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Molecular Structures of 1,1-Dimethyl-1-silacyclopent-3-ene, $(CH_3)_2SiC_4H_6$, and 1,1-Dimethyl-1-germacyclopent-3-ene, $(CH_3)_2GeC_4H_6$, Obtained by Gas-Phase Electron Diffraction and Theoretical Calculations

Kirsten Aarset, Elizabeth M. Page,* and David A. Rice*

Department of Chemistry, University of Reading, Whiteknights Park, Reading, RG6 6AD, U.K.

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The structures of 1,1-dimethyl-1-silacyclopent-3-ene and 1,1-dimethyl-1-germacyclopent-3-ene have been determined by gas-phase electron diffraction (GED), augmented by the results from ab initio calculations employing the second-order Møller−Plesset (MP2) level of theory and the 6-311+G(d) basis set. All the electrons were included in the correlation calculation. Both molecules were found to possess C_{2v} symmetry, thus the rings are planar. The results for the principal distances (r_g) and angles ($\angle_\alpha$) from the combined GED/ab initio study of 1,1-dimethyl-1-silacyclopent-3-ene (DMSiCP) (with estimated 2σ uncertainties) are $r(\mathrm{Si{-}C_r}) = 1.888(3)$ Å, $r(\mathrm{Si{-}C_t}) = 1.867(3)$ Å, $r(\mathrm{C{-}C}) = 1.503(9)$ Å, $r(\mathrm{C{=}C}) = 1.335(14)$ Å, $\langle r(\mathrm{C{-}H})\rangle = 1.109(7)$ Å, $\angle \mathrm{C_rSiC_r} = 96.3(5)°$, $\angle \mathrm{C_tSiC_t} = 110.6°$ (ab initio), $\angle \mathrm{SiC_rC_r} = 102.3(4)°$, $\angle(\mathrm{CCC})_r = 119.6(4)°$, $\angle \mathrm{HC_2H} = 106.1°$ (ab initio), $\angle \mathrm{C_4C_3H} = 120.7°$ (ab initio), $\angle(\mathrm{SiC_tH}) = 111.4°$ (ab initio) ($\mathrm{C_r}$ = ring C atom, $\mathrm{C_t}$ = methyl C atom). The results for the principal distances (r_g) and angles ($\angle_\alpha$) from the combined GED/ab initio study of 1,1-dimethyl-1-germacyclopent-3-ene (DMGeCP) (with estimated 2σ uncertainties) are $r(\mathrm{Ge{-}C_r}) = 1.963(4)$ Å, $r(\mathrm{Ge{-}C_t}) = 1.944(4)$ Å, $r(\mathrm{C{-}C}) = 1.504(12)$ Å, $r(\mathrm{C{=}C}) = 1.345(12)$ Å, $\langle r(\mathrm{C{-}H})\rangle = 1.096(11)$ Å, $\angle \mathrm{C_rGeC_r} = 93.4(9)°$, $\angle \mathrm{C_tGeC_t} = 111.0°$ (ab initio), $\angle \mathrm{GeC_rC_r} = 103.0(9)°$, $\angle(\mathrm{CCC})_r = 120.3(6)°$, $\angle \mathrm{HC_2H} = 106.6°$ (ab initio), $\angle \mathrm{C_4C_3H} = 120.1°$ (ab initio), $\angle(\mathrm{GeC_tH}) = 110.8°$ (ab initio).

Introduction

The study of the formation and reactions of gaseous silylenes and germylenes is of current interest as such species are likely to play an important part in the synthesis of silicon and germanium based electronic devices by metal-organic-chemical-vapor deposition (MOCVD). To facilitate a study of silylenes and germylenes, a number of them have been generated by the photolysis of 1,1-disubstituted-1-silacyclopent-3-enes and 1,1-disubstituted-1-germacyclopent-3-enes. Recently dimethylgermylene, which is likely to be formed when tetramethylgermanium is used in MOCVD, was detected in the gas phase for the first time, it being one of the products of the photolysis of 1,1-dimethyl-1-germacyclopent-3-ene.[1] In the same study it was also reported that dimethylsilylene can be obtained by the photolysis of 1,1-dimethyl-1-silylcyclopent-3-ene[1] at 193 nm. In view of the importance of dimethylsilylene and dimethylgermylene it was decided to study the structures of the molecules from which they are derived, namely 1,1-dimethyl-1-silacyclopent-3-ene, DMSiCP, and 1,1-dimethyl-1-germacyclopent-3-ene, DMGeCP, by gas-phase electron diffraction.

Experimental Section

1,1-dimethyl-1-silacyclopent-3-ene, DMSiCP, was obtained by reaction of MeMgI with 1,1-dichloro-1-silacyclopent-3-ene in dry ether.[2] The germanium compound, DMGeCP, was prepared similarly by treating 1,1-dichloro-1-germacyclopent-3-ene with an excess of MeMgBr in dry ether.[3] The precursor, 1,1-dichloro-1-germacyclopent-3-ene, was obtained by addition of 1,3-butadiene to a THF solution of the complex formed by reaction of $GeCl_2$ with 1,4-dioxan.[4] The electron-diffraction data were obtained with the electron diffraction apparatus at the University of Reading. Kodak Electron Image plates were used and the nozzle temperature was 25 °C. The electron wavelength was 0.058561 Å. The necessary voltage/distance calibration to measure the wavelength was achieved using benzene as reference. For both of the compounds studied one plate from each camera distance (short camera ca. 25 cm and long camera ca. 50 cm) was recorded. The optical densities were measured using a commercial AGFA II scanner.[5,6] The data covering the ranges $3.00 \le s/\text{Å}^{-1} \le 15.50$ and $8.00 \le s/\text{Å}^{-1} \le 27.00$, with $\Delta s = 0.25$ Å^{-1} (where $s = 4\pi\lambda^{-1}\sin\theta$ and 2θ is the scattering angle) were processed as previously described.[7] The experimental intensity curves are shown in Figure 1. The data are available as Supporting Information. Radial distribution (RD) curves (Figure 2) were calculated in the usual way by Fourier transformation of the functions $I'_m(s) = Z_xZ_C(A_xA_C)^{-1}sI_m(s)\exp(-Bs^2)$ (x = Si or Ge) with $B = 0.0020$ Å^{-2} and where $A = s^2F$ and F is the absolute value of the complex scattering amplitudes. The scattering amplitudes and phases were taken from tables.[8]

