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Highly Asymmetric Coordination in Alkenes: Gas-Phase Structures of *trans*-1,2-Dichloro-1,2-disilylethene and 1-Bromo-1-silylethene

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The molecular structures of *trans*-1,2-dichloro-1,2-disilylethene and 1-bromo-1-silylethene have been determined by gas-phase electron diffraction (GED) and ab initio molecular orbital calculations (MP2/6-311G*). Both compounds were found to have highly asymmetric coordination around the carbon atoms with [ab initio (r_e)/GED (r_a)] C=C—Cl [117.0/117.0(2)°] and C=C—Si [126.2/128.1(1)°] in the C_{2h} structure of *trans*-1,2-dichloro-1,2-disilylethene and C=C—Br [119.2/120.7(4)°] and C=C—Si [125.0/125.0(4)°] in the C_s structure of 1-bromo-1-silylethene. Other important structural parameters for *trans*-1,2-dichloro-1,2-disilylethene are C=C [135.2/134.5(3) pm], C—Si [189.4/187.9(2) pm], and C—Cl [175.1/174.9(1) pm], and C=C [134.2/133.4(2) pm], C–Si [187.8/187.2(3) pm], and C–Br [191.3/191.0(3) pm] for 1-bromo-1-silylethene. Further ab initio calculations were carried out on CH_2CRX and *trans*-$(CRX)_2$ (R = SiH_3, CH_3, or H; X = H, F, Cl, or Br) to gauge the effects of electron-withdrawing and electron-donating groups on the structures. They reveal some even more distorted structures. The asymmetric appearance of these molecules can largely be accounted for by valence shell electron pair repulsion theory.

Introduction

There are many literature references to the use of polysilylmethanes as precursors for chemical vapor deposition (CVD) of silicon/carbon alloys.[1−6] In a recently developed method of epitaxial deposition of silicon carbide, halogen-containing feedstock gases were introduced to improve reactivity due to increased reversibility during the deposition process. Substituted alkenes are expected to be more suited to epitaxial deposition than the corresponding alkanes, which show low thermal stability. However, although there is already structural information available for silyl alkanes halogenated at the carbon atom,[7,8] there is little on their unsaturated analogues. In the course of this study, the gas-phase electron diffraction structures of *trans*-1,2-dichloro-1,2-silylethene and 1-bromo-1-silylethene were obtained.

These two compounds are also of structural interest because they contain both electron-withdrawing and electron-donating substituents. This leads to extreme asymmetry in the coordination of the carbon atoms. In this paper we report measurements of structural parameters for two compounds and interpret the results with the aid of ab initio calculations, both for these two compounds and also for a wide range of derivatives.

Experimental Section

Synthesis. Samples of both $(SiH_3)ClC{=}CCl(SiH_3)$ (**1**) and $(SiH_3)BrC{=}CH_2$ (**2**) were prepared according to the literature method,[9] and no further purification was required prior to the electron diffraction experiment.

Computational Studies. All calculations were performed on a Dec Alpha 1000A workstation using the Gaussian98 program.[10]

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(1) Beyer, W.; Hager, R.; Schmidbaur, H.; Winterling, G. *Appl. Phys. Lett.* **1989**, *54*, 1666.

(2) Hölsch, J.; Rübel, H.; Schade, H. *Appl. Phys. Lett.* **1992**, *61*, 3029.

(3) Rübel, H.; Hölsch, J.; Schade, H. *Solid State Commun.* **1993**, *85*, 593.

(4) Zech, J.; Schmidbaur, H. *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 5.

(5) Zech, J.; Schmidbaur, H. *Chem. Ber.* **1990**, *123*, 2087.

(6) Bommers, S.; Schmidbaur, H. *Z. Naturforsch.* **1994**, *49b*, 337.

(7) Fritz, G.; Matern, E. *Z. Anorg. Allg. Chem.* **1976**, *426*, 28.

(8) Fritz, G.; Arnason, I. *Z. Anorg. Allg. Chem.* **1976**, *419*, 213.

(9) Rüdinger, C.; Beruda, H.; Schmidbaur, H. *Z. Naturforsch., B: Chem. Sci.* **1994**, *49*, 1348.

