J. Am. Chem. Soc. **1994,** *116,* 9287–9293

Resonance Stabilization in the Allyl Systems $CH_2CHXH_2^{+/-}$ (X = C, Si, Ge, Sn, Pb)

Alberto Gobbi and Gernot Frenking*

Contribution from the Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany

Received February 9, 1994⊗

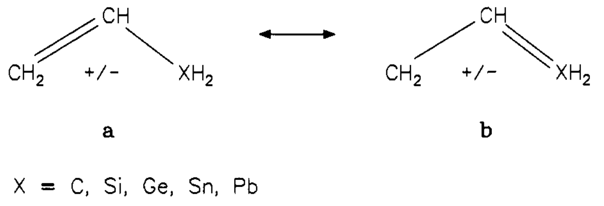
Abstract: The equilibrium structures and barriers for rotation around the C–X bond are calculated for the allyl cations and anions $CH_2CHXH_2^{+/-}$ (X = C, Si, Ge, Sn, Pb) using quantum mechanical ab initio methods. Effective core potentials are employed for the heavy atoms. The allyl cations are predicted with a planar geometry. All allyl cations are stabilized by π conjugative interactions. The strength of the resonance interactions as measured by the rotational barrier decreases from 37.8 kcal/mol (X = C) to 14.1 kcal/mol (X = Si), 12.0 kcal/mol (X = Ge), 7.2 kcal/mol (X = Sn), and 6.1 kcal/mol (X = Pb). The allyl cations are additionally stabilized by σ bonding and through-space charge interactions, which have the same magnitude as the resonance stabilization. The equilibrium geometries of the heavy atom allyl anions have strongly pyramidal XH_2 groups. The planar forms are much higher in energy. The calculations suggest that there is no resonance stabilization in the allyl anions, except in the parent anion $CH_2CHCH_2^-$. The electronic structure of the molecules is investigated using the Laplacian of the electron density distribution.

1. Introduction

Molecules with multiple bonds involving elements of the second or higher row of the periodic system (heavy atoms) have long been assumed to be nonexistent.[1] The observation and characterization of such species in the last 20 years is a success of modern chemical research, which is characterized by the interplay of ingenious experimental techniques and accurate quantum mechanical calculations. Of particular interest are molecules with multiple bonds between carbon and the heavier group 14 elements silicon, germanium, tin, and lead. Stable silaethenes,[2] germaethenes,[3] and stannaethenes[4] have been synthesized and characterized.[5] Theoretical studies show that the bond strength of the $H_2C{=}XH_2$ π bond (X = C, Si, Ge, Sn) decreases rapidly.[6] It is noteworthy that the theoretically predicted trend shows a large drop not only from C to Si but also from Ge to Sn [$D_e^{\pi}(H_2C{=}XH_2)$ = 64–68 kcal/mol (C); 35–36 kcal/mol (Si), 31 kcal/mol (Ge); 19 kcal/mol (Sn)].[6]

Another important property of the C=X π bond besides its bond energy is the strength of conjugative interactions with other double bonds, in particular C=C π bonds. The resonance stabilization of sila-, germa-, and stannabenzene has been studied theoretically.[7] Quantum chemical calculations of homodesmotic and isodesmic reactions suggest that the aromaticity of sila- and germabenzene is ~70% of benzene, while stannabenzene has only ~50 of the aromatic stabilization of benzene.[8] However, calculations of silacyclopentadienyl anion and silacyclopropenyl cation indicate that these compounds have very little aromatic stabilization.[9]

Chart 1



Other important species which are stabilized by conjugative interactions are the allyl cation and the allyl anion. In a previous study we showed that resonance stabilization in the allyl cation *and* the allyl anion is strong, because the conjugative interactions of the π electrons induces not only stronger covalent bonding, but also a favorable charge distribution.[10] In this paper we study the strength of conjugative interactions in the heterosubstituted 1-allyl cations and anions $H_2CCHXH_2^{+/-}$ (X = C, Si, Ge, Sn, Pb). We report the optimized geometries and the energies of the compounds. The electronic structure is analyzed using the topological analysis of the Laplacian of the electronic charge distribution[11] and the natural bond orbital (NBO) partitioning scheme.[12]

We investigate the importance of the resonance structure **b** in the allyl systems (Chart 1) by calculating the barrier for rotation around the C–X bond. The resonance form **b** is less important than **a** for the heavy atom systems, but the $XH_2^{+/-}$ moiety may additionally be stabilized through the C–X σ bond and the through-space charge interactions. We study the total stabilization of the $XH_2^{+/-}$ moiety in the allyl cation by calculating the reaction energies of isodesmic reactions.

Only one of the heterosubstituted allyl cations has been studied before. The 1-silaallyl cation $CH_2CHSiH_2^+$ was calculated at the STO-2G and 3-21G level of theory by Gordon and co-workers.[13] There are no other theoretical studies of

---

⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1994.

(1) Dasent, W. W. *Nonexistent Compounds*; Dekker: New York, 1965.

(2) Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981**, 191.

(3) (a) Wiberg, N.; Kim, C.-K. *Chem. Ber.* **1986**, *119*, 2966. (b) Meyer, H.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem.* **1987**, *99*, 790.

(4) Meyer, H.; Baum, G.; Massa, W.; Berger, S.; Berndt, A. *Angew. Chem.* **1987**, *99*, 559.

(5) For reviews, see: (a) Guselnikv, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (c) West, R. *Angew. Chem.* **1987**, *99*, 1231. (d) Gordon, M. S. In *Molecular Structure and Energetics*; Liegman, J. F., Greenberg, A., Eds.; VCH: Weinheim, 1986; Vol. 1. (e) Barrau, J.; Escudié J.; Satgé J.; *Chem. Rev.* **1990**, *90*, 283. (f) Baldridge, K. K.; Boatz, J. A.; Koseki, S.; Gordon, M. S. *Ann. Rev. Phys. Chem.* **1987**, *38*, 211.

(6) Dobbs, K. D.; Hehre, W. *Organometallics* **1986**, *5*, 2057.

