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Quantum Mechanical Study of Stabilization of Germaneselones

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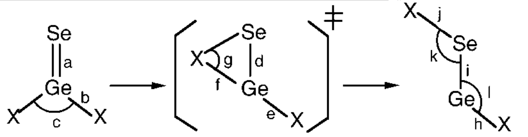
Substituent effects on the potential energy surfaces of $X_2Ge{=}Se$ (X = H, F, Cl, Br, and CH_3) were investigated by density functional theory and CCSD(T) methods. The theoretical findings suggest that both thermodynamic and kinetic stabilities of germaneselones are strongly dependent on the substituents, pointing to $F_2Ge{=}Se$ as a good candidate for experimental detection.

The existence of molecules containing a double bond between germanium and chalcogen[1] shows that the customary rule, according to which thermally stable compounds with multiple bonds would occur only for elements of the second period, must be loosened.[2] In fact, over the last fifteen years, our knowledge of molecular species exhibiting multiple bonds to germanium has expanded greatly due to both experimental progress and improvements in theoretical methods. Above all, kinetic stabilization by bulky substituents at both sides of Ge═Ge[3] and Ge═C[4] linkages has enabled experiments to synthesize and isolate numerous compounds that are thermally stable up to, and even above, room temperature and possess “formally” double-bonded germanium atoms. However, compounds containing germanium−chalcogen double bonds (Ge═Ch; Ch = O,[5] S,[6] Te,[7] etc.) provide only the germanium site to accommodate bulky substituents, and hence their oligomerization cannot be efficiently prevented. It is therefore not surprising that the first kinetically stabilized germaneselones (Tbt(Tip)Ge═Se and Tbt(Dis)Ge═Se) that are stable at ambient temperature were synthesized only recently.[8]

Indeed, monomeric germaneselones with trigonal planar geometry at germanium are kinetically unstable due to their lack of stabilization by bulky substituents. Although these species have been frequently postulated as intermediates, only very few of these short-lived intermediates have been detected experimentally.[9] Nevertheless, it seems intuitive that the presence of very bulky alkyl substituents in germaneselones may easily convert the double bond into the divalent species. With this notion in mind, it is important to consider the possibility of stabilizing this moiety with some small substituents. From a theoretical point of view, the simplest approach is to investigate single polar substituents, such as halogens. Fluorine is a particularly appealing candidate because of the strength of the Ge−F bonds. In the present work, the effect of dihalogen substitution on the relative stabilities of germaneselones is therefore investigated. Dimethyl substitution is also considered in this work for the sake of steric effects.

TABLE 1: Geometrical Parameters of Structures for Eq 1 at the B3LYP/6-311++G(d,p) and MP2(FC)/6-311++G(d,p) (in parentheses) Levels of Theory (Distances in Å, Angles in Degrees)



(1)

X	a	b	c	d	e	f	g	h	i	j	k	l
H	2.171	1.540	111.0	2.317	1.573	1.619	75.90	1.597	2.375	1.476	95.52	88.48
	(2.171)	(1.533)	(110.9)	(2.310)	(1.561)	(1.625)	(79.73)	(1.585)	(2.362)	(1.462)	(94.85)	(89.15)
CH_3	2.183	1.966	111.1	2.324	2.026	2.250	55.55	2.023	2.368	1.984	100.9	95.84
	(2.179)	(1.956)	(110.7)	(2.304)	(2.005)	(2.253)	(55.35)	(2.008)	(2.352)	(1.967)	(100.0)	(95.44)
F	2.152	1.742	99.24	2.447	1.772	1.822	64.41	1.804	2.415	1.828	92.65	92.51
	(2.143)	(1.753)	(98.33)	(2.443)	(1.778)	(1.848)	(67.34)	(1.818)	(2.398)	(1.825)	(92.36)	(92.45)
Cl	2.160	2.156	104.1	2.427	2.214	2.289	52.76	2.243	2.401	2.230	97.33	92.07
	(2.153)	(2.129)	(103.9)	(2.471)	(2.198)	(2.235)	(56.71)	(2.206)	(2.384)	(2.203)	(96.32)	(92.83)
Br	2.166	2.314	106.0	2.404	2.381	2.464	49.22	2.399	2.395	2.378	98.30	91.78
	(2.158)	(2.289)	(105.7)	(2.282)	(2.355)	(2.508)	(48.74)	(2.371)	(2.379)	(2.353)	(96.50)	(92.29)