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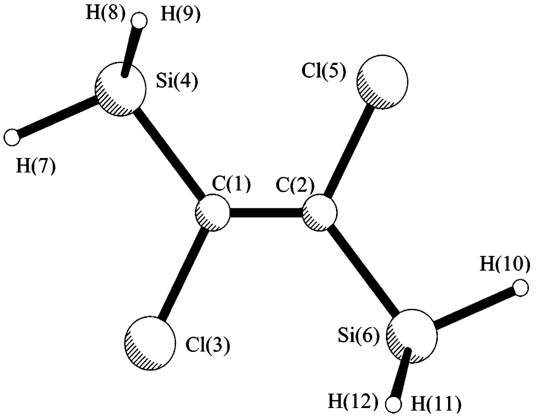

Figure 1. Molecular structure of *trans*-1,2-dichloro-1,2-disilylethene (**1**) in the gas phase, showing atom numbering.

Searches of the torsional potentials of the compounds were conducted at the HF/3-21G* level.[11−13] These resulted in the location of three conformers for **1** and one for **2**. Further optimizations for these four conformers were carried out at HF and MP2(fc) levels of theory using the standard 6-31G* and 6-311G*[14−17] basis sets. Analytical second derivatives of the energy with respect to the nuclear coordinates calculated at the HF/6-31G* level for **1** and **2** gave the force fields. These were used, without scaling, to provide estimates of the amplitudes of vibration (u) for use in the gas-phase electron-diffraction (GED) refinements. The force fields for the calculated structures were also used to calculate frequencies, which in turn provided information about the nature of the stationary points. The three conformers of **1** were all confirmed to be minima, two with C_{2h} symmetry and one with C_s, and only differed in the relative positions of the hydrogen atoms of the silyl groups. The sole conformer of **2** was also confirmed as a potential minimum with C_s symmetry. The structures of the lowest energy form of **1** and the only conformer of **2**, with the atom numbering schemes, are shown in Figures 1 and 2.

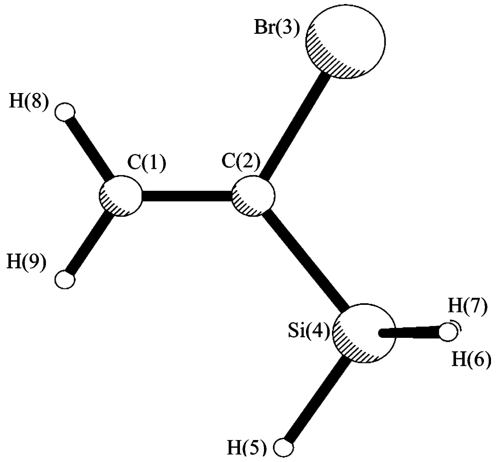

Figure 2. Molecular structure of 1-bromo-1-silylethene (**2**) in the gas phase, showing atom numbering.

Table 1. GED Experimental Conditions for **1** and **2**

compound	1		2	
camera distance/mm	127.65	255.00	127.71	285.11
Δs/nm^{-1}	4	2	4	2
s_{min}/nm^{-1}	100	40	100	40
s_1/nm^{-1}	120	60	120	60
s_2/nm^{-1}	256	128	264	110
s_{max}/nm^{-1}	300	150	308	130
correlation parameter	0.0287	0.4476	−0.2160	0.3252
scale factor	0.762(23)	0.843(12)	0.868(22)	0.847(3)
electron wavelength/pm	6.016	6.016	6.016	6.016

Gas-Phase Electron Diffraction Experiment. The Edinburgh gas-diffraction apparatus[18] was used to collect data for both compounds. For **1**, an accelerating voltage of ca. 40 kV (electron wavelength ca. 6.0 pm) was used, while maintaining the sample and nozzle temperatures at 283 and 293 K, respectively. Scattering intensities were recorded at nozzle-to-plate distances of 128 and 255 mm on Kodak Electron Image film. Three films were collected at each nozzle-to-plate distance. For **2**, an accelerating voltage of 40 kV was also used, and the sample and nozzle temperatures were both maintained at 293 K. Scattering intensities were recorded at nozzle-to-plate distances of 128 and 285 mm on Kodak Electron Image film. As with **1**, three films were recorded at each nozzle-to-camera distance. The weighting points for the off-diagonal weight matrixes, correlation parameters, and scale factors for the two camera distances are given in Table 1. The scattering patterns of benzene were also recorded for the purpose of calibration; these were analyzed in the same way as those for **1** and **2** to minimize systematic errors in wavelengths and camera distances. The electron-scattering patterns were converted into digital form using a Perkin-Elmer PDS densitometer at the Institute of Astronomy in Cambridge with a scanning program described elsewhere.[19] Data reduction and least-squares refinements were carried out using standard programs,[20,21] employing the scattering factors of Ross et al.[22]

Results

Ab Initio Calculations. Three minima were located for *trans*-1,2-dichloro-1,2-disilylethene, varying over an energy range of only 4.2 kJ mol^{-1}. However, as the three conformers differ just in the torsional position of the hydrogen atoms

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(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(11) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(12) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2979.

