermodynamic values for the dimerization reaction as those for the dimer structure assumed by Hilpert et al. Considering the shape of these dimers (see Figure 3) and the assumed D_{2h} symmetry structure in ref 1, to find such a good agreement is somewhat surprising. Apparently, the shape and geometry of these heavy molecules do not influence the thermodynamic functions as much as it is usually assumed.

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Supporting Information Available: Total electron diffraction molecular intensities at two different camera ranges. This material is available free of charge via the Internet at http://pubs.acs.org.

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