CHEMCOMM
Communication
www.rsc.org/chemcomm

Theoretical study of triple bonds to germanium: relative stabilities of germanitriles and germaimines

Chin-Hung Lai,[a] Ming-Der Su*[b] and San-Yan Chu*[a]

[a] *Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, R.O.C.*
[b] *School of Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan, R.O.C.*
E-mail: ggs@chu1.chem.nthu.edu.tw

Received (in Cambridge, UK) 14th February 2001, Accepted 18th April 2001
First published as an Advance Article on the web 31st May 2001

Both B3LYP and CCSD(T) computational results suggest that fluorine substitution can dramatically stabilize FGe≡N, with respect to Ge=NF, both from a kinetic and from a thermodynamic viewpoint.

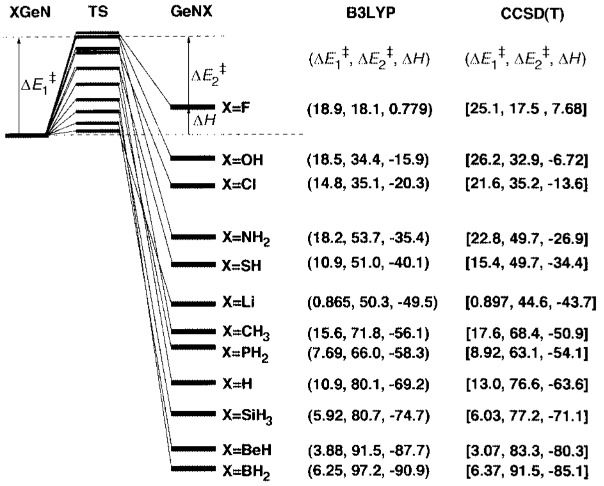
The chemistry of unsaturated organometallic compounds with multiple bonds between a group 14 atom and a heteroatom has assumed increasing importance during the last two decades, as shown by the large number of reviews[1] dealing with both experimental and theoretical aspects. In organogermanium chemistry, several very interesting new compounds with pπ–pπ bonds between the heteroatoms have been reported: Ge=C,[2] Ge=O,[3] Ge=S,[4] Ge=Ge[5] and Ge=N.[6] Of these species, the germaimines, compounds with a Ge=N double bond, have been studied extensively both experimentally[7] and theoretically.[8] Although there have been a great number of reports concerning the chemical and physical properties of these stable species, stable compounds with a Ge≡N triple bond (*i.e.* germanitriles) are still unknown. Naturally, the steric protection of the linear grouping of atoms in the triple bond system is much less possible than for a double bond system so that prospective syntheses are very problematical. Indeed, it has already been proposed that compounds of triply bonded germanium are the next frontier.[9,10]

These novel germanitriles raise a number of intriguing questions regarding their structures, energies, physical properties, and stabilities. Experimental difficulties have so far frustrated attempts to answer these questions. Nevertheless, this information can be obtained by the application of reliable computational methods. Thus, in this work we use carefully calibrated density functional theory (DFT) and high level *ab initio* computations to predict systems where XGe≡N is more stable than the isomeric Ge=NX, and where relatively large barriers separate the two isomers, hoping to stimulate experimental testing of these theoretical predictions.

To the best of our knowledge, no quantum chemical calculations for such compounds have yet been carried out, let alone a systematic theoretical study of substituent effects on the stabilities of germanitrile species. In view of the interest in isolating compounds containing a Ge≡N triple bond, we consider the possibility of stabilizing this moiety with various substituents. At present, we report a theoretical study concerning the effect of various substituents X (X = H, Li, BeH, BH_2, CH_3, SiH_3, NH_2, PH_2, OH, SH, F and Cl) on the relative stability of XGe≡N and Ge=NX isomers, as well as on the transition states connecting them.

