Contribution from the Department of Chemistry and Biochemistry, University of Arkansas,
Fayetteville, Arkansas 72701, and Structural Chemistry Research Group of the Hungarian Academy of Sciences,
Eötvös University, Pf. 117, Budapest, H-1431 Hungary

Structures, Energetics, and Vibrational Frequencies of the Silicon and Germanium Dichlorides and Dibromides and Their Dimers

J. M. Coffin,[†] T. P. Hamilton,[†] P. Pulay,*[,†] and I. Hargittai[‡]

Received July 29, 1988

The geometries and energies of the ground singlet ($^1A_1$) and first excited triplet ($^3B_1$) states of $SiCl_2$, $SiBr_2$, $GeCl_2$, and $GeBr_2$ and the ground states of their dimers were determined from ab initio Hartree–Fock calculations, in order to identify the additional component observed in the electron diffraction radial distribution of $GeBr_2$. The results show that the triplet states of these molecules are 140–200 kJ/mol higher in energy than the singlet states and can be thus excluded as the additional component at the experimental temperature. The bridged dimer of $GeBr_2$ is calculated to be weakly bound and is predicted to be the additional component. We have calculated the force constants and fundamental frequencies of the singlet monomers. The latter, after the usual scaling, agree well with the experimental frequencies. A matrix-infrared study of the system could positively identify the dimer as the additional component, and the predicted vibrational fundamental frequencies of Ge_2Br_4 are given to assist in this identification.

Introduction

The group IV dihalides $SiCl_2$, $SiBr_2$, $GeCl_2$, and $GeBr_2$ are halogenated analogues of carbenes. They are interesting, especially for their reactivity, and potentially important compounds. Experimentally, their structures have been investigated by electron diffraction,[1-3] by matrix-isolated infrared spectroscopy,[4-9] and by gas-phase ultraviolet spectroscopy.[10]

The performance of ab initio techniques for silicon and germanium compounds has been investigated in several recent theoretical studies.[11-15] Ab initio calculations on silicon compounds have been reviewed recently by Gordon et al.[16]

This theoretical study was initiated by the experimental observation of an additional component in vapor-phase germanium dibromide.[3] In a recent electron diffraction experiment,[3] the experimental radial distribution could not be fitted to a model containing only the ground-state singlet species of monomeric $GeBr_2$. It was suggested that $GeBr_2$ may have a low-lying triplet state that is appreciably populated at the experimental temperature (620 °C). In alternate models, a dimer with bridging bromines or with a Ge=Ge bond was suggested to account for the discrepancy. Due to the ambiguity in the electron diffraction radial distribution, the second component could not be positively identified. One of the goals of our study was the evaluation of these models to assist in establishing the identity of this unidentified component. The presence of an additional component has also been detected in the electron diffraction study of $SiCl_2$.[1]

The experimental method most likely to yield a positive identification of the dimers is matrix-infrared spectroscopy. An additional objective of this study was the calculation of fundamental vibrational frequencies from theoretically obtained force fields to assist in this assignment.

Computational Details

All calculations, except for the dimer frequencies, were performed by using the program TEXAS.[17] The MIDI-1* split-valence basis set of Huzinaga was used,[18,19] augmented with d-type valence polarization functions. The values for the d-orbital exponents are 0.28, 0.56, 0.43, and 0.336 for Si, Cl, Br,[18,19] and Ge (this work), respectively. The latter value has been optimized in GeH_4. The geometries of the singlet and first excited triplet states of $SiCl_2$, $SiBr_2$, $GeCl_2$, and $GeBr_2$ were optimized at the closed-shell Hartree–Fock and restricted open-shell Hartree–Fock levels, respectively. The geometries were relaxed until all internal forces were less than 0.001 mdyn.

Table I. Geometries and Energies[a] for the Singlet and Triplet States of the Silicon and Germanium Dichloride and Dibromide Series (Bond Distances in Å; Angles in deg)

molecule		calcd		exptl		tot.	triplet–singlet
		dist	angle	dist	angle	energy, E_h	energy splitting, kJ mol^{-1}
$SiCl_2$	S	2.102	101.40	2.083	102.8_1	−1202.2831	160.9
	T	2.073	116.92	*b*	*b*	−1202.2218	
$SiBr_2$	S	2.257	102.16	2.243	102.7_1	−5412.3573	139.7
	T	2.219	118.50	*b*	*b*	−5412.3041	
$GeCl_2$	S	2.177	100.35	2.183	100.3_2	−2981.7270	198.2
	T	2.145	117.30	*b*	*b*	−2981.6515	
$GeBr_2$	S	2.327	101.49	2.337	101.2_3	−7191.8064	174.2
	T	2.287	118.73	2.37[c]	141[c]	−7191.7400	

[a] 1 E_h = 2625.5 kJ/mol. [b] Not applicable. [c] Tentative value.