Theoretical Calculations

To aid in the elucidation of the structures of DMSiCP and DMGeCP theoretical calculations using GAUSSIAN94[9] (ab initio calculations) and ADF[10−12] (DFT calculations) were performed. The influences of the method, level of theory, and basis set (number of diffuse and polarization functions) employed on the structure parameters were studied by performing several calculations for each molecule. For both molecules Hartree−Fock (HF) and second-order Møller−Plesset (MP2)

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* To whom correspondence should be addressed. E-mail: d.a.rice@reading.ac.uk.

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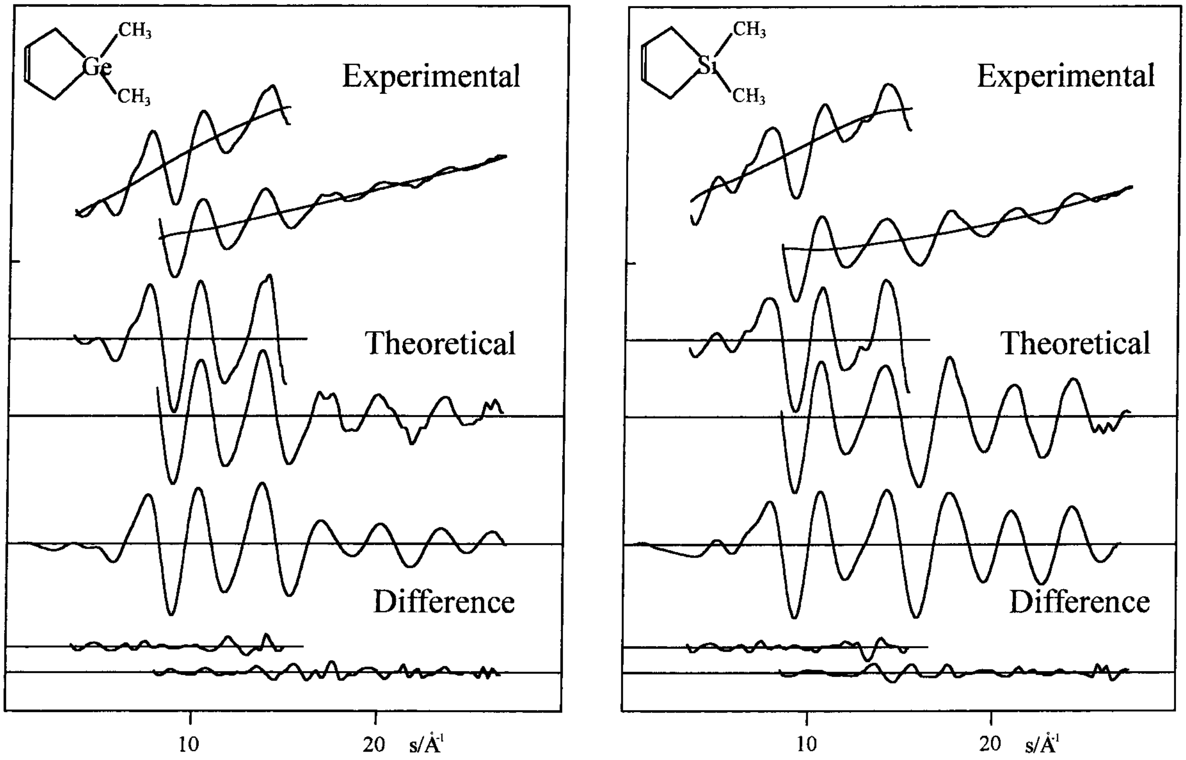

Figure 1. Experimental intensity curves $s^4I_t(s)$ for (a) 1,1-dimethyl-1-silacyclopent-3-ene (DMSiCP) and (b) 1,1-dimethyl-1-germacyclopent-3-ene (DMGeCP). Each plate is shown magnified 5× with respect to the final backgrounds on which they are superimposed.

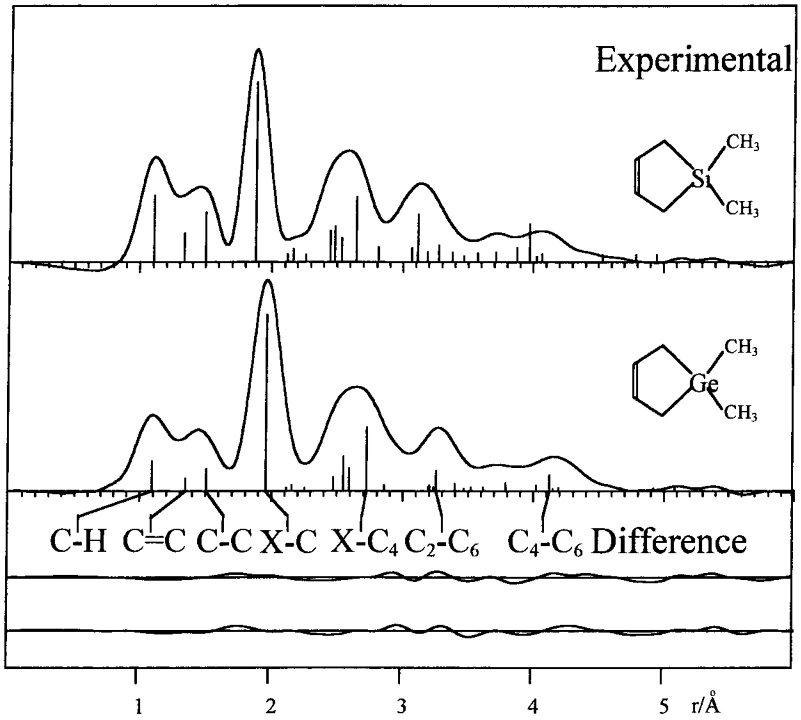

Figure 2. Radial distribution curves for 1,1-dimethyl-1-silacyclopent-3-ene (X = Si (DMSiCP)) and 1,1-dimethyl-1-germacyclopent-3-ene (X = Ge (DMGeCP)). The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 \leq s/\text{Å}^{-1} \leq 2.50$ and $B/\text{Å}^2 = 0.002$. Difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights.