Three regions on the potential energy surfaces are considered in this work: XGe≡N (germanitriles), the transition states, and Ge=NX (germaimines); see eqn. (1) in Table 1. The geometries and energetics of the stationary points on the potential energy surface of eqn. (1) have been calculated using non-localized DFT in conjunction with the 6-311++G(d,p) basis set, which is denoted as B3LYP/6-311++G(d,p).[11] All the stationary points have been positively identified as equilibrium structures (number of imaginary frequencies $N_{\text{imag}} = 0$) or transition states ($N_{\text{imag}} = 1$). Single-point energies were also calculated at CCSD(T)(frozen)/6-311++G(3df,3pd)//B3LYP/6-311++G(d,p) (hereafter designated CCSD(T)), to improve the treatment of electron correlation. Unless otherwise noted, relative energies given in the text are those determined at CCSD(T) and include vibrational zero-point energy (ΔZPE) corrections determined at B3LYP/6-311++G(d,p).[12]

The results of our theoretical study of unimolecular reaction [eqn. (1)] are summarized in the schematic reaction profiles in Scheme 1. Selected geometrical parameters of XGe≡N, Ge=NX, and the transition state for the reaction are collected in Table 1. Several intriguing results from Scheme 1 and Table 1 are as follows.

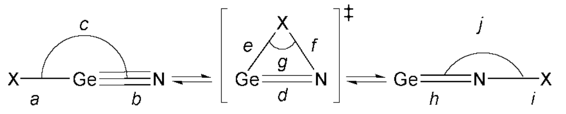


Scheme 1

First, as one can see in Scheme 1, the calculated energy difference between XGe≡N and Ge=NX, Δ*H*, is strongly dependent on the substituent X. Namely, for most substituents (*i.e.* X = H, Li, BeH, BH_2, CH_3, SiH_3, NH_2, PH_2, OH, SH and Cl), germaimines, Ge=NX, are more stable than the isomeric germanitriles, XGe≡N, by −6.7 to −85 kcal mol^{-1} at the B3LYP and CCSD(T) levels of theory. Additionally, it is apparent in Scheme 1 that electronegative substituents can reduce the energy difference between XGe≡N and GeN=X. Furthermore, Δ*H* is positive only for X = F. That is to say, FGe≡N is more stable than the corresponding Ge=NF by 7.7 kcal mol^{-1} at the same level of theory. It is therefore predicted that the more electronegative the substituent, the more stable the germanitrile (XGe≡N).

Secondly, it is found that the energy difference (Δ*H*) between XGeN and GeNX increases as the X element moves from left to right across both the first-row (from B to F) and second-row (from Si to Cl) in the periodic table. For instance, Δ*H* increases in the order (in kcal mol^{-1}) : BH_2 (−85) < CH_3 (−51) < NH_2 (−27) < OH (−6.7) < F (+7.7) and SiH_3 (−71) < PH_2 (−54) < SH (−34) < Cl (−14). In addition, there is a reduction in Δ*H* energies between the first- and second-row X substituents. That is, CH_3 > SiH_3, NH_2 > PH_2, OH > SH, and F > Cl. The

Table 1 Geometrical parameters of structures for eqn. (1) at the B3LYP/6-311++G(d,p) level of theory (distances in Å, angles in degrees)



(1)

X	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*
H	1.522	1.638	180.0	1.714	1.573	2.313	47.79	1.657	1.006	180.0
Li	2.415	1.660	180.0	1.666	2.414	3.755	18.90	1.677	1.748	180.0
BeH	2.160	1.649	180.0	1.672	2.177	3.246	27.99	1.677	1.499	180.0
BH_2	2.021	1.651	180.0	1.690	2.066	2.830	36.33	1.682	1.398	179.9
CH_3	1.959	1.642	180.0	1.715	2.089	2.696	39.51	1.663	1.423	179.9
SiH_3	2.400	1.646	180.0	1.686	2.443	3.289	29.81	1.671	1.723	180.0
NH_2	1.822	1.646	173.8	1.755	1.938	2.626	41.93	1.675	1.356	174.6
PH_2	2.342	1.647	172.3	1.703	2.414	3.163	32.15	1.675	1.694	171.1
OH	1.773	1.649	173.9	1.792	1.865	2.519	45.28	1.673	1.354	169.1
SH	2.221	1.648	176.5	1.736	2.298	2.967	35.72	1.679	1.657	171.9
F	1.748	1.651	180.0	1.834	1.827	2.413	48.88	1.670	1.346	180.0
Cl	2.145	1.649	180.0	1.770	2.241	2.867	38.13	1.673	1.660	180.0