The geometries of the bridged dimers were also optimized. Due to the large size of these calculations (between 140 and 160 contracted basis functions), the forces were only relaxed until they were less than 0.0025 mdyn. A correction for the basis set superposition error (BSSE) was calculated by using the Boys–Bernardi counterpoise correction method.[20] To estimate the BSSE, the energies for the following systems were calculated: half of a dimer (X_t–M–X_{br}) at the dimer geometry, in which the other three atoms were replaced by ghost atoms (E_1) and the same system after the ghost atoms were removed (along with their associated basis functions) (E_2). The difference between the two energies gives an estimate of the basis set superposition error. The counterpoise-corrected dissociation energy is given by

$$E_{\mathrm{dimer}} - 2E_{\mathrm{monomer}} - 2(\mathrm{BSSE})$$

The force fields for the ground state monomeric compounds were calculated at the SCF level. The forces were calculated analytically

---

[†] University of Arkansas.

[‡] Eötvös University.

(1) Hargittai, I.; Schultz, G.; Tremmel, J.; Kagramanov, N. D.; Maltsev, A. K.; Nefedov, O. M. *J. Am. Chem. Soc.* **1983**, *105*, 2895.
(2) Schultz, G.; Tremmel, J.; Hargittai, I.; Berecz, I.; Bokatka, S.; Kagramanov, N. D.; Maltsev, A. K.; Nefedov, O. M. *J. Mol. Struct.* **1979**, *55*, 207.
(3) Schultz, G.; Tremmel, J.; Hargittai, I.; Kagramanov, N. D.; Maltsev, A. K.; Nefedov, O. M. *J. Mol. Struct.* **1982**, *82*, 107.
(4) Miller, J. H.; Andrews, L. *J. Mol. Struct.* **1981**, *77*, 65.
(5) Milligan, D. E.; Jacox, M. A. *J. Chem. Phys.* **1968**, *49*, 1938.
(6) Maass, G.; Hauge, R. H.; Margrave, J. L. *Z. Anorg. Allg. Chem.* **1972**, *392*, 295.
(7) Svyatkin, V. A.; Maltsev, A. K.; Nefedov, O. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1977**, 2236.
(8) Andrews, L.; Frederick, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 775.
(9) Isabel, R. J.; Smith, G. R.; McGraw, R. K.; Guillory, W. A. *J. Chem. Phys.* **1973**, *58*, 818.
(10) Ruzsicska, B.; Jodhan, A.; Safarik, I.; Strausz, O. P.; Bell, T. N. *Chem. Phys. Lett.* **1987**, *139*, 72.
(11) Balasubramanian, K.; McLean, A. D. *J. Chem. Phys.* **1986**, *85*, 5117.
(12) Gordon, M. S.; Schmidt, M. W. *Chem. Phys. Lett.* **1986**, *132*, 294.
(13) Gosavi, R. K.; Strausz, O. P. *Chem. Phys. Lett.* **1986**, *123*, 65.
(14) Deeley, B.; Solt, G. *THEOCHEM* **1986**, *139*, 159.
(15) Haaland, A.; Schilling, B. E. R. *Acta Chem. Scand., Ser. A* **1984**, *38*, 217. Ha, T. K.; Nguyen, M. T.; Kerins, M. C.; Fitzpatrick, J. *Chem. Phys.* **1986**, *103*, 243.
(16) Baldridge, K. K.; Boatz, J. A.; Koseki, S.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1987**, *38*, 211.
(17) Pulay, P. *Theor Chim Acta* **1979**, *50*, 599–612.
(18) Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1980**, *1*, 205.
(19) Sakai, Y.; Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1982**, *3*, 6.
(20) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

0020-1669/89/1328-4092$01.50/0

Table II. Geometries and Energies of Dimers of Group IV Dihalides (Bond Lengths in Å; Angles in deg)[a]

molecule	R_1	R_2	angle *a* (X_b–M–X_b)	angle *b* (X_t–out of plane)	angle *c* (M–X_b–M)	energy, E_h
Si_2Cl_4 (br)	2.418	2.097	83.83	99.59	96.17	−2404.5684
Si_2Cl_4 (Si═Si)[b]						−2404.5425
Si_2Br_4	2.572	2.258	86.08	102.07	93.92	−10824.7154
Ge_2Cl_4	2.473	2.172	83.46	99.03	96.53	−5963.4689
Ge_2Br_4	2.643	2.322	86.21	101.18	93.79	−14383.6284
Ge_2Br_4[c]	2.45 ± 0.01	2.322	91 ± 3	173 ± 12		
$GeBr_2$[d]						−7191.7975
$GeBr_2$[e]						−7191.7909