(7) (a) Chandrasekhar, J.; Schleyer, P. v. R.; Baumgärtner, R. O. W.; Reetz, M. T. *J. Org. Chem.* **1983**, *48*, 3453. (b) George, P.; Bock, C. W.; Trachtman, M. *Theoret. Chim. Acta* **1987**, *71*, 289.

(8) Baldridge, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 4204.

(9) Gordon, M. S.; Bondjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972.

(10) Gobbi, A,; Frenking, G. *J. Am. Chem. Soc.*, preceeding paper in this issue.

(11) Bader, R. F. W. *Atom in Molecules: A Quantum Theory*; Oxford University Press: Oxford, 1990.

(12) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(13) Truong, T.; Gordon, M. S.; Boudjouk, P. *Organometallics* **1984**, *3*, 484.

0002-7863/94/1516-9287$04.50/0

$CH_2CHXH_2^{+/-}$ (X = Si-Pb) ions knows to us. The conjugation in trisilaallyl anion was theoretically studied by Korkin and Schleyer.[14] This work is the first systematic study of the structures of $CH_2CHXH_2^{+/-}$ (X = Si-Pb) compounds and the effect of resonance stabilization in these molecules.

2. Theoretical Details

The geometry optimizations and energy calculations have been carried out using the program package Gaussian 92.[15] We optimized the geometries and calculated the vibrational frequencies at the Hartree-Fock (HF) and MP2 (Møller-Plesset perturbation theory terminated at second order[16]) level of theory using a 6-31G(d) basis set for C and H.[17a-c] For the heavy atoms Si, Ge, Sn, Pb an effective core potential (ECP)[18] was employed with a double-ζ valence basis set augmented by a set of five d-type polarization functions[19] [21/21/1]. These levels of theory are denoted HF/VDZP and MP2/VDZP, respectively. The calculations of the anions have also been carried out using diffuse basis functions.[17d]

For the calculation of the Laplacian of the electron density distribution $\nabla^2\rho(\mathbf{r})$ the program GRID was used.[20] The NBO analysis[12] was carried out with the subroutine available in Gaussian 92.[15]

3. Allyl Cations $CH_2CHXH_2^+$ (X = C, Si, Ge, Sn, Pb)

Figure 1 shows schematically the optimized structures. The allyl cations CH_2CHXH_2 **1a–e** are predicted with a planar geometry as energy-minimum structures. The theoretically predicted bond lengths and angles and the calculated charge distribution of **1a–e** are shown in Table 1. The terminal XH_2 groups of **1b–e** always carry large positive charges. The NBO analysis calculates even partial charges > 1.0 for the XH_2 group of the heavy atom analogs (Table 1). This is an artifact of the NBO partitioning scheme, which assigns large negative partial charges to the central CH group of **1b–e**. The C–C bond lengths of **1b–e** are calculated shorter than for **1a**, but still longer than for ethylene (1.336 Å at MP2/6-31G(d)). The C–C and C–X interatomic distances of the allyl cations may be compared with the calculated bond lengths of the vinyl derivatives $H_2C{=}HC{-}XH_3$ shown in Table 2. The C–X bonds are clearly shorter and the C–C bonds are longer in **1a–e** than in the respective vinyl derivative. This is an indication of conjugative interactions in the allyl cations.

Table 1 also shows the optimized geometries and relative energies of the transition states for rotation of the XH_2 groups **2a–e**. As discussed in the previous paper,[10] the transition state **2a** could be located only at the HF/6-31G(d) level of theory.

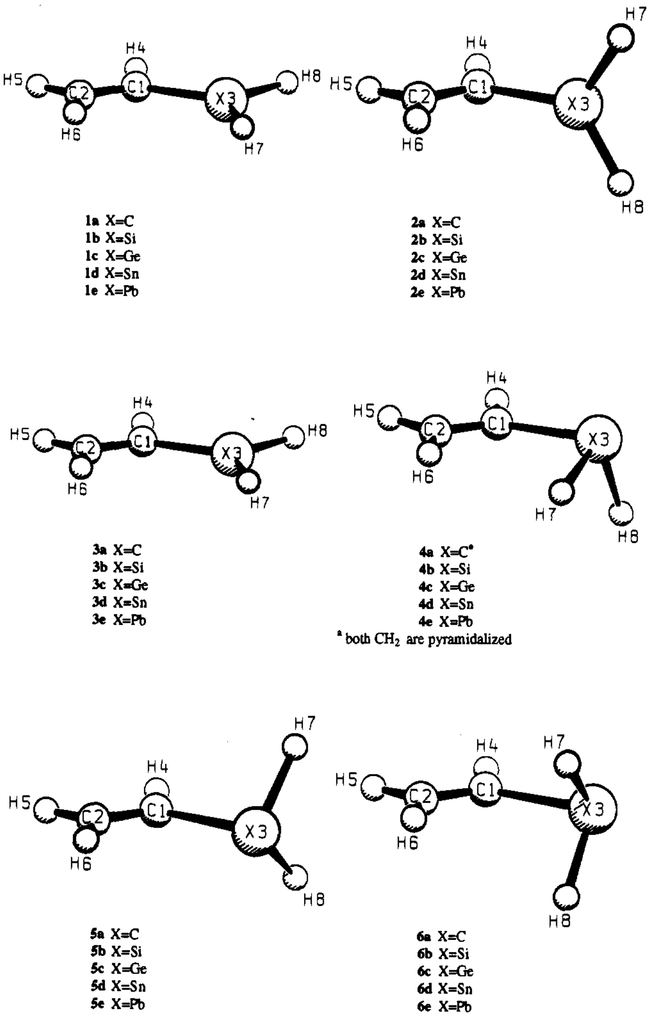


Figure 1. Schematic representation of the optimized geometries of the allyl cations **1a–2e** and the allyl anions **3a–6e**.

