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Substituent Effects on Germanium−Germanium and Tin−Tin Triple Bonds

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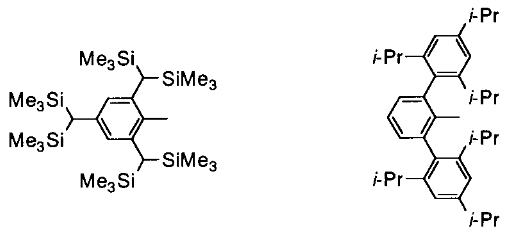
Summary: Effects of bulky aryl groups, C_6H_2*-2,4,6-*$\{CH(SiMe_3)_2\}_3$ *and* C_6H_3*-2,6-*$(C_6H_2$*-2,4,6-i-*$Pr_3)_2$*, on germanium−germanium and tin−tin triple bonds are investigated using density functional theory in search of stable digermynes (*$RGe{\equiv}GeR$*) and distannynes (*$RSn{\equiv}SnR$*).*

Multiple bonds between heavier main-group elements are of widespread interest.[1] Thus, a number of stable heavier analogues of alkenes, $R_2M{=}MR_2$ (M = Si, Ge, Sn, and even Pb), have been synthesized and isolated up to now.[1] However, stable heavier analogues of alkynes, $RM{\equiv}MR$, are still unknown despite several attempts,[2] which have attracted special interest as an important target in main-group chemistry.[3] A series of calculations of potential energy surfaces of $RM{\equiv}MR$ (R = H, Me, and SiH_3) reveal that the major difficulties in synthesis and isolation are due to their facile isomerization and high reactivity.[4] Recently, it has been suggested that bulky substituents could make disilynes ($RSi{\equiv}SiR$) a viable target as trans-bent structures.[4−6] It is an important question whether still heavier analogues are also synthetically accessible and isolable as stable molecules, when they bear the proper bulky substituents. Since 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl (Tbt) and 2,6-bis(2,4,6-triisopropylphenyl)phenyl (Ar*) are known as representative bulky groups (Chart 1) useful for the synthesis and stabilization of doubly bonded species,[7,8] we have investigated their effects on digermynes ($RGe{\equiv}GeR$) and distannynes ($RSn{\equiv}SnR$) as a typical example.

Chart 1



Tbt Ar*

Density functional calculations at the B3LYP level[9] were carried out with the 3-21G* basis set,[10] because of the size of the molecules, using the Gaussian 98 program.[11] To calibrate the calculations for the present purpose, we tested the parent $HGe{\equiv}GeH$, which has a trans-bent C_{2h} structure.[12] The Ge−Ge distance and Ge−Ge−H angle of 2.223 Å and 123.0° calculated at the B3LYP/3-21G* level are only 0.005 Å longer and 1.0−1.6° smaller than those of 2.218 Å and 124.0° at the B3LYP/6-311G(2d,2p) level and 2.218 Å and 124.6° at the MP2/6-311G(2d,2p) level. In addition, the energy difference of 8.6 kcal/mol (B3LYP/3-21G*) favoring $GeGeH_2$ over $HGe{\equiv}GeH$ agrees well with those of 8.8

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(4) (a) Nagase, S.; Kobayashi, K.; Takagi, N. *J. Organomet. Chem.* **2000**, *611*, 264. For R = Me and SiH_3, see: (b) Takagi, N.; Nagase, S. Manuscript in preparation.

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(6) Kobayashi, K.; Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 234.

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(12) All-electron density functional B3LYP and ab initio MP2 calculations give similar potential energy surfaces. This is not the case when effective core potentials (ECP) are employed for heavy atoms; for example, the trans-bent C_{2h} structure of $HGe{\equiv}GeH$ is a minimum for MP2 (as well as CCSD(T) and CASSCF (6,6)), as in all-electron calculations but is rather a transition state for B3LYP. As the calculated vibrational frequencies show, B3LYP tends to favor a twisted structure, in contrast to MP2 and CCSD(T), even in all-electron calculations. However, B3LYP is the only method applicable to large molecules.