calculations were performed together with the 6-311G basis set with differing numbers of diffuse and polarization functions added (see Tables 1 and 2). In addition, calculations with third-order Møller–Plesset (MP3), fourth order Møller–Plesset with single, double and quadruple substitutions (MP4(SDQ)), and configuration interaction with single and double substitutions (QCISD) levels of theory were performed for DMSiCP. The calculations using higher level than MP2 were all performed using the 6-311G(d) basis set and the core electrons were not included in the correlation calculations. In addition to calculations for the equilibrium C_{2v} form, ring puckering potentials were also calculated employing HF/6-311G(d,p) (see Figure 3). The constraints used for some of the structural parameters, in the theoretical model described below, were obtained using

TABLE 1: Results from Theoretical Calculations for 1,1-Dimethyl-1-silacyclopent-3-ene (DMSiCP)

	HF/6-311								
parameters[a]	G(d)	+G(d)	++G(d)	G(d,p)	+G(d,p)	++G(d,p)	G(2d,2p)	+G(2d,2p)	++G(2d,2p)
$r(\mathrm{Si-C_r})$	1.9048	1.9057	1.9056	1.9041	1.9047	1.9049	1.8999	1.9005	1.9005
$r(\mathrm{Si-C_t})$	1.8852	1.8859	1.8854	1.8840	1.8841	1.8842	1.8804	1.8805	1.8805
$r(\mathrm{C-C})$	1.5164	1.5166	1.5164	1.5164	1.5164	1.5164	1.5140	1.5140	1.5140
$r(\mathrm{C=C})$	1.3240	1.3254	1.3253	1.3238	1.3251	1.3251	1.3200	1.3218	1.3218
$r(\mathrm{C_2-H})$	1.0880	1.0881	1.0881	1.0887	1.0887	1.0887	1.0855	1.0854	1.0854
$r(\mathrm{C_3-H})$	1.0785	1.0787	1.0787	1.0787	1.0787	1.0787	1.0759	1.0758	1.0758
$r(\mathrm{C_t-H})_\mathrm{ave}$	1.0867	1.0868	1.0869	1.0878	1.0879	1.0879	1.0847	1.0847	1.0847
$\angle(\mathrm{SiC_rC_r})$	102.76	102.82	102.83	102.74	102.80	102.81	102.60	102.67	102.67
$\angle(\mathrm{CCC})_\mathrm{r}$	119.53	119.49	119.49	119.52	119.49	119.49	119.59	119.55	119.55
$\angle(\mathrm{C_rSiC_r})$	95.44	95.38	95.37	95.47	95.42	95.40	95.61	95.57	95.57
$\angle(\mathrm{C_tSiC_t})$	109.79	109.81	109.87	109.78	109.81	109.85	109.84	109.88	109.88
$\angle(\mathrm{C_rSiC_t})$	112.76	112.77	112.76	112.76	112.76	112.75	112.71	112.70	112.70
$\angle(\mathrm{SiC_rH})$	113.21	113.21	113.20	113.12	113.12	113.11	113.05	113.05	113.05
$\angle(\mathrm{C_3C_2H})$	110.86	110.81	110.84	110.84	110.79	110.81	110.96	110.91	110.91
$\angle(\mathrm{C_2C_3H})$	119.64	119.68	119.69	119.65	119.69	119.70	119.64	119.70	119.70
$\angle(\mathrm{C_4C_3H})$	120.84	120.83	120.83	120.83	120.82	120.81	120.77	120.75	120.75
$\angle(\mathrm{SiC_tH})_\mathrm{ave}$	111.46	111.45	111.47	111.23	111.23	111.23	111.10	111.08	111.08