The theoretically predicted rotational barrier is clearly higher for **1a** (37.8 kcal/mol) than for the heavier analogs **1b–e** (14.1–6.1 kcal/mol, Table 1). The rotational barrier is caused by the π delocalization in the planar forms as discussed in the preceding paper.[10] The delocalization of π charge should have an effect upon the partial charges at XH_2 in the two forms. The absolute values for the partial charges have no meaning, because they are based on an arbitrary partitioning scheme (like any other population analysis), but the *trend* should be in agreement with the charge flow. Table 2 shows that the positive charge flow from the XH_2 group to the vinyl moiety is much higher for the allyl cation **1a** (0.325 e) than for the heavy atom analogs **1b–e** (0.113–0.325 e). Figure 2 shows that there is nearly a linear relationship between the charge flow and the predicted rotational barrier. The calculated results indicate that the resonance stabilization by the π conjugation has the order **1a** ≫ **1b** > **1c** > **1d** > **1e**. It should be noted that the sequence shows a larger difference between the Ge compound **1c** and the Sn compound **1d** than between the other heavy atom compounds.

The allyl cations **1a–e** may be considered as vinyl-substituted XH_3^+ cations, which are stabilized by inductive and conjugative interactions. The total stabilization energy of the vinyl group can be calculated using the isodesmic reaction 1:

$$CH_2{=}CHXH_3\ (\mathbf{1}) + XH_3 \rightarrow CH_2CHXH_2^+ + XH_4 + \Delta E \qquad (1)$$

The calculated reaction energies are shown in Table 3. The stabilization energies $\Delta E(1)$ can be partitioned into (i) the π resonance stabilization given by the calculated rotational barrier, and (ii) the interaction through the σ bonds and the through-space electrostatic interactions ΔE(q) given by the difference between $\Delta E(1)$ and the rotational barrier. Table 3 shows that about half of the total stabilization energy of the allyl cations

---

[14] Korkin, A. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992,** *114,* 8720.

[15] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision C*; Gaussian, Inc.: Pittsburgh, PA, 1992.

[16] (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934,** *46,* 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975,** *9,* 229.

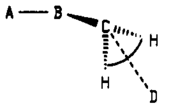
[17] (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972,** *56,* 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973,** *28,* 213. (c) Gordon, M. S. *Chem Phys. Lett.* **1980,** *76,* 163. (d) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983,** *4,* 294. The exponent for the diffuse functions of Si, Ge, Sn, Pb the exponent was calculated by taking the outermost function multiplied by 0.25.

[18] Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985,** *82,* 284.

[19] Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993,** *208,* 237.

[20] Biegler-König, F. W.; Bader, R. F. W.; Ting-Hua, T. *J. Comput. Chem.* **1982,** *3,* 317.

Table 1. Calculated Geometries, Energies and Partial Charges of the Allyl Cations $CH_2CHXH_2^+$ [a]



D=Dummy atom

	1a (X = C)	**1b** (X = Si)	**1c** (X = Ge)	**1d** (X = Sn)	**1e** (X = Pb)
sym	C_{2v}	C_s	C_s	C_s	C_s
E_{tot}	−116.55762 (−116.19321)	−82.41533 (−82.10691)	−82.29068 (−81.98190)	−81.85532 (−81.56601)	−81.92564 (−81.63402)
i	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
ZPE	43.9 (46.1)	37.8 (39.6)	36.6 (38.5)	35.0 (36.9)	34.6 (36.5)
$C^1–C^2$	1.382 (1.373)	1.364 (1.349)	1.360 (1.342)	1.354 (1.336)	1.350 (1.330)
$C^1–X^3$	1.382 (1.373)	1.784 (1.775)	1.871 (1.864)	2.053 (2.046)	2.103 (2.096)
$C^2–C^1–X^3$	117.6 (118.1)	116.8 (118.9)	116.9 (118.8)	119.9 (120.9)	119.5 (120.4)
$H^4–C^1–C^2$	121.2 (120.9)	120.7 (120.1)	121.6 (121.0)	120.2 (120.3)	121.7 (122.0)
$H^4–C^1–X^3$	121.2 (120.9)	122.6 (121.1)	121.5 (120.2)	119.9 (118.9)	118.8 (117.6)
$q(C^1)$	−0.465	−0.962	−0.914	−0.902	−0.813
$q(C^2)$	0.078	−0.097	−0.140	−0.190	−0.220
$q(X^3)$	0.078	1.630	1.636	1.820	1.691
$q(H^4)$	0.295	0.304	0.300	0.292	0.289
$q(H^5)$	0.264	0.260	0.260	0.256	0.259
$q(H^6)$	0.244	0.233	0.232	0.228	0.230
$q(H^7)$	0.244	−0.189	−0.193	−0.259	−0.226
$q(H^8)$	0.264	−0.180	−0.181	−0.246	−0.211
$q(C^1H^4)$	−0.170	−0.658	−0.614	−0.610	−0.524
$q(C^2H_2)$	0.586	0.396	0.352	0.294	0.269
$q(X^3H_2)$	0.586	1.261	1.262	1.315	1.254
	2a (X = C)	**2b** (X = Si)	**2c** (X = Ge)	**2d** (X = Sn)	**2e** (X = Pb)
Sym.	C_s	C_s	C_s	C_s	C_s
E_{tot}	−116.48286[b] (−116.13899)	−82.39291 (−82.08523)	−82.27160 (−81.96383)	−81.84387 (−81.55413)	−81.91587 (−81.62385)
E_{rel}	37.8[b] (34.0)	14.1 (13.6)	12.0 (11.3)	7.2 (7.4)	6.1 (6.4)
i	(1)	1 (1)	1 (1)	1 (1)	1 (1)
ZPE	(44.0)	36.8 (38.9)	35.8 (37.8)	34.6 (36.4)	34.1 (36.0)
$C^1–C^2$	(1.318)	1.351 (1.330)	1.347 (1.326)	1.346 (1.325)	1.342 (1.321)
$C^1–X^3$	(1.445)	1.816 (1.816)	1.908 (1.908)	2.084 (2.086)	2.138 (2.139)
$C^2–C^1–X^3$	(127.9)	119.7 (123.4)	120.6 (122.9)	122.3 (123.5)	121.9 (122.8)
$H^4–C^1–C^2$	(119.6)	120.4 (119.8)	121.3 (120.9)	120.1 (120.5)	121.8 (122.4)
$H^4–C^1–X^3$	(127.9)	119.9 (116.8)	118.1 (116.2)	117.6 (116.0)	116.3 (114.8)
$C^1–X^3–D$	(178.2)	179.1 (178.9)	179.5 (179.2)	179.9 (179.3)	179.7 (179.4)
$q(C^1)$	−0.494	−0.953	−0.889	−0.869	−0.771
$q(C^2)$	−0.251	−0.216	−0.243	−0.265	−0.286
$q(X^3)$	0.429	1.772	1.743	1.887	1.738
$q(H^4)$	0.322	0.307	0.299	0.291	0.287
$q(H^5)$	0.268	0.262	0.261	0.258	0.261
$q(H^6)$	0.243	0.227	0.228	0.223	0.226
$q(H^7)$	0.241	−0.199	−0.199	−0.262	−0.227
$q(H^8)$	0.241	−0.199	−0.199	−0.262	−0.227
$q(C^1H^4)$	−0.172	−0.646	−0.590	−0.578	−0.484
$q(C^2H_2)$	0.260	0.273	0.246	0.216	0.201
$q(X^3H_2)$	0.911	1.374	1.345	1.363	1.284