(13) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *103*, 5039.

(14) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(15) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(16) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(17) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(18) Huntley, C. M.; Laurenson, G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 954.

(19) Lewis, J. R.; Brain, P. T.; Rankin, D. W. H. *Spectrum* **1997**, *15*, 7.

(20) Cradock, S.; Koprowski, J. *J. Mol. Struct.* **1982**, *77*, 113.

(21) Boyd, A. S. F.; Laurenson, G. S.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *71*, 217.

(22) Ross, A. W.; Fink, M.; Hilderbrandt, R. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, p 245.

Table 2. Refined and Calculated Geometric Parameters (r_a Structure) from the GED Study of $(SiH_3)ClCCCl(SiH_3)$ (**1**) (Distances in pm, Angles in deg)[a,b]

	parameter	GED	MP2/6-311G*	restraint
p_1	C−C	134.5(3)	135.2	135.2(10)
p_2	C−Cl	174.9(1)	175.1	
p_3	C−Si	187.9(2)	189.4	
p_4	Si−H	147.4(7)	147.8	147.8(10)
p_5	∠CCSi	128.1(1)	126.2	126.6(3)
p_6	∠CCCl	117.0(2)	117.0	
p_7	∠CSiH	109.6(3)	108.2	108.2(5)
p_8	Φ H−Si−C=C	0.1(11)	0.0	0.1(10)
p_9	SiH_3 tilt	0.4(10)	1.6	0.1(10)
p_{10}	Φ Cl−C=C−Cl	0.1(11)	0.0	0.1(10)

[a] See text for parameter definitions. [b] Errors in parentheses are standard deviations in terms of the least significant digit.

on the silyl group, it was decided that only the lowest energy conformer should be considered in the refinement of the gas-phase data. It was thought that it would not be possible to distinguish between the three conformers using the GED data. Partial geometries obtained from the five highest-level calculations for the lowest-energy conformer of **1** are given in Supporting Information (SI) Table S1.

As the molecule contains both a double bond and the electronegative chlorine atoms, electron-correlation effects are especially important. Inclusion of electron-correlation results in a large increase in the length calculated for the C=C bond (from 132.5 to 135.2 pm) and a decrease in the C−Cl bond length (176.1 to 175.2 pm) from HF/6-31G* to MP2/6-31G*. The MP2/6-311G* calculation shows that basis set convergence has been attained as there is little difference between the values calculated at this and the previous MP2/6-31G* level. A further MP2 calculation was carried out using the 6-311+G* basis set, but this again made very little difference to the values calculated using the 6-311G* basis set. As basis set convergence had been achieved, it was not thought necessary or feasible to continue these calculations to a higher level, although, of course, other types of basis sets might produce slightly different parameters. Partial geometries obtained in the MP2/6-311G* calculations can be found with the electron-diffraction results in Table 2.

In the study of 1-bromo-1-silylethene (**2**), only one conformer was located. Partial geometries obtained from the five highest-level calculations for this conformer are given in SI Table S2. From this it can be seen that, as with **1**, including electron correlation is important for the C=C bond, increasing its length from 131.8 to 134.0 pm. The Hartree−Fock method appears to underestimate the C=C distance consistently. Including electron correlation, unlike in the previous case, has very little effect on the C−Br bond distance, probably because bromine is less electronegative than chlorine. Basis set convergence was achieved with the MP2/6-311G* level of calculation, apart from the C−Br bond length, which changed sizably between the MP2/6-31G* (192.5 pm) and MP2/6-311G* (191.3 pm) calculations. This can be attributed to the valence region of the double-ζ basis set being too restrictive for an atom the size of bromine. Addition of a diffuse function by using the 6-311+G* basis set can be seen to have little effect and confirms that basis set convergence was achieved using the MP2/6-311G* level, although, again, it may be possible to produce different results using a very different basis set. Partial geometries obtained in the MP2/6-311G* calculations can be found with the electron-diffraction results in Table 3.