There are two goals of this study: first, to predict systems where $X_2Ge{=}Se$ is more stable than the isomeric XGe−SeX and where relatively large barriers separate the two isomers; second, to predict trends in their molecular geometries and properties on substitution with progressively heavier atoms (F, Cl, Br) down the periodic table. Quantum mechanical methods can provide helpful information with regard to stability and structure of these types of molecules.[10] The only report of calculations on parent germaneselones has predicted the stability order for $H_2Ge{=}Se$, *trans*-HGeSeH, and *cis*-HGeSeH.[11] Computations on germaneselones with various substituents on germanium are nonexistent. In an attempt to characterize the structure and stability of germanium−selenium doubly bonded and divalent species, we shall present extensive and systematic theoretical calculations on the series $X_2Ge{=}Se$, XGeSeX (X = F, Cl, Br, CH_3), and transitions states (TS) connecting them (see eq 1 in Table 1). We shall provide accurate molecular parameters and spectroscopy data which may guide experimental studies on these species. As a consequence of this study, analogous research of germanium−selenium multiple bond compounds should soon be forthcoming and will open up new synthetic areas.

All geometries were fully optimized with the nonlocal hybrid density functional method at the B3LYP level.[12] The reason for using the B3LYP method is that it has been shown to be quite reliable both for geometries and energetics.[13] The 6-311++G(d,p) basis set has been used for Ge, Se, F, Cl, Br, C, and H (denoted B3LYP/6-311++G(d,p)).[14] The geometries were first optimized using the DFT models described above. For comparison, as suggested by one referee, structures for the germaneselone series were also optimized at the MP2(FC)/6-311++G(d,p) level. The harmonic vibrational frequencies

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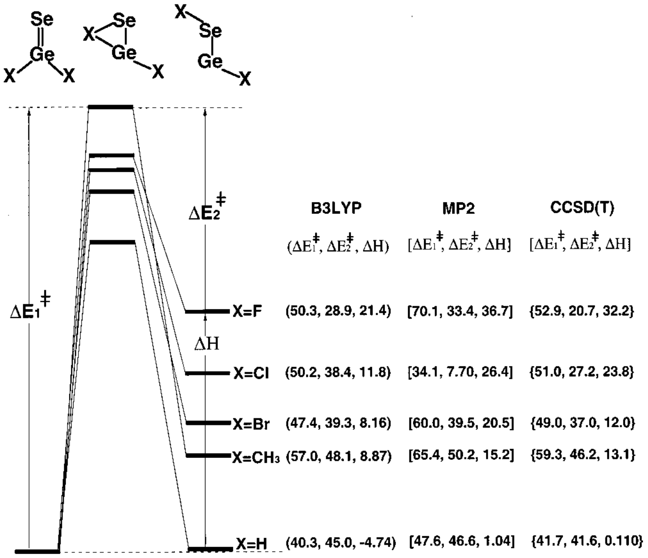
SCHEME 1



were then calculated at the same level of theory to confirm the nature of the stationary points. For all species, single-point calculations were made at the CCSD(T) [15] level using the 6-311++G(df,p) basis set. Unless otherwise noted, relative energies given in the text are those determined at CCSD(T)/6-311++G(df,p)//B3LYP/6-311++G(d,p) (hereafter designed CCSD(T)) and include vibrational zero-point energy (ZPE, without scale) corrections determined at B3LYP/6-311++G(d,p). All calculations were carried out on the IBM computers at the National Center for High-Performance Computing, with the GAUSSIAN98 programs.[16]