[a] The results are given at MP2/VDZP, results at HF/VDZP are given in parentheses, *i* gives the number of imaginary frequencies; total energies, E_{tot}, in atomic units; zero point vibrational energies, ZPE, in kcal/mol; bond distances, A–B in Å; bond angles, A–B–C, in deg. [b] Calculated at MP2/VDZP//HF/VDZP.

Table 2. Calculated Geometries and Energies of the Molecules CH_2CHXH_3 at MP2/VDZP and HF/VDZP[a]

	X = C	X = Si	X = Ge	X = Sn	X = Pb
sym	C_s	C_s	C_s	C_s	C_s
E_{tot}	−117.46966 (−117.07147)	−83.29812 (−82.96857)	−83.15817 (−82.82899)	−82.70268 (−82.39905)	−82.75700 (−82.45079)
i	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
ZPE	51.2 (53.6)	43.0 (45.1)	41.5 (43.6)	39.4 (41.4)	38.8 (40.8)
$C^1–C^2$	1.337 (1.318)	1.345 (1.324)	1.344 (1.323)	1.346 (1.325)	1.344 (1.323)
$C^1–X^3$	1.498 (1.503)	1.869 (1.868)	1.950 (1.949)	2.123 (2.121)	2.169 (2.164)
$C^2–C^1–X^3$	124.6 (125.2)	122.5 (123.5)	122.3 (123.2)	122.7 (123.3)	122.3 (123.0)

[a] For details see Table 1.

1a–e is caused by resonance stabilization, while the other half is due to σ bond interactions and through-space electrostatic interactions. The π resonance stabilization is calculated as 37.8 kcal/mol for **1a**, 14.1 kcal/mol for **1b**, 12.0 kcal/mol for **1c**, 7.2 kcal/mol for **1d**, and 6.1 kcal/mol for **1e**. The stabilization due to the σ interactions and Coulomb interactions is calculated as 22.2 kcal/mol for **1a**, 13.4 kcal/mol for **1b**, 11.2 kcal/mol for **1c**, 8.5 kcal/mol for **1d**, and 8.2 kcal/mol for **1e**.

The differences of the electronic structure of the C–X bonds and the change in the C–X bond upon rotation of the XH_2 group become clearly visible by comparison of the Laplacian distribution of the electron density $\nabla^2\rho(\mathbf{r})$ in the π plane. Figure 3 shows the contour line diagrams of the Laplacian distribution for the C–X bond of the equilibrium structures **1a–e** and the transition states **2a–e**.[21] Visual inspection of the C–X bond region shows that only for X = C, Si, and to a smaller extent for X = Ge there is

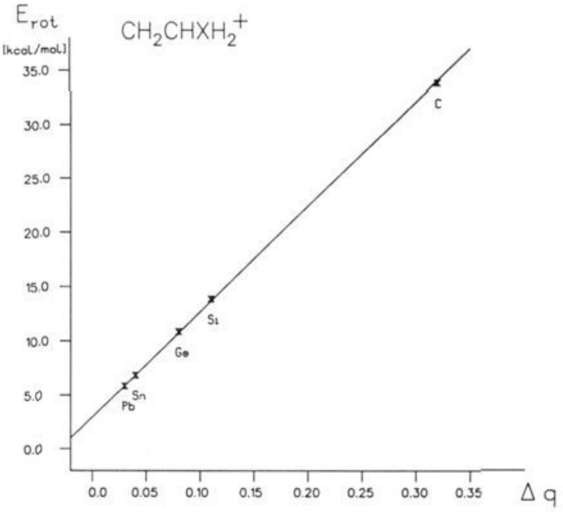


Figure 2. Correlation of the calculated barriers for rotation of the XH_2 group and the change in the partial electronic charge at XH_2 for the allyl cations $CH_2CHXH_2^+$.