[a] See Figure 1 for explanation of bond lengths and angles. [b] The geometry was calculated to be R(Si═Si) = 2.089 Å and R(Si–Cl) = 2.048 Å and 123.62 and 112.76° for SiSiCl and ClSiCl bond angles, respectively. [c] Reference 3. Note that the experimental values are rather uncertain. [d] At the dimer geometry, with ghost atoms. [e] At the dimer geometry, without ghost atoms.

followed by a numerical differentiation step to obtain the force constants.[21] The fundamental vibrational frequencies were obtained by scaling the theoretically obtained force fields to the experimental vibrational fundamental frequencies with the SQM method,[22] scaling the stretching and bending motions separately, while scaling all molecules together.

Results and Discussion

The first problem considered was the existence of the triplet monomeric species of $GeBr_2$ as suggested in ref 3. The size of the singlet–triplet energy separation (see Table I) renders the presence of the first excited triplet state practically impossible under the experimental conditions. The calculated singlet–triplet energy separation for the triplet state of $GeBr_2$ is 174.23 kJ/mol. This large energy separation would only get larger if correlation were added to the Hartree–Fock energy calculation, as the correlation energy must be larger in the singlet state. Note also that the singlet–triplet energy separation for $SiBr_2$ is smaller than that of $GeBr_2$ according to analogous calculations (Table I), yet nothing in the electron diffraction data suggests that the triplet species was observed for $SiBr_2$ in an experiment at an even higher temperature[1] than for $GeBr_2$.[3]

Concerning the geometries, the calculated and experimental parameters agree well (Table I) for the singlet monomers. For the supposed $GeBr_2$ triplet, a longer bond (2.37 Å) and a wider angle (141°) fit the experimental radial distribution function best, as compared with those for the singlet state (2.34 Å and 101°). In view of the good agreement for the ground-state singlet, the discrepancy between theory and experiment for the triplet again points to the fact that such a model is highly unlikely. The disagreement is especially important for the bond angles, since this parameter could have been more reliably determined experimentally than the bond length.

The other model investigated was that of the dimers present in the vapor sample. The geometries and energies of the dimers are listed in Table II. The bridging halogen type geometries were used instead of the double-bonded structures, since it was found that for $SiCl_2$ the bridging structure is 65.6 kJ/mol lower in energy than the double-bond structure. The best dimer geometry has a planar (trans) or an essentially planar (cis) four-membered ring, with its halogen atoms in symmetrical positions below or above the ring plane (Figure 1). As expected, the cis and trans forms of the molecules were essentially equal in energy. The remaining three dimer geometries were calculated only in the cis bridging conformation.

As is shown in Table II, the geometry for Ge_2Br_4 is quite different from the sharply puckered model deduced from fitting the electron diffraction radial distributions.[3] This is not surprising: due to the relatively low concentration of the additional component, the structure of the model is quite uncertain. The three other dimer geometries were optimized in order to complete the study and get an approximation of the structures of these molecules should they exist.

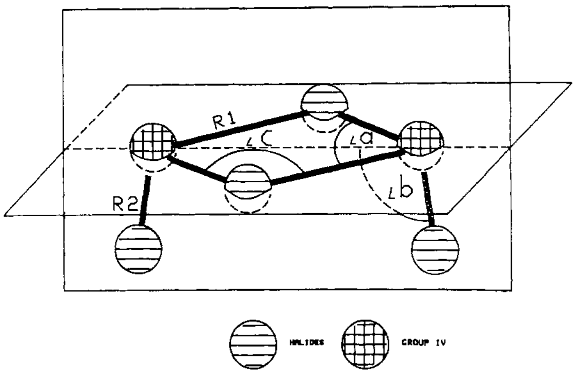

Figure 1. Reference geometry for all cis dimers.

Table III. Force Constants of Germanium and Silicon Dichlorides and Dibromides[a]

force const	$SiCl_2$	$SiBr_2$	$GeCl_2$	$GeBr_2$
$F_{R,R}$	2.661	2.146	2.486	2.039
$F_{\alpha,\alpha}$	1.225	1.121	1.089	1.005
$F_{R,\alpha}$	0.131	0.121	0.071	0.066
$F_{R,R'}$	0.280	0.261	0.242	0.226

[a] Stretching force constants are in aJ $Å^{-2}$, bending force constants are in aJ rad^{-2}, and stretch–bending force constants are in aJ $Å^{-1}$ rad^{-1}.