The geometries of the critical structures in the present calculations at the B3LYP and MP2 levels of theory are shown in Table 1 (the MP2 values are in parentheses). The relative reaction energies for the isomerization reactions obtained at the same level of theory are collected in Scheme 1. Of course, the experimental geometries for the stationary points of the isomerization of $X_2Ge{=}Se$ to $XGe{-}SeX$ are not available and it is hard to determine the accuracy of stationary point geometries generated by computational methods. Nevertheless, the prediction of geometric parameters seems to be consistent with changing the theory level of both ab initio and DFT methods. Moreover, as can be seen in Scheme 1, the trends for both B3LYP and MP2 results are qualitatively the same. Besides these, all we concern in this work is to find out the key factors that can greatly stabilize the germaneselone species. Thus, unless otherwise noted, we shall use only the B3LYP and CCSD(T) results in the following discussion for the sake of convenience. The calculated vibrational frequencies, rotational constants, dipole moments, and net atomic charges of substituted germaneselones, $X_2Ge{=}Se$, and their derivatives are collected in Table S1 of the Supporting Information. There are four important conclusions from these results to which attention should be drawn.

(1) Our B3LYP results suggest that the Ge=Se bond length of the $X_2Ge{=}Se$ species varies inversely with the electronegativity of the substituent X. For instance, the Ge=Se bond length increases along the series F (2.152 Å) < Cl (2.160 Å) < Br (2.166 Å) < CH_3 (2.183 Å). This effect on the Ge=Se bond distance in the germaneselones can be explained in terms of the bond polarity. The Ge=Se double bond is polarized, so that the Ge atom is positively charged and the Se atom carries a negative charge (i.e., $Ge^{\delta+}{=}Se^{\delta-}$). The electron-withdrawing substituents, in particular F, increase the positive charge at the germanium (see Table S1) and thus increase the ionic character of the Ge=Se bond as well. As a consequence, the more electronegative the substituent X attached to germanium, the shorter the Ge=Se double bond becomes. The opposite is true for the XGe−SeX species, where electron-withdrawing substituents reduce the polarization and thus lengthen the Ge−Se single bond (see below). Similarly, the increasing ∠XGeX bond angle in germaneselones is due to the steric effects of substituent X. Namely, since the size of the substituent X is in the order F < Cl < Br < CH_3, the ∠XGeX bond angle for the $X_2Ge{=}Se$ species increases in the order F (99.24°) < Cl (104.1°) < Br (106.0°) < CH_3 (111.1°). On the other hand, our DFT calculations show that halogen substitution results in a longer Ge−Se single bond, which decreases in the order F (2.415 Å) > Cl (2.401 Å) > Br (2.395 Å) > CH_3 (2.368 Å). Consequently, if bond energy−bond length relationships are valid, it appears that fluorine substitution strengthens the Ge=Se bond, with substitution at Ge having a greater effect (vide infra).

(2) As Scheme 1 shows, the most striking result reported in this work is that the relative stabilities of $X_2Ge{=}Se$ and XGe−SeX are dramatically reversed when two hydrogens are replaced by two halogens. In particular, germaneselones containing more electronegative substituents are considerably more stable. This situation may lead to a larger activation energy ($\Delta E_1^{‡}$) and a larger enthalpy (ΔH) for the unimolecular rearrangement (left to right in eq 1), but also the lower the heat ($\Delta E_2^{‡}$) of reverse reaction (right to left in eq 1). For instance, at the CCSD(T) level of theory, since the electron-withdrawing ability is in the order F > Cl > Br,[17] the barrier height ($\Delta E_1^{‡}$) for the $X_2Ge{=}Se \rightarrow XGe{-}SeX$ reaction decreases in the order F (53 kcal/mol) > Cl (51 kcal/mol) > Br (49 kcal/mol), while the activation energy ($\Delta E_2^{‡}$) for the $XGe{-}SeX \rightarrow X_2Ge{=}Se$ process increases in the order F (21 kcal/mol) < Cl (27 kcal/mol) < Br (37 kcal/mol). Similarly, the order of reaction enthalpy (ΔH) follows the same trend as that of the forward activation barrier ($\Delta E_1^{‡}$): F (32 kcal/mol) > Cl (24 kcal/mol) > Br (12 kcal/mol). In consequence, our theoretical results suggest that the more electronegative the halogen, the more stable the germaneselone ($X_2Ge{=}Se$).