reason for these trends can easily be understood in terms of the X–Ge *vs.* X–N bond energies. Generally speaking, elements which are more electronegative than Ge increase the XGe≡N *vs.* XN=Ge energy differences (relative to X = H), while more electronegative elements decrease them. For example, ΔH is positive for X = F, where a very strong F–Ge bond and a very weak F–N bond[13] can overturn the large (*ca.* 64 kcal mol^{-1}) intrinsic preference of HN=Ge over HGe≡N.

Thirdly, as we can see in Scheme 1, electronegative substitution not only reduces the energy gap (ΔH) between XGe≡N and Ge=NX, but it also raises the barrier ($\Delta E_1^{\ddagger}$) to the XGe≡N → Ge=NX isomerization, thus increasing the kinetic stability of the germanitrile molecules. For instance, our CCSD(T) calculations suggest that the barrier for the isomerization of XGe≡N to Ge=NX decreases in the order (in kcal mol^{-1}): X = OH (26) > X = F (25) > X = NH_2 (23) > X = Cl (22) > X = CH_3 (18) > X = SH (15) > X = H (13) > X = PH_2 (8.9) > X = BH_2 (6.4) ≈ X = SiH_3 (6.0) > X = BeH (3.1) > X = Li (0.90). Likewise, the barrier height ($\Delta E_2^{\ddagger}$) for the reverse reaction (from Ge=NX to XGe≡N) is also dependent on the electronegativity of substituents X. That is to say, the more electronegative the substituent, the smaller the activation barrier from Ge=NX to XGe≡N. For example, our CCSD(T) results indicate that the trend in activation energy ($\Delta E_2^{\ddagger}$; in kcal mol^{-1}) mirrors the trend in electronegativity of the substituent: X = F (18) < X = OH (33) < X = Cl (35) < X = Li (45) < X = NH_2 (50) ≈ X = SH (50) < X = PH_2 (63) < X = CH_3 (68) < X = H (77) ≈ X = SiH_3 (77) < X = BeH (83) < X = BH_2 (91). Taken together, our theoretical findings suggest that fluorine is a particularly appealing possibility because of the strength of the Ge–F bond.

In summary, from our survey of the unimolecular isomerization of XGe≡N → Ge=NX reactions, the present computational results predict that germanitrile XGe≡N itself lies at the minimum of the potential energy surface, and can be strongly stabilized in both a kinetic and thermodynamic sense with a proper choice of substituents. In particular, based on the DFT and CCSD(T) results, we confidently predict that FGe≡N should be stable with respect to the products of unimolecular isomerization and should be the most likely of the species to be detected experimentally.

We encourage experimentalists to carry out further experiments to confirm our predictions.

We are grateful to the National Center for High-Performance Computing of Taiwan for generous amounts of computing time. We also thank the National Science Council of Taiwan for their financial support.

Notes and references

1 For recent reviews, see: (*a*) G. Raabe and J. Michl, in *The Chemistry of Organic Silicon Compounds*, ed. S. Patai and Z. Rappoport., John Wiley, New York, 1989, ch. 17, p. 1015; (*b*) J. Barrau, J. Esoudié and J. Satgé, *Chem. Rev.*, 1990, **90**, 283; (*c*) R. S. Grev, *Adv. Organomet. Chem.*, 1991, **33**, 125; (*d*) J. Esoudié, C. Couret, H. Ranaivonjatovo and J. Satgé, *Coord. Chem. Rev.*, 1994, **130**, 427; (*e*) R. Okazaki and R. West, *Adv. Organomet. Chem.*, 1996, **39**, 31; (*f*) K. W. Klinkhamme, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2320; (*g*) J. Barrau and G. Rina, *Coord. Chem. Rev.*, 1998, **178**, 593; (*h*) P. P. Power, *J. Chem. Soc., Dalton Trans.*, 1998, 2939; (*i*) N. Tokitoh, T. N. Matsumoto and R. Okazaki, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 1665; (*j*) G. H. Robinson, *Acc. Chem. Res.*, 1999, **32**, 773; (*k*) P. P. Power, *Chem. Rev.*, 1999, **99**, 3463; (*l*) W. J. Leigh, *Pure Appl. Chem.*, 1999, **71**, 453; (*m*) N. Tokitoh, *Pure Appl. Chem.*, 1999, **71**, 495; (*n*) R. Okazaki and N. Tokitoh, *Acc. Chem. Res.*, 2000, **33**, 625.