Table 3. Refined and Calculated Geometric Parameters (r_a Structure) from the GED Study of SiH_3BrCCH_2 (**2**) (Distances in pm, Angles in deg)[a,b]

		GED	MP2/6-311G*	restraint
	Independent Parameters			
p_1	Si−H	150.0(5)	148.0	
p_2	C−Si/C−Br average	189.1(1)	189.6	
p_3	C−Si/C−Br difference	3.8(6)	3.5	3.5(8)
p_4	C−C	133.4(2)	134.2	
p_5	C−H	109.0(6)	108.7	108.6(3)
p_6	∠CSiH	108.2(4)	108.9	108.9(5)
p_7	∠CCBr	120.7(4)	119.2	
p_8	∠CCSi	125.0(4)	125.0	125.0(5)
p_9	∠CCH	120.9(4)	121.3	121.3(5)
p_{10}	Φ H−Si−C=C	1.0(10)	0.0	1.0(10)
p_{11}	SiH_3 tilt	0.2(8)	1.5	1.0(10)
p_{12}	Φ Br−C=C−H	1.0(10)	0.0	1.0(10)
	Dependent Parameters			
p_{13}	C−Si	187.2(3)	187.8	
p_{14}	C−Br	191.0(3)	191.3	

[a] See text for parameter definition. [b] Errors in parentheses are standard deviations in terms of the least significant digit.

Table 4. Selected Calculated Geometric Parameters for CH_2CRX, Where R = SiH_3, CH_3, or H and X = H, Br, Cl, or F at the MP2(fc)/6-311G* Level (Distances in pm, Angles in deg)

	H	Br	Cl	F
R = SiH_3				
C(1)=C(2)	134.7	134.3	134.3	133.8
X(3)−C(2)	109.1	191.4	175.2	137.0
Si(4)−C(2)	186.8	187.9	188.0	188.4
C(1)−C(2)−X(3)	117.5	119.1	119.3	118.2
C(1)−C(2)−Si(4)	122.9	125.1	124.8	127.3
R = CH_3				
C(1)=C(2)	134.1	133.9	133.8	133.4
X(3)−C(2)	109.0	191.0	174.7	136.1
C(4)−C(2)	150.1	149.8	149.7	148.9
C(1)−C(2)−X(3)	118.8	119.6	119.9	119.0
C(1)−C(2)−C(4)	126.1	126.0	125.9	124.6
R = H				
C(1)=C(2)	133.8	133.5	133.5	133.0
X(3)−C(2)	108.5	189.0	173.1	134.9
H(4)−C(2)	108.5	108.4	108.4	108.4
C(1)−C(2)−X(3)	121.6	122.9	123.1	121.5
C(1)−C(2)−H(4)	121.6	123.7	123.6	126.3

Ab initio calculations were also carried out for CH_2CRX and $(CRX)_2$ (R = SiH_3, CH_3, or H; X = H, F, Cl, or Br) to the MP2/6-311G* level. Basis set convergence had been achieved at this level as with **1** and **2**, and no further calculations were felt to be necessary. Partial geometries for the calculations are given in Tables 4 and 5.

Electron Diffraction Analysis for *trans*-1,2-Dichloro-1,2-disilylethene. The refinement of the gas-phase structure of **1** was carried out using a model of the lowest-energy conformation from the ab initio calculations. The model was written using C_2 symmetry, allowing for both twisting of the silyl groups and twisting about the C=C bond, which lowers the molecular symmetry from C_{2h}, as found in the ab initio calculations. The structure was defined in terms of 10 independent geometric parameters. These comprised four

Table 5. Selected Calculated Geometric Parameters for *trans*-$(CRX)_2$ (R = SiH_3, CH_3, or H; X = H, Br, Cl, or F) at the MP2(fc)/6-311G* Level (Distances in pm, Angles in deg)