		MP2[c]/6-311										
parameters[a]	MP2[b]/ 6-311G(d)	G(d,p)	+G(d)	+G(d,p)	G(d)	G(d,p)	+G(d)	+G(d,p)	MP3[b]/ 6-311G(d)	MP4(SDQ)[b]/ 6-311G(d)	QCISD/ 6-311G(d)	BLYP/ TZ[d]
$r(\mathrm{Si-C_r})$	1.9014	1.9008	1.9018	1.9013	1.8988	1.8981	1.8993	1.8988	1.9028	1.9044	1.9046	1.9291
$r(\mathrm{Si-C_t})$	1.8789	1.8779	1.8788	1.8781	1.8766	1.8757	1.8765	1.8760	1.8803	1.8818	1.8823	1.9051
$r(\mathrm{C-C})$	1.5144	1.5148	1.5147	1.5150	1.5124	1.5126	1.5127	1.5128	1.5202	1.5200	1.5209	1.5253
$r(\mathrm{C=C})$	1.3480	1.3482	1.3499	1.3501	1.3466	1.3469	1.3486	1.3487	1.3426	1.3456	1.3462	1.3469
$r(\mathrm{C_2-H})$	1.0974	1.0977	1.0977	1.0978	1.0969	1.0970	1.0971	1.0970	1.0974	1.0997	1.1002	1.1015
$r(\mathrm{C_3-H})$	1.0899	1.0893	1.0902	1.0896	1.0894	1.0888	1.0897	1.0891	1.0891	1.0912	1.0917	1.0916
$r(\mathrm{C_t-H})_\mathrm{ave}$	1.0941	1.0950	1.0946	1.0954	1.0936	1.0943	1.0941	1.0947	1.0950	1.0971	1.0978	1.0987
$\angle(\mathrm{SiC_rC_r})$	102.95	102.99	103.07	103.09	102.93	102.97	103.04	103.06	102.97	103.00	103.02	103.17
$\angle(\mathrm{CCC})_\mathrm{r}$	119.13	119.09	119.06	119.03	119.13	119.10	119.06	119.04	119.14	119.12	119.10	119.37
$\angle(\mathrm{C_rSiC_r})$	95.83	95.83	95.75	95.76	95.87	95.87	95.79	95.80	95.78	95.75	95.76	94.93
$\angle(\mathrm{C_tSiC_t})$	110.32	110.33	110.59	110.58	110.33	110.34	110.59	110.58	110.16	110.18	110.15	111.03
$\angle(\mathrm{C_rSiC_t})$	112.51	112.51	112.45	112.45	112.50	112.50	112.44	112.44	112.57	112.57	112.58	112.51
$\angle(\mathrm{SiC_rH})$	112.96	112.83	112.99	112.86	112.94	112.80	112.98	112.83	113.05	113.07	113.08	112.72
$\angle(\mathrm{C_3C_2H})$	110.99	110.96	110.93	110.90	111.00	110.94	110.94	110.88	110.88	110.90	110.88	111.36
$\angle(\mathrm{C_2C_3H})$	120.17	120.22	120.27	120.31	120.16	120.22	120.26	120.31	119.83	119.93	119.93	119.81
$\angle(\mathrm{C_4C_3H})$	120.70	120.68	120.67	120.65	120.71	120.68	120.68	120.65	121.03	120.95	120.97	120.82
$\angle(\mathrm{SiC_tH})_\mathrm{ave}$	111.25	111.07	111.35	111.16	111.23	111.01	111.34	111.09	111.30	111.36	111.37	111.30

[a] The distances are in angstroms and the angles are in degrees. [b] The core electrons excluded from the correlation calculations. [c] All the electrons included in the correlation calculations. [d] Triple-ζ basis set with two polarization functions.

Møller−Plesset level of theory, with all the electrons included in the correlation calculation, denoted MP2(FU), and the 6-311+G(d) basis set. To perform the electron diffraction refinements vibrational parameters (l = root-mean-square amplitudes of vibration, K = perpendicular amplitude corrections, δr = centrifugal distortions) are also needed and these were calculated, with the force field obtained in the HF/6-311G(d,p) calculation (scaled by a factor of 0.9), using ASYM40.[13] One DFT calculation was performed for each molecule, using BLYP level of theory and a triple-ζ basis set with two polarization functions.

Analysis of the Structures. The theoretical calculations performed indicate that DMSiCP and DMGeCP have planar rings and thus possess C_{2v} symmetry. Our findings are in accord with the results of a study of the vibrational spectra of DMGeCP[14] and the results of electron diffraction and/or spectroscopic studies on three molecules related to DMSiCP, namely, $\mathrm{R_2SiC_4H_6}$ (R = H, Cl, and F[16] (electron diffraction) and R = H,[15] and Cl[14] (spectroscopy)) which were also reported to have C_{2v} symmetry.

The molecules DMSiCP and DMGeCP are depicted in Figure 4, which contains the atom numbering scheme. As the theoretical calculations indicated that DMSiCP and DMGeCP have C_{2v} symmetry, models with this symmetry were adopted in the analyses of the electron diffraction data. Such models can be defined by the following parameters (X = Si or Ge): $\langle r(\mathrm{X-C})\rangle = 0.5[r(\mathrm{X-C_r}) + r(\mathrm{X-C_t})]$, $\Delta r(\mathrm{X-C}) = [r(\mathrm{X-C_r}) - r(\mathrm{X-C_t})]$, $\langle r(\mathrm{C-C})\rangle = 0.5[r(\mathrm{C-C}) + r(\mathrm{C=C})]$, $\Delta r(\mathrm{C-C}) = [r(\mathrm{C-C}) - r(\mathrm{C=C})]$, $\langle r(\mathrm{C-H})\rangle = (1/3)[r(\mathrm{C_2-H_8}) + r(\mathrm{C_3-H_{10}}) + r(\mathrm{C_6-H_{14}})]$, $\Delta r_1(\mathrm{C-H}) = [r(\mathrm{C_2-H_8}) - r(\mathrm{C_3-H_{10}})]$, $\Delta r_2(\mathrm{C-H}) = [r(\mathrm{C_2-H_8}) - r(\mathrm{C_6-H_{14}})]$, $\angle\mathrm{C_rXC_r}$, $\angle\mathrm{C_tXC_t}$, $\angle\mathrm{XC_tH}$, $\angle\mathrm{HC_2H}$, $\angle\mathrm{C_4C_3H}$ (r = ring, t = terminal). Local C_{3v} symmetry was assumed for the methyl groups.

The electron diffraction refinements were carried out by the least-squares method,[17] adjusting a theoretical $sI_\mathrm{m}(s)$ curve simultaneously to the two intensity curves (one from each camera distance) using a unit weight matrix. The geometries were calculated on the basis of r_α parameters. These were converted to the r_a type required by the scattering intensity formula by using values of centrifugal distortions (δr), perpendicular amplitude corrections (K), and root-mean-square amplitudes of vibration (l).