Table 3. Stabilization Energies (kcal/mol) of the Isodesmic Reactions $\Delta E(1)$ and $\Delta E(2)$ and Rotational Barriers of the Cations $\Delta E_{rot}(1)$ and Anions $\Delta E_{rot}(2)$ Calculated at MP2/VDZP[a]

	X = C	X = Si	X = Ge	X = Sn	X = Pb
$\Delta E(1)$	60.0 (54.1)	27.5 (27.1)	23.2 (22.8)	15.7 (16.9)	14.3 (15.6)
$\Delta E_{rot}(1)$	37.8[b] (34.0)	14.1 (13.6)	12.0 (11.3)	7.2 (7.4)	6.1 (6.4)
$\Delta E(2)$[c]	29.8 (26.9)	1.7 (–0.7)	1.1 (–1.0)	2.8 (0.0)	4.1 (1.5)
$\Delta E_{t}r_{ot}(2)$	23.2 (20.4)	3.6 (3.4)	2.5 (2.4)	1.5 (1.5)	1.3 (1.3)

[a] The results at HF/VDZP are shown in parentheses. [b] Calculated at MP2/VDZP//HF/VDZP. [c] Calculated with inclusion of diffuse functions (ref 17d).

a visible difference of the Laplacian distribution around the X atom between the equilibrium structure and the transition state. The holes in the Laplacian distribution at Si in **2b** are filled in **1b** by electronic charge concentration, which demonstrates the effect of π conjugation. The germanium analog shows only a polarization of the valence electronic charge in **1c** compared with **2c**. The Laplacian distribution around the Sn and Pb atoms is nearly invariant to the rotation of the XH_2 group, the differences between **1d**, **1e** and the corresponding transition states **2d**, **2e** are hardly visible. This agrees with the calculated small barrier for rotation around the XH_2 group of 7.2 kcal/mol for **1d** and 6.1 kcal/mol for **1e**.

4. Allyl Anions $CH_2CHXH_2^-$ (X = C, Si, Ge, Sn, Pb)

Now we turn to the calculated results for the allyl anions $CH_2CHXH_2^-$. Table 4 shows the data for the planar structures **3a–e** (Figure 1). The optimized structures of the planar heavy atom molecules **3b–e** are not minima on the potential energy surface. The release of symmetry constraints yields the energy minimum structures **4b–e**, which have strongly pyramidal XH_2 groups and nearly planar CH_2 groups. The nonplanar forms **4b–e** are much lower in energy than the planar forms **3b–e**, which are transition states for the inversion of the XH_2 group. The barrier for inversion is between 23.7 kcal/mol for X = Si and 54.8 kcal/mol for X = Pb (Table 4).

The lone pair orbitals of the energy-minimum structures **4b–e** at atom X are parallel to the C–C π bond (Figure 1). But there is practically no π interaction between the C–C π bond and the lone pair electrons at the heteroatom X. The inward rotation of the XH_2 group leads to the C_s-symmetric structures **5b–e**, which have the lone pair electrons orthogonal to the C–C π bond (Figure 1). The rotatamers **5b–e** are also minima on the potential energy surface. The calculated energy differences between the energy-minimum structures **4b–e** and **5b–e** are very small (<1 kcal/mol at MP2/VDZP, Table 4). The outward rotation of the XH_2 groups needs also very little energy. The C_s-symmetric structures **6b–e** are transition states for the rotation of the XH_2 groups (Table 4). The calculated barriers are very low (<4 kcal/mol). The calculations indicate that the allyl anions $CH_2CHXH_2^-$ (X = Si, Ge, Sn, Pb) have nearly no energy barrier for rotation around the C–X bond. The lack of π conjugation in the energy-minimum structures **4b–e** and **5b–e** is also demonstrated by the calculated C–C and C–X bond lengths. The optimized C–X interatomic distances are even slightly longer in the anions than in the respective neutral compounds $CH_2{=}CHXH_3$ (Table 2). This is caused by the *repulsive* interaction between the lone pair electrons at the XH_2 group and the C=C π electrons. The C–C interatomic distances of **4b–e** and **5b–e** are nearly the same as in $CH_2{=}CHXH_3$ (Table 2).

The strongly pyramidal XH_2 groups, the calculated C–C and C–X bond lengths and the nearly identical energies of the energy minimum structures **4b–e** and the rotamers **5b–e** suggest that π

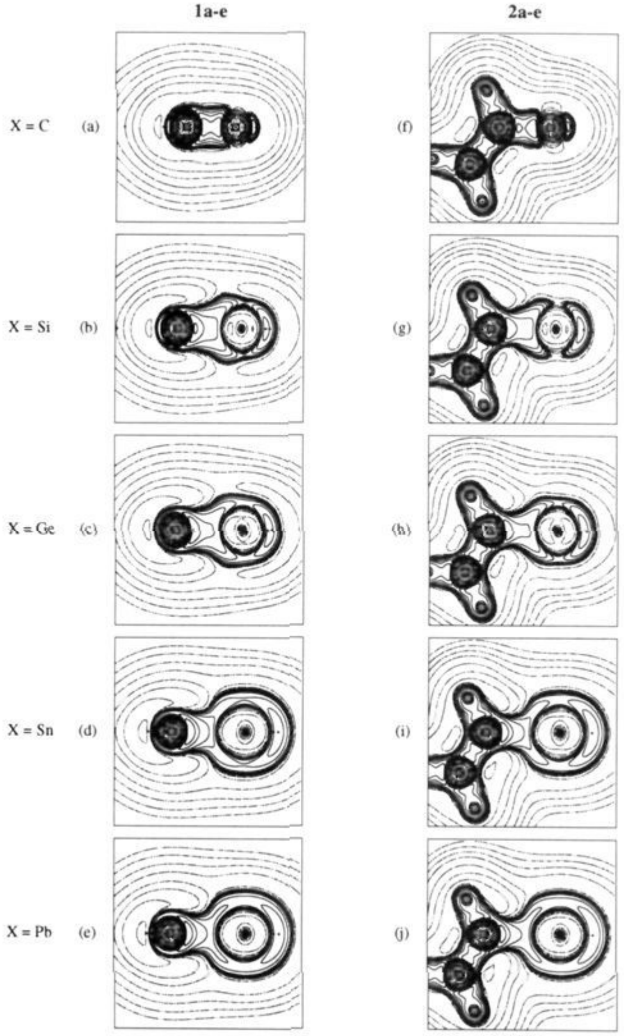


Figure 3. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$ at MP2/VDZP/MP2/VDZP for the allyl cations: (a–e) the π plane of the C–X bond in the equilibrium structures **1a–e**. (f–j) the C^2–C^1–X^3 plane of the transition states **2a–e**. Dashed lines indicate charge depletion ($\nabla^2\rho(\mathbf{r}) > 0$); solid lines indicate charge concentration ($\nabla^2\rho(\mathbf{r}) < 0$). The Laplacian distribution of **2a** is calculated at MP2/VDZP/HF/VDZP.