	H	Br	Cl	F
R = SiH_3				
C(1)═C(2)	135.6	135.4	135.4	134.6
X(3)−C(2)	109.3	191.9	175.1	137.1
Si(4)−C(2)	187.3	189.6	189.5	188.9
C(1)−C(2)−X(3)	117.9	116.4	116.9	116.2
C(1)−C(2)−Si(4)	123.5	127.4	126.1	129.8
R = CH_3				
C(1)═C(2)	134.3	134.8	134.8	133.8
X(3)−C(2)	109.3	191.4	174.7	136.3
C(4)−C(2)	150.1	149.7	149.6	148.5
C(1)−C(2)−X(3)	118.6	118.8	119.1	117.3
C(1)−C(2)−C(4)	124.7	128.8	127.9	128.8
R = H				
C(1)═C(2)	133.8	133.7	133.6	133.1
X(3)−C(2)	108.5	188.5	172.4	134.7
H(4)−C(2)	108.5	108.4	108.4	108.3
C(1)−C(2)−X(3)	121.6	121.2	121.4	119.9
C(1)−C(2)−H(4)	121.6	124.0	123.5	125.6

bond lengths, three bond angles, and two torsions (one about the C−Si bond, the other about the C═C bond) and a tilt of the silyl group. The four bond lengths were C═C (p_1), Si−H (p_2), C−Cl (p_3), and C−Si (p_4), and the independent angles were CCSi (p_5), CCCl (p_6), and CSiH (p_7). The remainder of the parameters were a twist of the silyl group around the x axis (p_8), a tilt of the silyl group in the z direction (p_9) (defined as positive if tilted away from the adjacent chlorine atom), and a Cl−C═C−Cl torsion [180° − (p_{10})]. A full description of the model used can be found in the SI.

The starting values for the 10 geometric parameters used in the refinement were taken from the ab initio calculation (MP2/6-311G*). Theoretical (HF/6-31G*) Cartesian force fields were obtained and converted into force fields described by a set of symmetry coordinates using ASYM40.[23] The model was refined as an r_a structure (i.e., without any perpendicular amplitude corrections). In total, all 10 geometric parameters and 11 groups of amplitudes were refined. Flexible restraints were used during the refinement (seven geometric and two amplitude) using the SARACEN method and are listed in Tables 6 and 7.[24]

The final refinement, for which $R_G = 0.073$, led to the satisfactorily small difference curves for the combined molecular scattering intensity (Figure 3) and radial distribution (Figure 4). Although it appears that the short and long data do not overlap well in Figure 3, it should be noted that this is merely due to the scaling of the data with different s intervals. Final refined parameters are listed in Table 2 and interatomic distances and the corresponding amplitudes of vibration in Table 7. The least-squares correlation matrix is given in SI Table S3.

Table 6. Interatomic Distances (r_a/pm) and Amplitudes of Vibration (u/pm) for the Restrained GED Structure of $(SiH_3)ClCCCl(SiH_3)$ (**1**)

	atom pair	r_a	u	restraint
u_1	Cl(5)···Si(4)	329.7	13.9(4)	
u_2	Si(4)···Cl(3)	306.0	7.8(3)	
u_3	Cl(3)−C(1)	174.9	3.7(6)	
u_4	Si(4)−C(1)	187.9	3.8(6)	
u_5	Cl(3)···C(2)	264.6	5.8(3)	
u_6	Cl(5)···Cl(3)	428.1	5.7(3)	
u_7	Si(4)···C(2)	291.2	6.5(6)	
u_8	Si(6)···Si(4)	471.5	8.1(4)	6.9(7)
u_9	C(2)═C(1)	134.5	3.4(8)	
u_{10}	H(9)−Si(4)	148.6	9.8 (tied to u_{12})	
u_{11}	H(8)−Si(4)	148.6	9.8 (tied to u_{12})	
u_{12}	H(7)−Si(4)	148.6	9.8(6)	
u_{13}	H(8)···Cl(5)	339.1	32.6(32)	36.6(36)
u_{14}	H(9)···Cl(5)	339.6	32.6 (tied to u_{13})	