In the earlier electron diffraction study of $\mathrm{R_2SiC_4H_6}$ (R = H, Cl, F)[16] it was found that these molecules have a large amplitude ring puckering motion. The calculations performed in this study gave fairly low frequencies for the ring puckering modes in DMSiCP and DMGeCP (44 and 54 cm^{-1}, respectively). The shape of the calculated puckering potential (see Figure 3) is steep (or "narrow"), and a good fit to the experimental data was obtained using nondynamic C_{2v} models. These observations, plus a consideration of the calculated vibrational parameters, provided convincing evidence that the use of dynamic models

TABLE 2: Results from Theoretical Calculations for 1,1-Dimethyl-1-germacyclopent-3-ene (DMGeCP)

	HF/6-311									MP2[b]/6-311		MP2[c]/6-311		BLYP
parameters[a]	G(d)	+G(d)	++G(d)	G(d,p)	+G(d,p)	++G(d,p)	G(2d,2p)	+G(2d,2p)	++G(2d,2p)	G(d)	+G(d)	G(d)	+G(d)	TZ[d]
$r(Ge-C_r)$	1.9822	1.9826	1.9827	1.9814	1.9817	1.9819	1.9798	1.9803	1.9803	1.9836	1.9838	1.9724	1.9722	2.0167
$r(Ge-C_t)$	1.9651	1.9657	1.9657	1.9638	1.9637	1.9638	1.9641	1.9642	1.9642	1.9625	1.9625	1.9519	1.9517	1.9997
$r(C-C)$	1.5142	1.5145	1.5145	1.5144	1.5144	1.5144	1.5121	1.5121	1.5121	1.5120	1.5124	1.5096	1.5101	1.5199
$r(C{=}C)$	1.3244	1.3259	1.3258	1.3243	1.3256	1.3257	1.3205	1.3223	1.3223	1.3487	1.3506	1.3472	1.3492	1.3438
$r(C_2-H)$	1.0868	1.0868	1.0868	1.0874	1.0874	1.0874	1.0844	1.0843	1.0843	1.0967	1.0970	1.0961	1.0964	1.1005
$r(C_3-H)$	1.0790	1.0791	1.0791	1.0791	1.0791	1.0791	1.0763	1.0761	1.0761	1.0904	1.0907	1.0899	1.0902	1.0920
$r(C_t-H)_{ave}$	1.0851	1.0852	1.0851	1.0862	1.0863	1.0863	1.0832	1.0832	1.0832	1.0930	1.0935	1.0923	1.0928	1.0977
$\angle(GeC_rC_r)$	102.63	102.69	102.70	102.61	102.66	102.66	102.50	102.56	102.56	102.88	102.99	102.89	103.00	102.77
$\angle(CCC)_r$	120.84	120.80	120.80	120.84	120.80	120.80	120.94	120.90	120.90	120.50	120.42	120.36	120.27	121.03
$\angle(C_rGeC_r)$	93.05	93.02	93.01	93.11	93.07	93.06	93.13	93.09	93.09	93.24	93.17	93.50	93.44	92.39
$\angle(C_tGeC_t)$	110.13	110.16	110.18	110.11	110.13	110.14	110.07	110.08	110.08	110.71	110.94	110.72	110.99	110.56
$\angle(C_rGeC_t)$	113.20	113.20	113.20	113.20	113.20	113.20	113.21	113.21	113.21	112.98	112.93	112.92	112.85	113.27
$\angle(GeC_rH)$	112.88	112.87	112.85	112.79	112.78	112.77	112.79	112.78	112.78	112.46	112.48	112.38	112.42	112.22
$\angle(C_3C_2H)$	111.05	111.00	111.01	111.03	110.99	111.00	111.09	111.05	111.05	111.30	111.23	111.32	111.25	111.47
$\angle(C_2C_3H)$	119.00	119.04	119.06	119.00	119.06	119.06	118.97	119.03	119.03	119.51	119.60	119.56	119.67	118.83
$\angle(C_4C_3H)$	120.16	120.16	120.14	120.16	120.14	120.14	120.09	120.08	120.08	119.99	119.98	120.08	120.06	120.14
$\angle(GeC_tH)_{ave}$	111.02	111.01	110.99	110.79	110.78	110.77	110.73	110.72	110.72	110.73	110.81	110.69	110.81	110.34

[a] The distances are in angstroms and the angles are in degrees. [b] The core electrons excluded from the correlation calculations. [c] All the electrons included in the correlation calculations. [d] Triple-ζ basis set with two polarization functions.

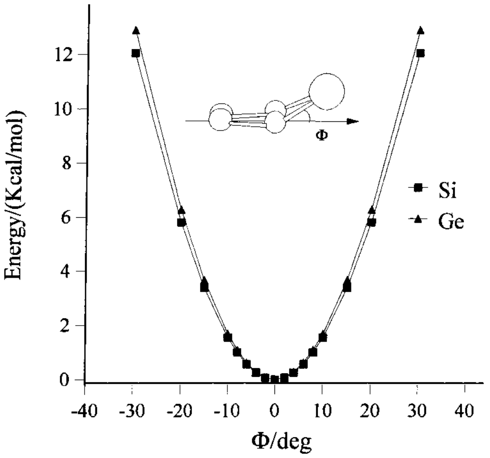

Figure 3. Ring puckering potential obtained by ab initio calculations employing HF/6-311G(d,p).

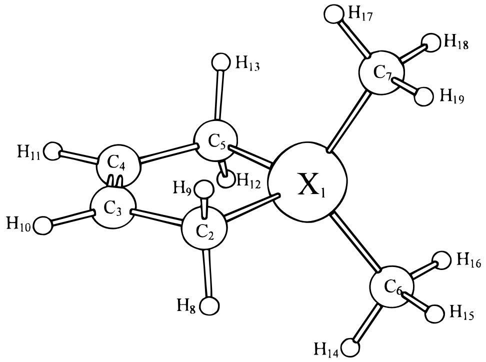

Figure 4. Diagram showing the numbering scheme of 1,1-dimethyl-1-Xcyclopent-3-ene (X = Si or Ge).

to describe the structures of DMSiCP and DMGeCP was not needed. Unsuccessful attempts were made to refine the puckering angle. In DMGeCP the angle did not converge while for DMSiCP the uncertainty on the value was very large 5(24)°. Including it in the refinements did not lead to an improvement in the fit between the theoretical and experimental data. The other important structural parameters were not affected significantly by changes in the puckering angle for either molecule.