---

(21) It was not possible to locate the bond critical points for the C–X bonds of the heavier analogs of the allyl ions, because the effective core potentials gave no minima along the C–X bond path. Therefore, the zero-flux surfaces could not be determined.

Table 4. Calculated Geometries, Energies, and Partial Charges of the Allyl Anions CH_2CHX_2[a]

	3a (X = C)	**3b** (X = Si)	**3c** (X = Ge)	**3d** (X = Sn)	**3e** (X = Pb)
sym	C_{2v}	C_s	C_s	C_s	C_s
E_{tot}	116.79852 (–116.39349)	–82.64454 (–82.29514)	–82.51450 (–82.16723)	–82.06938 (–81.76409)	–82.12433 (–81.81677)
E_{rel}	0.2 (0.0)	23.7 (29.6)	30.7 (36.7)	40.5 (42.5)	54.8 (57.1)
i	2 (0)	1 (1)	1 (1)	1 (1)	1 (1)
ZPE	39.7 (42.1)	35.0 (36.8)	34.2 (36.0)	32.9 (34.8)	32.6 (34.6)
$C^1–C^2$	1.391 (1.382)	1.369 (1.346)	1.365 (1.340)	1.363 (1.335)	1.363 (1.333)
$C^1–X^3$	1.391 (1.382)	1.827 (1.835)	1.910 (1.921)	2.086 (2.113)	2.118 (2.145)
$C^2–C^1–X^3$	133.3 (133.7)	134.5 (134.9)	133.6 (133.5)	132.9 (131.8)	132.1 (131.0)
$H^4–C^1–C^2$	113.4 (113.1)	114.3 (114.4)	115.4 (115.4)	115.1 (115.8)	116.3 (116.8)
$H^4–C^1–X^3$	113.4 (113.1)	111.1 (110.8)	111.0 (111.1)	111.9 (112.3)	111.5 (112.2)
$q(C^1)$	–0.132	–0.621	–0.596	–0.627	–0.571
$q(C^2)$	–0.819	–0.629	–0.605	–0.554	–0.556
$q(X^3)$	–0.819	0.143	0.095	0.153	–0.004
$q(H^4)$	0.155	0.201	0.202	0.207	0.207
$q(H^5)$	0.153	0.165	0.168	0.177	0.180
$q(H^6)$	0.154	0.173	0.177	0.185	0.188
$q(H^7)$	0.154	–0.217	–0.221	0.273	–0.226
$q(H^8)$	0.153	–0.215	–0.220	–0.267	–0.219
$q(C^1H^4)$	0.023	–0.420	–0.394	–0.420	–0.364
$q(C^2H_2)$	–0.512	–0.291	–0.260	–0.192	–0.188
$q(X^3H_2)$	–0.512	–0.289	–0.346	–0.387	–0.449

	4a (X = C)	**4b** (X = Si)	**4c** (X = Ge)	**4d** (X = Sn)	**4e** (X = Pb)
sym	C_2	C_1	C_1	C_1	C_1
E_{tot}	–116.79883	–82.68232 (–82.34232)	–82.56346 (–82.22571)	–82.13400 (–81.83187)	–82.21163 (–81.90772)
E_{rel}	0.0	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
i	0	0 (0)	0 (0)	0 (0)	0 (0)
ZPE	40.7	35.7 (37.3)	34.5 (36.1)	33.1 (34.7)	32.3 (33.9)
$C^1–C^2$	1.393	1.351 (1.330)	1.349 (1.328)	1.349 (1.329)	1.349 (1.329)
$C^1–X^3$	1.393	1.933 (1.939)	2.038 (2.045)	2.231 (2.235)	2.311 (2.315)
$C^2–C^1–X^3$	132.9	129.4 (130.3)	128.8 (129.7)	128.2 (128.6)	128.1 (128.6)
$H^4–C^1–C^2$	113.5	114.5 (114.6)	114.8 (114.8)	114.3 (114.7)	114.3 (114.7)
$H^4–C^1–X^3$	113.5	115.7 (114.9)	115.9 (115.2)	117.1 (116.4)	117.2 (116.4)
$C^1–C^2–D$	161.1	178.9 (179.4)	178.7 (179.2)	178.7 (179.2)	178.6 (179.1)
$C^1–X^3–D$	161.1	100.1 (101.1)	97.5 (98.8)	96.1 (97.4)	94.8 (96.1)
$C^2–C^1–X^3–D$	85.8	77.0 (76.4)	73.4 (74.1)	66.9 (67.5)	65.5 (68.0)
$q(C^1)$	–0.125	–0.573	–0.572	–0.630	–0.600
$q(C^2)$	–0.818	–0.535	–0.527	–0.509	–0.519
$q(X^3)$	–0.818	0.181	0.236	0.436	0.435
$q(H^4)$	0.154	0.174	0.170	0.173	0.163
$q(H^5)$	0.151	0.161	0.160	0.164	0.160
$q(H^6)$	0.152	0.182	0.184	0.190	0.189
$q(H^7)$	0.152	–0.295	–0.326	–0.412	–0.414
$q(H^8)$	0.151	–0.295	–0.326	–0.411	–0.415
$q(C^1H^4)$	0.029	–0.399	–0.402	–0.457	–0.437
$q(C^2H^2)$	–0.515	–0.192	–0.183	–0.155	–0.170
$q(X^3H_2)$	–0.515	–0.409	–0.416	–0.387	–0.394