(3) The effect of dihalogen substitution is quite encouraging (in particular for fluorine) since it strongly stabilizes double bond ($X_2Ge{=}Se$) relative to single bond (XGe−SeX).[18] For instance, in the case of monofluorine substitution,[19] HFGe=Se was found to be more stable than HGe−SeF, but less stable than FGe−SeH. These effects of dihalogen substitution are explained most probably in terms of the strength of Ge−X vs Se−X bonds. For example, according to the experimental studies, bond dissociation energies (in kcal/mol) are as follows: Ge−F = 116 ± 5, Se−F = 82 ± 20; Ge−Cl = 103, Se−Cl = 77; Ge−Br = 71 ± 7, Se−Br = 61 ± 20; Ge−H < 77, Se−H = 75; Ge−C = 110, Se−C = 141.[20] From these data, it is readily seen that very strong germanium−halogen bond can enhance the large preference of $X_2Ge{=}Se$ over XGe−SeX. In addition, as discussed in point (1), it was predicted that halogen substitution causes the shortening of the germanium−selenium double bond lengths. Again, this provides strong evidence for the fact that dihalogen substitution strengthens the Ge=Se double bond, as far as bond energy−bond distance relationships are valid. This, in turn, would reinforce relative stability of $X_2Ge{=}Se$ relative to XGe−SeX.

(4) It must be emphasized that $Me_2Ge{=}Se$ is now calculated to be 13 kcal/mol more stable than MeGe−SeMe at the CCSD(T) level of theory. This is very unusual, since bulky substituents

are expected to destabilize $X_2Ge{=}Se$ relative to $XGe{-}SeX$, due to the steric effects. Moreover, the barrier height for the $Me_2Ge{=}Se \rightarrow MeGe{-}SeMe$ reaction is sizable (59 kcal/mol at CCSD(T)). Likewise, the reverse activation barrier ($MeGe{-}SeMe \rightarrow Me_2Ge{=}Se$) is large (46 kcal/mol) as well. All of these results indicate that $Me_2Ge{=}Se$ will have both thermodynamic and kinetic stabilities for such a migration reaction.

In summary, our theoretical calculations suggest a possibly promising strategy for the synthesis of a relatively stable germaneselone based on the high energy of the divalent species $XGe{-}SeX$ and the low barrier for its rearrangement. Given the importance of the presence of the electronic effect on the germaneselone species, it is therefore predicted that either highly electronegative or bulky substitutions should greatly stabilize germaneselones $X_2Ge{=}Se$, with respect to $XGe{-}SeX$, from both a thermodynamic and a kinetic viewpoint. As such, one may then foresee that dihalogen-substituted and bulky substituted germaneselones would be good candidates for experimental observation. In other words, the detection of such species as a monomer should be achieved in either the low-pressure gas phase (e.g. as low as 10^{-4} Torr) or in cryogenic matrixes.

This work paves the way to the chemistry of unstabilized germaneselones.

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Supporting Information Available: Supporting Information: The calculated vibrational frequencies, rotational constants, dipole moments, and net atomic charges of substituted germaneselones, $X_2Ge{=}Se$, and their derivatives are collected in Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For the most recent reviews, see: (a) Okazaki, R.; Tokitoh, N. *Acc. Chem. Res.* **2000**, *33*, 625. (b) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1665.

(2) For reviews, see: (a) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: New York, 1989; Chapter 17, p 1015. (b) Barrau, J.; EsoudiÇ, J.; SatgÇ, J. *Chem. Rev.* **1990**, *90*, 283. (c) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125. (d) EsoudiÇ, J.; Couret, C.; Ranaivonjatovo, H.; SatgÇ, J. *Coord. Chem. Rev.* **1994**, *130*, 427. (e) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 31. (f) Klinkhammer, K. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2320. (g) Barrau, J.; Rina, G. *Coord. Chem. Rev.* **1998**, *178*, 593.

(3) (a) Escudié, J.; Couret, C.; Ranaivonjatovo, H. *Coord. Chem. Rev.* **1998**, *178*, 565. (b) Leigh, W. J. *Pure Appl. Chem.* **1999**, *71*, 453. (c) Tokitoh, N. *Pure Appl. Chem.* **1999**, *71*, 495.