It was possible to refine all the important structural parameters for the ring ($\langle r(X-C)\rangle$, $\langle r(C-C)\rangle$, $\Delta r(C-C)$, $\langle r(C-H)\rangle$, and $\angle C_rXC_r$). The terminal CXC angle and all the angles depending on the position of the hydrogen atoms could not be refined. The structural parameters that could not be refined were constrained at the values obtained from the ab initio calculations (MP2(FU)/6-311+G(d)). The amplitudes associated with bond distances were all refined except for those associated with $r(C-C)$ and $r(C{=}C)$ in DMGeCP.

Results from the final refinements for DMSiCP and DMGeCP are given in Table 3. Intensity curves calculated for the final models are shown in Figure 1, together with experimental and difference curves. Figure 2 contains the corresponding RD-curves, and the correlation matrixes for the refined parameters are given in Tables 4 and 5.

Discussion

All the bonded distances and the C_rXC_r angle (X = Si and Ge, r = ring) in both DMSiCP and DMGeCP were refined; thus, the geometry of the ring was well determined from the electron diffraction data. It was not possible to refine the angles subtended by the methyl groups ($\angle C_tXC_t$; X = Si or Ge) or

TABLE 3: Structural Parameters for 1,1-Dimethyl-1-silacyclopent-3-ene (DMSiCP) and 1,1-Dimethyl-1-germacyclopent-3-ene (DMGeCP)

parameters[a]	1,1-dimethyl-1-silacyclopent-3-ene				1,1-dimethyl-1-germacyclopent-3-ene			
	electron diffraction		ab initio[b]		electron diffraction		ab initio[b]	
	$r_\alpha/\angle_\alpha$		$r_e/\angle_e$		$r_\alpha/\angle_\alpha$		$r_e/\angle_e$	
$\langle r(X-C)\rangle$	1.874 (3)		1.888		1.953 (4)		1.962	
$\Delta r(X-C)$	[0.023]		0.023		[0.021]		0.021	
$\langle r(C-C)\rangle$	1.414 (10)		1.431		1.422 (14)		1.430	
$\Delta r(C-C)$	0.164 (11)		0.164		0.158 (17)		0.161	
$\langle r(C-H)\rangle$	1.099 (7)		1.094		1.086 (10)		1.093	
$\Delta r_1(C-H)$	[0.007]		0.007		[0.006]		0.006	
$\Delta r_2(C-H)$	[0.003]		0.003		[0.004]		0.004	
$\angle(C_rXC_r)$	96.3 (5)		95.8		93.4 (9)		93.4	
$\angle(C_tXC_t)$	[110.6]		110.6		[111.0]		111.0	
$\angle XCH_t$	[111.4]		111.4		[110.8]		110.8	
$\angle HC_2H$	[106.1]		106.1		[106.6]		106.6	
$\angle C_4C_3H$	[120.7]		120.7		[120.1]		120.1	
	$r_g/\angle_\alpha$	$l_{refined}$	$r_e/\angle_e$	$l_{calculated}$	$r_g/\angle_\alpha$	$l_{refined}$	$r_e/\angle_e$	$l_{calculated}$
$r(X-C_r)$	1.888 (3)	0.058 (5)[c]	1.899	0.053	1.963 (4)	0.060 (6)[c]	1.972	0.053
$r(X-C_t)$	1.867 (3)	0.057 (5)[c]	1.877	0.053	1.944 (4)	0.060 (6)[c]	1.952	0.053
$r(C-C)$	1.503 (9)	0.048 (13)[c]	1.513	0.051	1.504 (12)	[0.051]	1.510	0.051
$r(C=C)$	1.335 (14)	0.039 (13)[c]	1.349	0.041	1.345 (12)	[0.041]	1.349	0.041
$r(C-H)_{av}$	1.109 (7)	0.070 (9)	1.094	0.078	1.096 (11)	0.073 (12)	1.094	0.077
$r(X\cdots C_4)$	2.647 (10)	0.073 (8)	2.682	0.059	2.723 (18)	0.112 (16)	2.741	0.058
$r(C_2\cdots C_4)$	2.450 (14)	[0.057]	2.468	0.057	2.470 (19)	[0.057]	2.481	0.057
$r(C_2\cdots C_5)$	2.811 (11)	[0.065]	2.818	0.065	2.858 (21)	[0.066]	2.872	0.066
$r(C_2\cdots C_6)$	3.116 (6)	[0.108]	3.139	0.108	3.253 (7)	[0.115]	3.269	0.115
$r(C_4\cdots C_6)$	3.987 (10)	[0.257]	4.033	0.257	4.120 (17)	0.167 (69)	4.146	0.205
$r(C_6\cdots C_7)$	3.067 (5)	[0.104]	3.085	0.104	3.201 (6)	[0.115]	3.212	0.115
$\angle(XC_rC_r)$	102.3 (4)		103.0		103.0 (9)		103.0	
$\angle(CCC)_r$	119.6 (4)		119.1		120.3 (6)		120.3	
R-factor	0.117				0.127			

[a] Distances (*r*) and amplitudes (*l*) are in angstroms and angles (∠) are in degrees. Parenthesized values are 2σ and include estimates of uncertainties in voltage/nozzle height and of correlation in experimental data. Values in square brackets were kept constant at the calculated values. [b] MP2 level of theory and 6-311+G(d) basis set used. [c] Refined as a group.