Table 7. Interatomic Distances (r_a/pm) and Amplitudes of Vibration (u/pm) for the Restrained GED Structure of SiH_3BrCCH_2 (**2**)

	atom pair	r_a	u	restraint
u_1	Si(3)···Br(4)	317.7	8.5(1)	
u_2	Br(3)−C(2)	191.0	5.4(2)	
u_3	Br(3)···C(1)	283.4	5.2(2)	
u_4	Si(4)−C(2)	187.2	5.3 (tied to u_2)	
u_5	Si(4)···C(1)	285.5	6.0 (tied to u_3)	
u_6	H(5)−Si(4)	150.0	9.9(5)	
u_7	C(2)−C(1)	133.4	4.3(3)	4.0(4)
u_8	H(8)−C(1)	109.0	7.3(4)	
u_9	H(8)···Br(3)	295.6	14.2 (fixed)	
u_{10}	H(7)···Br(3)	350.1	18.3(10)	21.5(20)
u_{11}	H(6)···Br(3)	352.2	18.3 (tied to u_{10})	

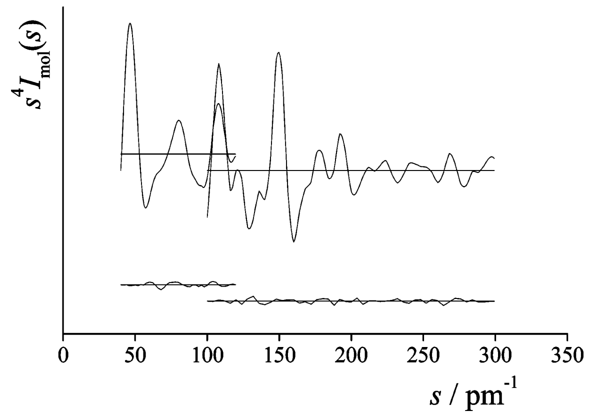

Figure 3. Experimental and final weighted difference (experimental − theoretical) molecular-scattering intensities for (**1**).

Electron Diffraction Analysis for 1-Bromo-1-silylethene. The refinement of the gas-phase structure of **2** was carried out using a model of C_s symmetry, assuming local C_{3v} symmetry within the silyl group and C_{2v} for C═CH_2. The structure was defined using 12 independent geometric parameters, comprising five bond lengths, four bond angles, and two torsions (one about the C−Si bond and one about the C═C bond) and a tilt of the silyl group. The five bond lengths were Si−H (p_1), C−Si and C−Br, which were described in terms of the average of the two distances (p_2) and the difference between them (p_3), C═C (p_4), and C−H (p_5). The average value was used for the CSiH (p_6) angles, thus defining HSiH, although the CSiH angles were subsequently changed as the group was tilted. The angles CCBr (p_7), CCSi (p_8), and CCH (p_9) were also used in the model description. The remaining parameters were a twist of the silyl group around the x axis (p_{10}), a tilt of the silyl group in the z direction (p_{11}) (defined as positive if tilted away from the adjacent bromine atom), and a C═C torsional parameter

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(23) Hedberg, L.; Mills, I. M. *J. Mol. Struct.* **1993**, *160*, 117.

(24) (a) Blake, A. J.; Brain, P. T.; McNab, H.; Millar, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A. *J. Phys. Chem.* **1996**, *100*, 12280. (b) Brain, P. T.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1996**, 4589.

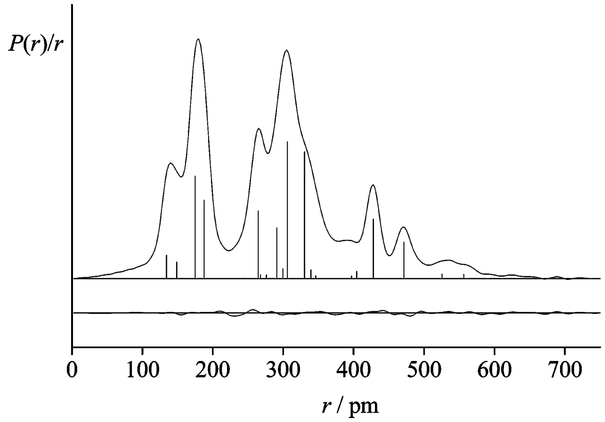

Figure 4. Experimental and difference (experimental − theoretical) radial-distribution curves, $P(r)/r$, for **1**. Before Fourier inversion, the data were multiplied by $s \exp(-0.00002s^2)/(Z_{Cl} - f_{Cl})/(Z_{Si} - f_{Si})$.