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Figure 1. Optimized structures of (a) TbtGe≡GeTbt and (b) GeGeTbt$_2$. Atoms are denoted by the following colors: pink, Ge; purple, Si; green, C; and white, H.

kcal/mol (B3LYP/6-311G(2d,2p)) and 6.5 kcal/mol (CCSD-(T)/6-311G(2d,2p)//MP2/6-311G(2d,2p)). The results below are based on the B3LYP/3-21G* calculations, and the M−M−R bond angle and R−M−M−R dihedral angle of RM≡MR are denoted by the symbols θ and ω, respectively.

The optimized structure of TbtGe≡GeTbt is shown in Figure 1a and has C_2 symmetry. Obviously, the two bulky Tbt groups help to protect the Ge−Ge bond from the attack of reactive reagents. The trans bending in TbtGe≡GeTbt ($\theta = 121.8°$) is 9.1° larger than that in TbtSi≡SiTbt ($\theta = 130.9°$), and its skeleton is twisted 7.0° around the Ge−Ge bond ($\omega = 173.0°$), unlike the silicon case ($\omega = 180°$). The Ge−Ge distance of 2.231 Å lengthens slightly from that of HGe≡GeH. It is worth noting that the Ge−Ge distance is short and deserves to be a triple bond,[13] compared with the Ge−Ge double-bond distance of 2.304 Å calculated for H$_2$Ge=GeH$_2$ (C_{2h}) and those in the range 2.30−2.44 Å observed for the X-ray crystal structures of R$_2$Ge=GeR$_2$ with trans-bent angles of 30−46°.[1,14] The bulky Tbt groups help to destabilize the 1,2-Tbt shifted isomer GeGeTbt$_2$, since they crowd more around one end of the Ge−Ge bond, as shown in Figure 1b. Thus, TbtGe≡GeTbt is 17.5 kcal/mol more stable than GeGeTbt$_2$. This energy difference is sufficiently large to prevent the 1,2-Tbt shift in TbtGe≡GeTbt, while HGe≡GeH isomerizes readily with a very small barrier of 3.4 kcal/mol.[4a]

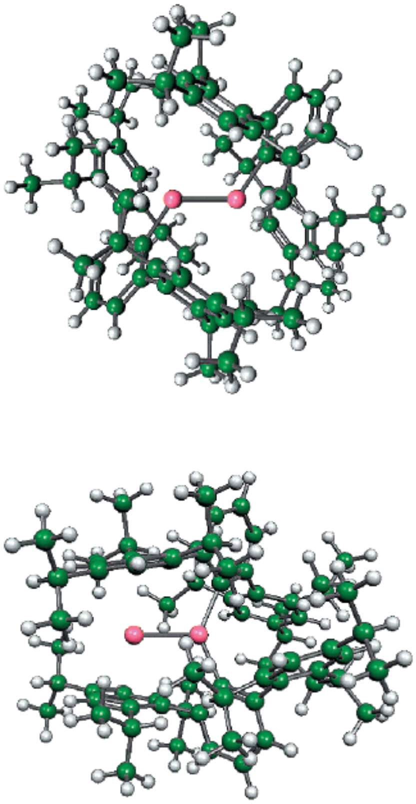

Figure 2. Optimized structures of (a) Ar*Ge≡GeAr* and (b) GeGeAr*$_2$. Atoms are denoted by the following colors: pink, Ge; green, C; white, H.