	5a (X = C)	**5b** (X = Si)	**5c** (X = Ge)	**5d** (X = Sn)	**5e** (X = Pb)
sym	C_s	C_s	C_s	C_s	C_s
E_{tot}	–116.76185 (–116.36094)	–82.68089 (–82.34184)	–82.56343 (–82.22657)	–82.13487 (–81,83337)	–82.21300 (–81.90970)
E_{rel}	23.2 (20.4)	0.9 (0.3)	0.02 (–0.5)	–0.5 (–0.9)	–0.9 (–1.2)
i	1 (1)	0 (0)	0 (0)	0 (0)	0 (0)
ZPE	40.1 (42.0)	35.7 (37.4)	34.6 (36.1)	33.1 (34.8)	32.2 (34.0)
$C^1–C^2$	1.348 (1.331)	1.348 (1.328)	1.347 (1.327)	1.348 (1.329)	1.348 (1.330)
$C^1–X^3$	1.493 (1.508)	1.954 (1.955)	2.052 (2.054)	2.236 (2.238)	2.312 (2.314)
$C^2–C^1–X^3$	124.6 (125.9)	124.3 (125.4)	124.0 (124.9)	124.6 (124.9)	124.0 (124.3)
$H^4–C^1–C^2$	111.8 (112.7)	115.0 (115.2)	115.5 (115.4)	114.9 (115.3)	115.0 (115.4)
$H^4–C^1–X^3$	123.6 (121.5)	120.7 (119.4)	120.6 (119.7)	120.4 (119.8)	120.9 (120.4)
$C^1–X^3–D$	114.6 (113.9)	97.6 (98.7)	96.0 (97.1)	95.1 (96.2)	94.3 (95.2)
$q(C^1)$	–0.102	–0.574	–0.571	–0.625	–0.590
$q(C^2)$	–0.561	–0.505	–0.513	–0.508	–0.527
$q(X^3)$	–0.998	0.162	0.231	0.437	0.440
$q(H^4)$	0.108	0.173	0.174	0.180	0.175
$q(H^5)$	0.151	0.161	0.162	0.166	0.164
$q(H^6)$	0.184	0.187	0.184	0.183	0.177
$q(H^7)$	0.108	–0.303	–0.333	–0.417	–0.420
$q(H^8)$	0.108	–0.303	–0.333	–0.417	–0.420
$q(C^1H^4)$	0.006	–0.401	–0.397	–0.445	–0.415
$q(C^2H_2)$	–0.226	–0.157	–0.167	–0.159	–0.186
$q(x^3H_2)$	–0.782	–0.444	–0.435	–0.397	–0.400

Table 4. (Continued)

	6a (X = C)	**6b** (X = Si)	**6c** (X = Ge)	**6d** (X = Sn)	**6e** (X = Pb)
sym	C_s	C_s	C_s	C_s	C_s
E_{tot}	–116.75793 (–116.35733)	–82.67666 (–82.33693)	–82.55949 (–82.22190)	–82.13154 (–81.82947)	–82.20962 (–81.90568)
E_{rel}	*25.7 (22.7)*	*3.6 (3.4)*	*2.5 (2.4)*	*1.5 (1.5)*	*1.3 (1.3)*
i	1 (1)	1 (1)	1 (1)	1 (1)	1 (1)
ZPE	40.2 (42.1)	35.6 (37.2)	34.4 (36.0)	32.9 (34.6)	32.2 (33.8)
C^1–C^2	1.351 (1.334)	1.347 (1.327)	1.347 (1.326)	1.348 (1.328)	1.348 (1.328)
C^1–X^3	1.503 (1.518)	1.971 (1.974)	2.069 (2.072)	2.251 (2.252)	2.330 (2.331)
C^2–C^1–X^3	130.9 (131.3)	128.4 (129.2)	128.6 (129.4)	128.6 (128.9)	129.3 (129.7)
H^4–C^1–C^2	111.8 (112.5)	114.2 (114.3)	114.6 (114.6)	114.3 (114.7)	114.2 (114.5)
H^4–C^1–X^3	117.2 (116.2)	117.4 (116.5)	116.8 (116.0)	117.2 (116.4)	116.5 (115.8)
C^1–X^3–D	115.9 (115.5)	98.5 (100.5)	96.9 (98.8)	96.4 (98.0)	95.5 (97.0)
$q(C^1)$	–0.085	–0.575	–0.578	–0.638	–0.608
$q(C^2)$	–0.580	–0.491	–0.493	–0.484	–0.499
$q(X^3)$	–1.035	0.140	0.209	0.418	0.423
$q(H^4)$	0.136	0.170	0.167	0.170	0.160
$q(H^5)$	0.153	0.158	0.158	0.162	0.158
$q(H^6)$	0.169	0.187	0.189	0.191	0.190
$q(H^7)$	0.121	–0.295	–0.326	–0.410	–0.412
$q(H^8)$	0.121	–0.295	–0.326	–0.410	–0.412
$q(C^1H^4)$	0.051	–0.405	–0.411	–0.468	–0.448
$q(C^2H_2)$	–0.258	–0.146	–0.146	–0.131	–0.151
$q(X^3H_2)$	–0.793	–0.450	–0.443	–0.402	–0.401

[a] For Details see Table 1.

resonance stabilization is very low or absent in the anions. Table 3 shows the calculated energies for the isodesmic reaction 2.[22]

$$CH_2{=}CHXH_3\ (\mathbf{4})^a + XH_3^- \rightarrow CH_2CHXH_2^- + XH_4 + \Delta E \qquad (2)$$

(^a Structure **5** is used for for X = Sn, Pb)

The theoretically predicted reaction energies $\Delta E(2)$ show that there is practically *no* extra stabilization of the negative charge in the heavy atom allyl systems relative to XH_3^-. The calculated reaction energies $\Delta E(2)$ for the heteroallyl anions are very small (1.7–4.1 kcal/mol). Unlike the allyl cations, the heavy atom allyl anions are stabilized neither by Coulomb interactions nor by conjugative interactions. The parent allyl anion **4a** has a calculated stabilization energy $\Delta E(2)$ = 29.8 kcal/mol, which is only slightly higher than the rotational barrier (23.2 kcal/mol). The reaction energy $\Delta E(2)$ for the parent system is just the difference between the gas-phase acidities of propene (390.8 kcal/mol) and methane (416.6 kcal/mol) or 25.8 kcal/mol.[23] The calculated value for $\Delta E(2)$ = 29.8 kcal/mol (29.7 kcal/mol with inclusion of zero-point vibrational energy contributions) is in good agreement with the experimental value of 25.8 kcal/mol.