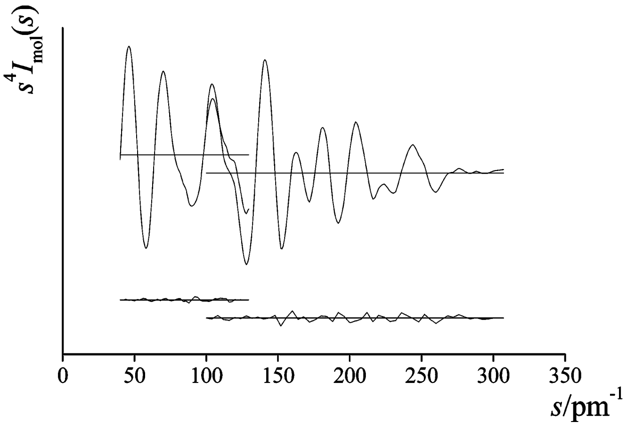

Figure 5. Experimental and final weighted difference (experimental − theoretical) molecular-scattering intensities for **2**.

around the x axis (p_{12}). A more comprehensive description of the model used can be found in the SI.

The starting values for the geometric parameters were obtained by the ab initio calculation (MP2/6-311G*), and the theoretical force field was obtained and refined exactly as described previously. In total, all 12 geometric parameters and 7 groups of amplitudes were refined. Flexible restraints were used during the refinement (eight on geometric parameters and two on amplitudes), again using the SARACEN method, and are listed in Tables 3 and 7.[24]

In the final refinement R_G was 0.054. The experimental and final difference combined molecular scattering intensity curves are shown in Figure 5 and the radial distribution curves in Figure 6. Refined parameters are listed in Table 3 and interatomic distances and the corresponding amplitudes of vibration in Table 7. The correlation matrix can be found in SI Table S4.

Discussion

The same asymmetry about the carbon−carbon double bond found in **1** and **2** is noticeably present in the results of the calculations for the series of analogous compounds, CH_2-CRX and *trans*-$(CRX)_2$ (Tables 4 and 5). The largest difference (13.6°) between ∠CCX and ∠CCR is found in *trans*-$[C(SiH_3)F]_2$, with the angles CCSi 129.8° and CCF 116.2°, the largest and smallest angles in the whole group of compounds. This can be explained by looking at the electron density, which in the C−F bond is pulled toward the fluorine atom, whereas in the C−Si bond the electron density is closer to the carbon atom. The angle at the carbon atom to the silyl group must therefore increase, while the angle to the fluorine atom must reduce. This high asymmetry is less extreme but still present in other molecules in the series *trans*-$[C(SiH_3)X]_2$. The difference between the CCSi and CCBr angles in *trans*-$[C(SiH_3)Br]_2$ (127.4° and 116.4°) is greater than the equivalent difference in $[C(SiH_3)Cl]_2$, suggesting that the effects of the electronegativities of the substituents are partially countered by steric effects of the large bromine atom. A similar trend is noticed in the series *trans*-$[C(CH_3)X]_2$, with the largest difference between the CCC and CCX angles occurring when X = F. These, and other trends, are consistent with valence shell electron pair repulsion theory (VSEPR).

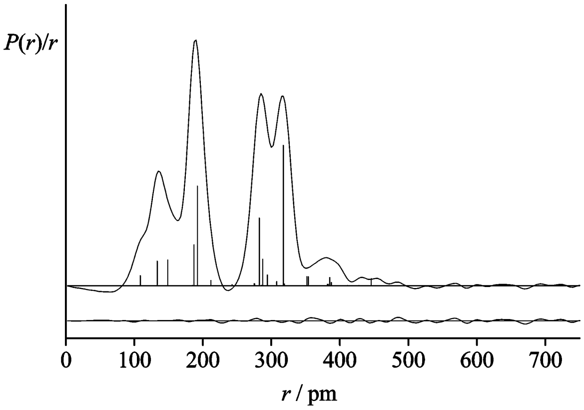

Figure 6. Experimental and difference (experimental − theoretical) radial-distribution curves, $P(r)/r$, for **2**. Before Fourier inversion, the data were multiplied by $s \exp(-0.00002s^2)/(Z_{Br} - f_{Br})/Z_{Si} - f_{Si})$.

The asymmetry is also present in the series of compounds studied that are only substituted at one end of the carbon−carbon double bond, $CH_2{=}CRX$. As with the previous examples, the highest asymmetry is exhibited in $CH_2{=}C(SiH_3)F$, where the difference between the CCSi and CCF angles is 11.5° (127.3 and 118.2°, respectively). It is also worth noting that the CCX angles are slightly larger than in the *trans*-$(CRX)_2$ analogues. This is because of the lack of steric repulsion from the hydrogen atoms at the nonsubstituted end of the carbon−carbon double bond, allowing the CCX angle to increase to avoid the R substituent.