2 J. Escudié, C. Couret and H. Ramaivonjatovo, *Coord. Chem. Rev.*, 1998, **178**, 565 and references therein; J. Satgé, *Adv. Organomet. Chem.*, 1982, **21**, 241.

3 (*a*) M. Rivière-Baudet, J. Satgé and F. El-Baz, *J. Chem. Soc., Chem. Commun.*, 1995, 1687; (*b*) T. Tsumuraya and W. Ando, *Chem. Lett.*, 1989, 1043; (*c*) C. Glidewell, D. Lloyd, K. W. Lumbard and J. S. McKechnie, *Tetrahedron Lett.*, 1987, **28**, 343; (*d*) A. Meller, G. Ossig, W. Maringgele, D. Stalke, R. Herbst-Irmer, S. Freitag and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1991, 1123; (*e*) H. G. Ang and F. K. Lee, *J. Chem. Soc., Chem. Commun.*, 1989, 310.

4 P. G. Harrison, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, New York, 1987, vol. 3, ch. 26; J. Satgé, *Pure Appl. Chem.*, 1984, **56**, 137; T. Tsumuraya, S. A. Batcheller and S. Masamune, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 902; J. Satgé, *J. Organomet. Chem.*., 1990, **400**, 121; R. Okazaki, N. Tokitoh, A. Ishii, N. Ishii, Y. Matsuhashi, T. Matsumoto and H. Suzuki, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1992, **67**, 49.

5 N. Wiberg, *J. Organomet. Chem.*, 1984, **273**, 141; P. B. Hitchcock, M. F. Lappert, J. J. Miles and A. Thorne, *J. Chem. Soc., Chem. Commun.*, 1984, 480; J. T. Snow, S. Murakami, S. Masamune and D. J. Williams, *Tetrahedron Lett.*, 1984, **25**, 419; W.-C. Chen, M.-D. Su and S.-Y. Chu, *Organometallics*, 2001, **20**, 564 and references therein.

6 N. C. Norman, *Polyhedron*, 1993, **12**, 2431; W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 272; L. E. Guselñikov and N. S. Nametkin, *Chem. Rev.*, 1979, **79**, 529.

7 The germaimines were first characterized indirectly using various trapping reagents [see ref. 3(*a*)]. Only in the last ten years have sufficiently stable germaimines been stabilized to allow their analysis in the solid state, solution, and in the gas phase [see refs. 3(*b*)–(*e*)].

8 G. Trinquier, J.-C. Barthelat and J. Satgé, *J. Am. Chem. Soc.*, 1982, **104**, 5931.

9 See ref. 1(*h*) and 3(*a*); P. Jutzi, *Angew. Chem., Int. Ed.*, 2000, **39**, 3797.

10 For XSiN study see: Y. Apeloig and K. Albrecht, *J. Am. Chem. Soc.*, 1995, **117**, 7263 and references therein.

11 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

12 M. J. Frisch, *et al.* Gaussian 94, Gaussian, Inc., Pittsburgh, PA, 1995.

13 Bond dissociation energetics (kcal mol^{-1}): Ge–F 116, N–F 82.0, Ge–Cl ≈ 103, N–Cl 79.8 ± 2.29, Ge–O 158 ± 3.01, N–O 151 ± 0.031, Ge–S 132 ± 0.598, N-S 111 ± 5.02, Ge–C 110 ± 5.02, N–C 180 ± 2.39, Ge–Si 71.9 ± 5.02, N–Si 112 ± 3.59. See: D. R. Lide and H. P. R. Frederikse, *CRC Handbook of Chemistry and Physics*, CRC Press, New York, 1998, pp. 9–51.