The direct ab initio calculation of the dimerization energy of a weakly bound dimer with such heavy atoms is an essentially unsolved problem at present. The reason for this is the large basis set superposition error (BSSE). Disregarding the BSSE, our data predict a significant bonding energy (41.0 and 39.1 kJ/mol for Ge_2Br_4 and Ge_2Cl_4, respectively) for both germanium dihalides, and much lower values for Si_2Cl_4 (≈5.8 kJ/mol) and Si_2Br_4 (≈2.1 kJ/mol). These values are probably overestimates. On the other hand, inclusion of the full counterpoise correction leads to a dissociation energy in Ge_2Br_4 of only 6.98 kJ/mol. In a system like this, the full counterpoise correction is certainly an overestimation. There also must be significant dispersion forces, not accounted for in an SCF calculation, which lead to a further stabilization of the dimer. At the present time, we can only state that Ge_2Br_4 and also Ge_2Cl_4 are bound and the dimerization energy is less than 40 kJ/mol. The silicon dihalides are predicted to be essentially unbound. There is thus some contradiction with the experimental results, in that no dimer has been observed in $GeCl_2$, while an additional component was detected in $SiCl_2$ vapor.[1-3]

In order to positively identify the species present, a matrix-infrared determination must be completed. We calculated the force constants and vibrational spectra for the singlet monomeric species of the series. The force constants are listed in Table III. As usual, the frequencies calculated from the ab initio force field overestimate the experimental fundamental frequencies. We correct for this empirically by the SQM[22] scaling procedure. The calculated frequencies can be remarkably well fitted to the experimental matrix-IR values[4-9] by using only two scale factors: 0.870 for the stretchings and 0.918 for the bendings. The scaled vibrational frequencies, as well as the experimental frequencies,[8] are listed in Table IV. These scaled frequencies exhibit very good

---

(21) Fogarasi, G.; Pulay, P. *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: New York, 1985; Vol. 14, pp 125–220.

(22) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037.

Table IV. Experimental and Scaled[a] Theoretical Vibrational Fundamental Frequencies (in cm^{-1})

molecule		ν_1	ν_2	ν_3
$SiCl_2$	expt[6]	512.5	202.2	501.4
	calcd	505.5	204.1	501.0
$SiBr_2$	expt[6]	402.6	*b*	399.5
	calcd	395.9	128.2	394.6
$GeCl_2$	expt[4]	396	*b*	372
	calcd	400.8	168.7	384.2
$GeBr_2$	expt[9]	286	110	276
	calcd	284.8	109.4	278.1

[a] Scale factors: 0.870 for stretches and 0.918 for bends. [b] Not observed experimentally.

Table V. Scaled Theoretical Fundamental Vibrational Frequencies and Intensities of *cis*-Ge_2Br_4 (in cm^{-1} and km mol^{-1}, Respectively)

	symmetry	description	freq	intens
ν_1	a_1	terminal str	318.0	104.0
ν_2	b_1	terminal str	309.0	8.5
ν_3	a_1	ring str/terminal bend	201.5	0.6
ν_4	b_2	ring str	194.8	52.4
ν_5	b_1	ring str	187.1	171.8
ν_6	a_1	ring def/ring str	144.4	0.9
ν_7	b_1	terminal bend	96.4	1.0
ν_8	a_1	ring def/terminal bend	94.6	0.2
ν_9	b_2	terminal bend	92.8	0.3
ν_{10}	a_2	terminal bend	84.7	0.0
ν_{11}	a_2	ring str	64.9	0.0
ν_{12}	a_1	ring puckering	15.4	0.1

agreement with the known experimental frequencies. The correct assignment of the two close-lying stretching frequencies in these compounds has not been quite resolved.[5,8] Unfortunately, chlorine isotopic data are of little help.[5,8] Our calculations predict that the totally symmetrical vibration, ν_1 is higher than ν_3 in each case. This agrees with the latest assignment of Miller and Andrews[4] and their earlier preference based on analogy with $SnCl_2$.[8]

We also determined the fundamental vibrational frequencies and intensities of the bridged cis dimer Ge_2Br_4 to assist in the assignment of any future infrared data. These calculations were done by using the program package CADPAC.[23] The results of this study are shown in Table V. We predict three strong infrared bands, at 318, 195 and 187 cm^{-1}, and a number of weaker ones. The observation of the three strong bands near their predicted positions would constitute, in our opinion, conclusive proof for the bridged structure of the dimer, Ge_2Br_4. No calculations have been performed for the trans form, but in view of the small splitting of the terminal Ge–Br frequencies (9 cm^{-1}), the position of the three strong infrared bands should be nearly the same.