TABLE 4: Correlation Matrix (×100) for Parameters Refined in the Final Least-Square Refinements for 1,1-Dimethyl-1-silacyclopent-3-ene (DMSiCP)

	σ_{LS}[a]	r_1	r_2	r_3	r_4	$\angle_5$	l_6	l_7	l_8	l_9
1 $\langle r(Si-C)\rangle$	0.0008	100	−22	12	1	−12	−23	−25	−18	3
2 $\langle r(C-C)\rangle$	0.0037		100	−54	23	65	36	18	59	−22
3 $\Delta r(C-C)$	0.0040			100	−30	−17	−1	19	−29	7
4 $\langle r(C-H)\rangle$	0.0025				100	11	−4	−28	6	4
5 $\angle(C_rSiC_r)$	0.1790					100	18	10	34	−20
6 $l(Si-C_r)$	0.0015						100	54	46	0
7 $l(C-C)$	0.0045							100	36	4
8 $l(C-H)$	0.0029								100	−4
9 $l(Si\cdots C_4)$	0.0028									100

[a] Standard deviations from least-squares refinements. Distances (*r*) and amplitudes (*l*) are in angstroms, angles (∠) in degrees.

TABLE 5: Correlation Matrix (×100) for Parameters Refined in the Final Least-Square Refinements for 1,1-Dimethyl-1-germacyclopent-3-ene (DMGeCP)

	σ_{LS}[a]	r_1	r_2	r_3	r_4	$\angle_5$	l_6	l_7	l_8	l_9
1 $\langle r(Ge-C)\rangle$	0.0011	100	−21	6	−5	−12	−9	−7	7	−2
2 $\langle r(C-C)\rangle$	0.0049		100	−49	7	43	16	45	−18	0
3 $\Delta r(C-C)$	0.0060			100	−10	−2	−8	−29	−2	2
4 $\langle r(C-H)\rangle$	0.0037				100	−2	5	1	23	−2
5 $\angle(C_rGeC_r)$	0.3181					100	−11	11	−31	−1
6 $l(Ge-C_r)$	0.0020						100	28	19	6
7 $l(C-H)$	0.0040							100	1	1
8 $l(Ge\cdots C_4)$	0.0056								100	−3
9 $l(C_4\cdots C_6)$	0.0242									100

[a] Standard deviations from least-squares refinements. Distances (*r*) and amplitudes (*l*) are in angstroms, angles (∠) in degrees.

angles involving hydrogen, so these were not well determined by the electron diffraction refinements.

The model assuming a planar ring for $(CH_3)_2XC_4H_6$ (X = Si, Ge) gave excellent agreement with the electron diffraction data and with the results from theoretical calculations. The finding is also in accord with those geometries found for related molecules. [14-16] The parent molecule, cyclopentene, is known to have a nonplanar ring structure. The departure from planarity is ascribed to strain experienced by adjacent CH_2 groups in the eclipsed orientation.[18] If the central CH_2 group is replaced by −O− as in 2,5-dihydrofuran [19] or the C atom by Si as in $R_2SiC_4H_6$ (R = H, Cl, F) [14-16] the eclipsing strain is relieved and the ring able to resume C_{2v} symmetry. Thus it would appear that the longer Si−C and Ge−C distances in DMSiCP and DMGeCP allow the molecules to assume a planar structure, albeit with large amplitude ring puckering motion. It would be interesting to compare the planar ring geometry of the title molecules with that of the ring in the C analogue 1,1-dimethylcyclopent-3-ene but no structural information appears to be available for this molecule. Using the theory put forward above based on the geometries of analogous molecules we would predict 1,1-dimethylcyclopent-3-ene to have a puckered ring structure. In the absence of structural information relating to 1,1-dimethylcyclopent-3-ene we have carried out ab initio calculations using the Hartree−Fock and Møller−Plesset levels of theory with the 6-311+G(d) basis set in which the ring was indeed found to be nonplanar with a ring-puckering angle of 12.4° (MP^2) and 16.2° (HF). The value of the puckering angle is somewhat less than that found experimentally for cyclopentene (29(2)°)[18] but still demonstrates the preference of the CH_2

TABLE 6: Comparison of Structure Parameters for $R_2SiC_4H_6$ (R = H, CH_3, Cl, F)

	$H_2SiC_4H_6$		$(CH_3)_2SiC_4H_6$		$Cl_2SiC_4H_6$		$F_2SiC_4H_6$	
parameters[a]	GED	ab initio[b]	GED	ab initio[b]	GED	ab initio[b]	GED	ab initio[b]
$r(Si-C_r)$	1.899 (3)	1.897	1.886 (3)	1.899	1.876 (6)	1.871	1.847 (3)	1.863
$r(C-C)$	1.533 (4)	1.514	1.501 (9)	1.512	1.526 (7)	1.514	[1.519]	1.516
$r(C=C)$	1.359 (5)	1.348	1.334 (14)	1.347	1.330 (10)	1.349	1.378 (7)	1.350
$\angle(C_rSiC_r)$	95.8 (5)	96.3	96.3 (5)	95.9	99.6 (30)	98.4	98.7 (4)	99.1
$\angle(SiC_rC_r)$	103.7 (5)	102.6	102.3 (4)	102.9	100.0 (34)	101.5	102.7 (4)	101.1
$\angle(CCC)_r$	118.4 (2)	119.2	119.6 (4)	119.1	120.3 (10)	119.3	117.9 (3)	119.3
$l(Si-C_r)$	0.062 (4)		0.058 (5)		[0.06]		0.064 (5)	
$l(C-C)$	0.044 (7)		0.048 (13)		0.053 (10)		[0.047]	
$l(C=C)$	0.037(11)		0.039 (13)		[0.038]		[0.038]	
$l(C-H)_{ave}$	0.099(8)		0.070 (9)		0.052 (14)		0.105 (15)	
ref	16	this work	this work	this work	16	this work	16	this work

[a] Distances (r_a) and amplitudes (l) are in angstroms and angles ($\angle_\alpha$) are in degrees. Values in square brackets were kept constant. [b] MP2 level of theory and 6-311+G(d) basis set used.

groups for avoiding an eclipsed orientation and results in a nonplanar ring.