The calculated charge distribution for **4a–e** reveals further details about the interactions in the allyl systems. The negative charge of **4a** is localized at the terminal CH_2 groups (–0.515 e), while the central CH group is nearly neutral (0.029 e, Table 4). In the heavy atom analogs **4b–e**, however, the negative charge is mainly at the terminal XH_2 group and the central CH group, while the terminal CH_2 group carries only a small negative charge (Table 4). This is, because there is no π conjugation in **4b–e**. Therefore, the charge distribution in the rotated forms **5b–e** are nearly the same as in **4b–e**.

Figure 4 shows the contour line diagrams of the Laplacian distribution for the C–X bonds of the planar forms **3a–e** and the energy-minimum structures **4a–e** in the plane bisecting the XH_2

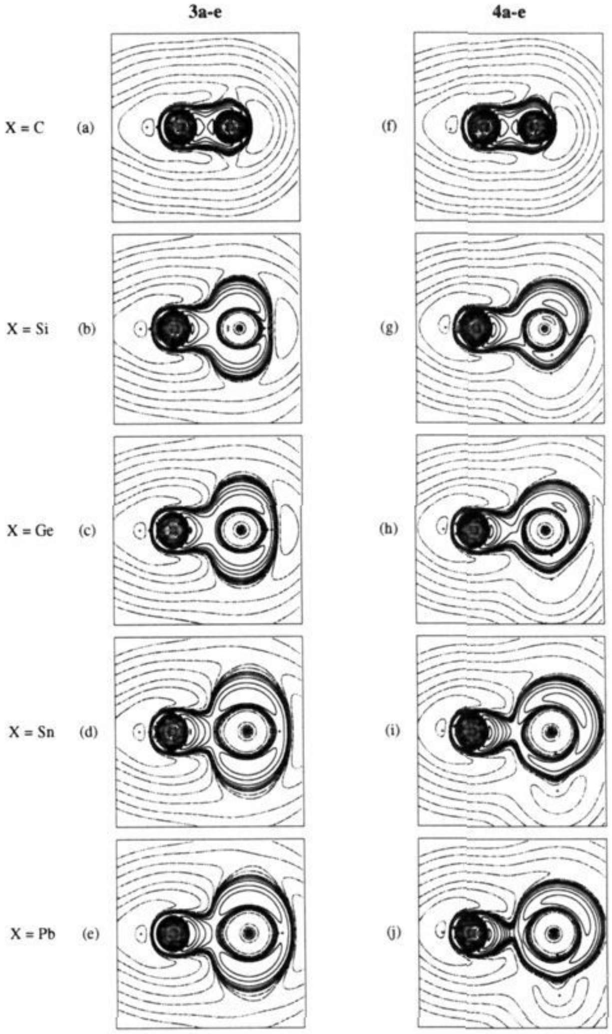


Figure 4. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$ at MP2/VDZP/HF/VDZP for the allyl anions: (a–e) the π plane of the C–X bond in the planar structures **3a–e**; (f–j) the C–X–lp plane of **4a–e**, where lp is the electron lone pair at X. Dashed lines indicate charge depletion ($\nabla^2\rho(\mathbf{r}) > 0$); solid lines indicate charge concentration ($\nabla^2\rho(\mathbf{r}) < 0$).

---

(22) The total energies for calculating $\Delta E(2)$ of the anions have been obtained using the VDZP++ basis set, which include a set of diffuse functions for all atoms.[17d] This was necessary, because in reaction 2 the negative charge of the XH_3^- molecules is localized, while it is delocalized in the allyl anions. The diffuse functions are not necessary if similar structures are compared. For example, the calculated rotational barrier of the allyl anion is 23.2 kcal/mol at MP2/6-31G(d) and 21.9 kcal/mol at MP2/6-31++G(d).

(23) Bartmess, J. E.; McIver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., ed;, Academic Press: New York, 1979; Vol. 2, p 87.

plane. The shape of the Laplacian distribution shows nicely the concentration of the electronic charge in the p(π) orbital at atom X in the planar forms **3a–e** (left side of Figure 4). The change of the Laplacian distribution at atom X in the pyramidal forms **4b–e** shows clearly the formation of the lone pair electrons.

5. Summary

The heavy atom analogs of the allyl cation $CH_2CHXH_2^+$ (X = Si, Ge, Sn, Pb) have planar equilibrium geometries. The energy profile for rotation around the C–X bond shows that the allyl cations are stabilized by π conjugative interaction. The strength of the resonance interactions as measured by the rotational barrier decreases from 37.8 kcal/mol (X = C) to 14.1 kcal/mol (X = Si), 12.0 kcal/mol (X = Ge), 7.2 kcal/mol (X = Sn), and 6.1 kcal/mol (X = Pb). The allyl cations are additionally stabilized by σ C–X and through-space charge interactions. The calculated energies of isodesmic reactions indicate that the σ bond and through-space charge interactions have the same magnitude as the resonance stabilization.

In contrast to the allyl cations the heavy atom allyl anions $CH_2CHXH_2^-$ (X = Si, Ge, Sn, Pb) show no stabilization by π conjugative interactions. The equilibrium structures of the anions have strongly pyramidal XH_2 groups, which can rotate with little or no energy around the C–X bond. The planar forms are much higher in energy; they are transition states for the inversion of the XH_2 group. The C–X bond length in the equilibrium structures of the allyl anions is even longer than the C–X bond in the neutral molecules $CH_2{=}CHXH_3$. It is only the parent allyl anion $CH_2CHCH_2^-$ which exhibits resonance stabilization. The calculated energies of isodesmic reactions show that the heavy atom allyl anions are not stabilized relative to XH_3^- anions.

Acknowledgment. We are grateful to one anonymous referee for very helpful comments. This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. We acknowledge excellent service by the computer HRZ Marburg. Additional computer time was given by the HHLR Darmstadt, HRZ Frankfurt, HRZ Giessen, and HLRZ Jülich.