The experimental C═C bond length obtained for 1-bromo-1-silylethene (**2**) [133.4(2) pm] is about 1 pm less than that observed for **1**. This can be attributed to the presence of another electron-donating silyl group in **1** increasing the C═C bond length, overriding the effect of an additional electron-withdrawing atom. Having observed this shortening of C═C in **2** compared to **1**, it is appropriate to extend the discussion to the series of compounds $CH_2{=}CRX$ (R = CH_3, SiH_3, or H; X = H, F, Cl, or Br) (Table 4). By observing how the C═C bond length varies on changing R and X, we can gain an understanding of how the effects of electronegativity of X compare with the consequences of changing the R group.

We have also extended these calculations to the XRC═CRX analogues (Table 5), to complete our understanding of these effects.

For the series CH_2═CRX, when X is varied and R = SiH_3 (Table 4), we see the expected systematic decrease in the length of the C═C bond as the electronegativity of X increases. This is accompanied by a lengthening of the C−X bond compared to the same bonds in $CHXCH_2$, where there is no electron-donating group adjacent to X.

Similar consequences of varying X are observed when R = CH_3. Again, the C═C bond shortens as the electronegativity of X increases, while the C−X bond is longer than that in the analogous compounds with R = H. The results for R = CH_3 show that bromine and chlorine have approximately the same effect, slightly decreasing the length of the C═C bond compared to X = H, reflecting their similar electronegativities. Hydrogen, which is less electronegative, gives a longer C═C bond length, whereas fluorine, which is much more electronegative, is seen to promote a shorter C═C bond length.

For R = CH_3 and H, the C−R bond length decreases as the electronegativity of X increases. However, for R = SiH_3, the opposite occurs, with the C−Si bond length actually increasing as the electronegativity of X increases. This can be attributed to electrostatic repulsion occurring between the carbon and silicon atoms. As the electronegativity of X increases, more electron density is drawn away from carbon making it more electropositive. This in turn repels the positive silyl group, making the C−Si bond longer. This is not observed when R = CH_3 or H as neither is as positive as the SiH_3 group.[25]

Similar trends are observed in a series of calculations carried out on XRC═CRX (R = SiH_3, CH_3, or H; X = H, F, Cl, or Br). On comparison of the lengths of the C═C bonds in CH_2CH_2, $[C(SiH_3)H]_2$ (both Table 5), and $(SiH_3)HCCH_2$ (Table 4), an increase from 133.8 and 134.7 pm to 135.6 pm is observed. This is expected, as the addition of another electron-donating silyl group further increases the length of the neighboring C═C bond.

However, unlike the examples of the ethenes substituted on one side of the C═C bond, the lengths of the Si−C bonds in Table 5 do not show the same increase as the electronegativity of X increases. In fact, the Si−C bond length in $[C(SiH_3)F]_2$ is shorter than that of $[C(SiH_3)Br]_2$ and $[C(SiH_3)Cl]_2$. This can be attributed to having competing effects at the two ends of the carbon−carbon double bond. Although both the carbon atoms in the double bond are slightly positive due to the electron- withdrawing effect of the fluorine atoms, the effect is not as pronounced as in the other examples as it is not possible to have two substantial positive charges on adjacent carbon atoms.

Conclusions

Overall, high-level calculations provide excellent estimates of differences between geometrical parameters for series of related molecules, but absolute values of some parameters are significantly unreliable. At the other extreme, VSEPR theory gives a simple explanation of many of the observed features. These simple molecules, perhaps the simplest showing such extreme distortions from idealized symmetric coordination at the central atom, provide an elegant illustration of VSEPR theory.

Supporting Information Available: Detailed descriptions of the molecular models and tables containing calculated geometric parameters and least-squares correlation matrixes for compounds **1** and **2** are available in PDF format. This information is available free of charge via the Internet at http://acs.pubs.org.

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(25) Rempfer, B.; Pfafferott, G.; Oberhammer, H.; Beckers, H.; Bürger, H.; Eujen, R.; Boggs, J. *Rev. Chim. Miner.* **1986**, *23*, 551.