In Table 3 the structural parameters of DMSiCP and DMGeCP are given. The $Si-C_r$ ($r_g = 1.888(3)$ Å) and $Si-C_t$ ($r_g = 1.867(3)$ Å) bonds were found to be about 0.08 Å shorter than the $Ge-C_r$ ($r_g = 1.963(4)$ Å) and $Ge-C_t$ ($r_g = 1.944(4)$ Å) bonds. The C−C single bonds were similar in DMSiCP ($r_g = 1.503(9)$ Å) and DMGeCP ($r_g = 1.504(12)$ Å), while the carbon−carbon double bond in DMSiCP ($r_g = 1.335(14)$ Å) was refined to be shorter than the corresponding distance in DMGeCP ($r_g = 1.345(12)$ Å), but within the uncertainty limits. The C_rXC_r angle (X = Si and Ge) was found to be larger in DMSiCP (96.3(5)°) than in DMGeCP (93.4(9)°), which might result from the shorter $X-C_r$ distance in the Si compound. Only small differences between the two molecules were found for the other bond angles in the ring (Table 3).

In Table 1 the results from the theoretical calculations for DMSiCP are given. The structural parameters obtained by ab initio calculations show, for a given parameter, only small changes when diffuse and polarization functions are added to the 6-311G basis set or when the level of theory was changed, except for the carbon−carbon double bond. The length of this bond was found to be sensitive to the change in level of theory, as expected from the importance of including electron correlation in determining the length of double bonds. The bond length, using HF, was about 0.02−0.03 Å shorter than that obtained with a MP level of theory. The distance did not change significantly through the MP series (MP2, MP3, MP4(SDQ)), neither did it change when using QCISD. All the calculations using a level of theory higher than MP2 were performed with the core electrons excluded from the correlation calculations, since it was observed in the MP2 calculations that only minor differences occurred when the core electrons were included in the correlation calculations. In the DFT calculation both the $Si-C_r$ and $Si-C_t$ bonds were found to be about 0.03 Å longer than those obtained ab initio.

It was not possible to perform calculations at a level of theory higher than MP2 for DMGeCP because of the limitations on the computational resources. The results from the calculations for this molecule are given in Table 2. As for DMSiCP only minor differences were observed when adding diffuse and polarization functions to the 6-311G basis set and the carbon−carbon double bond was calculated to be about 0.02−0.03 Å shorter when using HF than MP2. For DMGeCP slightly larger differences were observed for $Ge-C_r$ and $Ge-C_t$ bonds when changing the level of theory used. The values obtained for these bonds using HF and MP2(FC) (with the core electrons excluded from the correlation calculation) levels of theory were similar, but when using MP2(FU) the values were found to be slightly shorter as can be seen in Table 2.

In general the bond lengths obtained in the ab initio calculations were slightly longer than those determined experimentally (ca. 0.01−0.02 Å), except for the carbon−carbon double bond. The agreement between experimental and calculated carbon−carbon bond lengths depends, of course, on which calculation is chosen. The experimentally determined length of the carbon−carbon double bond in DMGeCP (1.345(12) Å) is closer to the one obtained by the MP rather than by the HF calculations, while in DMSiCP the experimental length (1.335(14) Å) lies between that obtained by HF and MP (MP2, MP3, MP4). For the bond angles it can be seen from Tables 1, 2, and 3 that there is excellent agreement between experiment and theory. It can also be seen that the difference in the C_rXC_r angle between DMSiCP and DMGeCP, found in the electron diffraction analysis, was also predicted by the theoretical calculations. The amplitudes obtained by refinement of the electron diffraction data and those calculated are in reasonable agreement, except for the amplitude associated with the $Ge-C_4$ distance, which was refined to be somewhat larger than the calculated value. Constraining this amplitude to the calculated values led to a larger R-factor ($R = (\sum[w_i(s_iI_i(\text{obs})\text{-}s_iI_i(\text{calc}))/\sum w_i(s_iI_i(\text{obs}))^2]^{1/2}$).

In Table 6 some of the important structural parameters determined for DMSiCP are compared with those obtained for $R_2SiC_4H_6$ (R = H, Cl, F).[16] In the earlier electron diffraction investigation, structural changes in the ring were observed when the hydrogen atom on the Si atom was replaced by a halogen atom. Replacement of H by a methyl group seems to bring about similar changes. The most significant is the shortening of the $Si-C_r$ bond length which is reduced from 1.899(3) Å in $H_2SiC_4H_6$ [16] to 1.886(3) Å when R = CH_3, 1.876(6) Å when R = Cl and 1.847(3) Å when R = F.[16] This bond shortening is accompanied by a slight widening of $\angle C_rSiC_r$ and a reduction of $\angle SiC_rC_r$, except for R = F. However, there is no straightforward relationship between the $Si-C_r$ distance and the ring angles and such possible trends should be treated with caution as the uncertainties in some of the angles are rather large. In addition not all the structural trends derived from electron-diffraction measurements are reproduced by the ab initio calculations. It can be seen from Table 6 that the ab initio calculations predict the structural parameters for $H_2SiC_4H_6$ to be close to those of $(CH_3)_2SiC_4H_6$, whereas the results from the electron diffraction show some differences. The C−C bond distance was found to be shorter in DMSiCP than in the three molecules studied earlier**.** If the experimental values for this distance are compared with the calculated ones it can be seen that the C−C bond length in DMSiCP is slightly shorter than the calculated value whereas in the molecules studied previously it was found to be longer.

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Supporting Information Available: Tables giving total scattered intensities, molecular intensities, and Cartesian coordinates from the final electron diffraction refinements for 1,1-dimethyl-1-silacyclopent-3-ene and 1,1-dimethyl-1-germacyclopent-3-ene. Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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