Conclusions

Our study shows that the triplet state is not energetically accessible at 600 °C and therefore is not a possible model for the electron diffraction data obtained. The most likely model is the presence of a halogen-bridged dimer species of $GeBr_2$. The dimers, Ge_2Br_4 and Ge_2Cl_4, are probably bound by a dimerization energy of less than 40 kJ/mol. Continuing study of the matrix-infrared spectrum of the system in question should be completed in order to positively identify all species present. Our prediction of the experimental spectrum of Ge_2Br_4 should assist in this identification.

Acknowledgment. This project was supported in part by the National Science Foundation (Grant CHE-8500387). We are thankful to the J. W. Fulbright College of Arts and Sciences for the Fulbright College–Clare Hall Cambridge Dissertation Fellowship, which was awarded to J.M.C. for 1 year of research in Cambridge, England, where part of this study was completed. J.M.C. wishes to thank Dr. N. C. Handy and R. D. Amos for their help and advice and the use of their computing facilities. J.M.C. also wishes to extend a special thanks to Clare Hall, Cambridge, England, for their hospitality.

---

(23) Amos, R. D.; Rice, J. E. "CADPAC: The Cambridge Analytic Derivatives Package", issue 4.0; University of Cambridge, 1987.

Contribution from the Anorganisch-Chemisches Institut,
Universität Münster, D-4400 Münster, West Germany

Band Structure and Bonding of $Er_8Rh_5C_{12}$ and Other Carbides with C_2 Pairs

Stephen Lee,* Wolfgang Jeitschko, and Rolf-Dieter Hoffmann

Received September 15, 1988

The electronic structure of $Er_8Rh_5C_{12}$ is treated by using standard one-electron (extended Hückel) calculations that rationalize the varying Rh–C distances within the $[Rh_5C_{12}]^{24-}$ polyanion as well as the various Rh–C–Rh and Rh–C–C bond angles. Two separate models are contrasted. In the first the erbium atoms are treated as mere three-electron donors, while in the second the erbium orbitals are included. While some geometric features of $Er_8Rh_5C_{12}$ may be understood purely with the first model, others can be rationalized only with the active participation of the erbium atomic orbitals. For comparison the electronic structures of several hypothetical and real RhC_2^{3-} systems are studied including the polyanion of the $CeNiC_2$ type structure.

Introduction

In recent years a great number of ternary rare-earth transition-metal carbides have been synthesized.[1] The compound $Er_8Rh_5C_{12}$, whose synthesis and structure was reported in a previous paper,[2] is a typical example of such a compound. Little work has yet been done to characterize the band structure of these carbides. Here we report on the electronic structure of $Er_8Rh_5C_{12}$ by using a standard one-electron treatment. The especial advantage of the $Er_8Rh_5C_{12}$ system is that while the system is small enough to be amenable to one electron (extended Hückel) calculations,[3] it is also large enough to afford a diverse set of bond distances and bond angles. These geometrical variables are used throughout this work to assess the accuracy and utility of our simple electronic model.

Table I. Bond Lengths (pm) and Bond Angles (deg) in the Rh_5C_{12} Unit of $Er_8Rh_5C_{12}$[a]

Rh1–C1 (d_1)	193.7 (11)	Rh1–C11–C2 (θ_1)	167.9 (9)
Rh2–C2 (d_2)	203.8 (11)	Rh2–C2–C1 (θ_2)	149.2 (9)
Rh2–C3 (d_3)	200.8 (10)	Rh3–C3C4 (θ_3)	135.7 (7)
Rh3–C3 (d_4)	209.6 (10)	Rh3–C5–C6 (θ_4)	126.1 (8)
Rh3–C5 (d_5)	230.4 (12)		
		C1–Rh1–C1 (ϕ_1)	180.0 (0)
C1–C2 (l_1)	126.9 (16)	C2–Rh2–C3 (ϕ_2)	171.1 (4)
C3–C4 (l_2)	132.2 (14)	C3–Rh3–C5 (ϕ_3)	104.2 (4)
C5–C6 (l_3)	133.0 (16)		
Rh2–Rh3	270.8 (1)		

[a] Standard deviations in the position of the least significant digit are given in parentheses; d_i, l_i, θ_i, and ϕ_i all refer to the bonds and angles as shown in Figure 1.

---

* To whom correspondence should be addressed at the Department of Chemistry, University of Michigan, Ann Arbor, MI 48109.