(4) (a) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939. (b) Robinson, G. H. *Acc. Chem. Res.* **1999**, *32*, 773. (c) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.

(5) (a) Withnall, R.; Andrews, L. *J. Phys. Chem.* **1990**, *94*, 2351. (b) Norman, N. C. *Polyhedron* **1993**, *12*, 2431. (c) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Chem. Lett.* **1995**, 1087. (d) Lin, C.-L.; Su, M.-D.; Chu, S.-Y. *Chem. Phys.* **1999**, *249*, 145; and references therein.

(6) (a) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237. (b) Veith, M.; Detemple, A.; Huch, V. *Chem. Ber.* **1991**, *124*, 1135. (c) Tokitoh, N.; Matsumoto, T.; Manmara, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855. (d) Kuchta, C. M.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1351. (e) Khabashesku, V. N.; Boganov, S. E.; Zuev, P. S.; Nefedov, O. M. *J. Organomet. Chem.* **1991**, *402*, 161. (f) Lin, C.-L.; Su, M.-D.; Chu, S.-Y. *J. Phys. Chem. A* **2000**, *104*, 9250.

(7) (a) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 2337. (b) Ref 4(b). (c) Ref 3(c). (d) Tokitoh, N.; Matsuhashi, Y.; Shibata, K.; Matsumoto, T.; Suzuki, H.; Saito, M.; Manmara, K.; Okazaki, R. *Main Group Met. Chem.* **1994**, *17*, 55. (e) Tokitoh, N.; Matsumoto, T.; Ichida, H.; Okazaki, R. *Tetrahedron Lett.* **1991**, *32*, 6877. (f) Tokitoh, N.; Saito, M.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2065.

(8) (a) Ref 3(d). (b) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2316. (c) Foley, S.; Bensimon, C.; Richeson, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 10359. (d) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1999**, *121*, 8811.

(9) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1988**, *7*, 2015.

(10) (a) Lin, C.-L.; Su, M.-D.; Chu, S.-Y. *Chem. Phys.* **1999**, *249*, 145. (b) Liao, H.-Y.; Su, M.-D.; Chu, S.-Y. *Chem. Phys.* **2000**, *261*, 275. (c) Liao, H.-Y.; Su, M.-D.; Chu, S.-Y. *Inorg. Chem.* **2000**, *39*, 3522.

(11) Nowek, A.; Sims, R.; Babinec, P.; Leszczynski, J. *J. Phys. Chem. A* **1998**, *102*, 2189.

(12) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(13) (a) Su, M.-D.; Chu, S.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 4229. (b) Su, M.-D.; Chu, S.-Y. *J. Phys. Chem.* **1999**, *103*, 11011. (d) Lin, C.-L.; Su, M.-D.; Chu, S.-Y. *Chem. Commun.* **1999**, 2383.

(14) (a) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265. (b) Krishnan, R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (c) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(15) (a) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968. (b) Lee, T. J.; Scuseria, G. *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langoff, S. F., Ed.; Kluwer Academic Press: Dordrecht, 1995.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen,W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(17) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*; HarperCollins College Publishers: New York, 1993; p 187.

(18) A reviewer suggests that the energy ordering of isomers containing the second and third row elements can often be reversed when extra d orbitals are used on the heavy central atoms such as Ge and Se here. Therefore, to make sure the results presented in this work are reliable, we have done a B3LYP/6-311++G(3df,p) optimization on both $X_2Ge{=}Se$ and XGeSeX (X = H and F) species. Our computational results show that HGeSeH is more stable than $H_2Ge{=}Se$ by 3.97 kcal/mol, while $F_2Ge{=}Se$ is more stable than FGeSeF by 24.1 kcal/mol. These results are consistent with the energy ordering of the B3LYP/6-311++G(d,p) results in Scheme 1. We therefore believe that the B3LYP/6-311++G(d,p) level employed in this work can provide reliable results.

(19) Liao, H.-Y.; Su, M.-D.; Chu, S.-Y. *J. Phys. Chem. B* **2001**, *105*, (in print).

(20) Lide, D. R.; Frederikse, H. P. R. *CRC Handbook of Chemistry and Physics*; CRC Press: New York, 1998; pp 9−51.