Figure 2 shows the optimized structures of Ar*Ge≡GeAr* and its isomer GeGeAr*$_2$. The bulkier Ar* groups make Ar*Ge≡GeAr* 29.5 kcal/mol more stable than GeGeAr*$_2$. The trans bending in Ar*Ge≡GeAr* ($\theta = 123.2°$) differs little from that in TbtGe≡GeTbt ($\theta = 121.8°$). However, Ar*Ge≡GeAr* suffers a larger twisting ($\omega = 157.6°$) around the Ge−Ge bond with C_2 symmetry than TbtGe≡GeTbt, owing to the bulkier Ar* groups. As a result, the Ge−Ge distance of 2.277 Å is 0.046 Å longer than that for TbtGe≡GeTbt. A much less twisted ($\omega = 171.0°$) but more trans-bent ($\theta = 131.2°$) structure was also located for Ar*Ge≡GeAr*. This structure has a shorter Ge−Ge distance of 2.218 Å but is 46.3 kcal/mol less stable than the structure shown in Figure 2a.[15] In an attempt to reduce the crowding of substituents, the *i*-Pr groups on Ar* were replaced by

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[13] Upon substitution by electropositive silyl groups such as Si(*t*-Bu)$_3$ and SiDep$_3$ (Dep = 2,6-diethylphenyl), the Ge−Ge distance becomes ca. 0.1 Å shorter. However, the digermynes undergo facile dimerization when silyl groups are not sufficiently bulky.

[14] For a short Ge−Ge distance of 2.213 Å for the less trans-bent R$_2$Ge=GeR$_2$, see: (a) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191. (b) Schäfer, H.; Saak, W.; Weidenbruch, M. *Organometallics* **1999**, *18*, 3159.

[15] In a recent study of Ar*Si≡SiAr*, only a slightly twisted structure ($\omega = 177.4°$, $\theta = 133.5°$, and Si−Si = 2.094 Å) was located; therefore, Ar*Si≡SiAr* was calculated to be 12.9 kcal/mol less stable than SiSiAr*$_2$.[6] However, it has been recently found that a more twisted C_2 structure of Ar*Si≡SiAr* ($\omega = 163.9°$, $\theta = 130.5°$, and Si−Si = 2.126 Å) is 31.7 kcal/mol more stable than SiSiAr*$_2$, which is also very stable to dimerization (Takagi, N.; Nagase, S. *Chem. Lett.* **2001**, 966).

H atoms. Upon this replacement, the digermyne structure was not only highly trans-bent ($\theta = 99.2°$) but also highly twisted ($\omega = 92.5°$) in such a way that Ge interacts with two benzene rings of both sides of the *m*-terphenyl group, and the Ge−Ge distance was elongated to 2.509 Å, which is longer than the Ge−Ge single bond of 2.424 Å in $H_3Ge{-}GeH_3$. In addition, the 1,2-shifted isomer was only 10.7 kcal/mol less stable. Obviously, the *i*-Pr groups on Ar* are not ornamental but essential to maintain a digermyne structure.[16] When smaller groups such as Ph are adopted instead of Ar*, the digermyne undergoes facile isomerization leading to a dibridged structure (Ge−Ge = 2.506 Å, $\theta = 98.8°$, and $\omega = 88.4°$)[17] or the 1,2-shifted isomer $GeGePh_2$. These results suggest that it is very important to prepare carefully substituent groups in order to realize a digermyne structure.

We turn to the tin case, RSn≡SnR. As found for the germanium case, the energy difference of 29.4 kcal/mol favoring RSn≡SnR over $SnSnR_2$ is larger for R = Ar* than that of 10.4 kcal/mol for R = Tbt. The trans bending and twisting in TbtSn≡SnTbt ($\theta = 122.0°$ and $\omega = 169.3°$) is only 0.2 and 3.7° larger than those in TbtGe≡GeTbt, respectively. It is interesting that the Sn−Sn distance of 2.659 Å for TbtSn≡SnTbt is considerably shorter than those of 2.737 Å for $H_2Sn{=}SnH_2$ (C_{2h}) and 2.77−3.64 Å for the X-ray crystal structures of $R_2Sn{=}SnR_2$.[1] On the other hand, Ar*Sn≡SnAr* has a more trans-bent and twisted structure ($\theta = 111.0°$ and $\omega = 125.3°$) than TbtSn≡SnTbt. As a result, the Sn−Sn distance of 2.900 Å is rather longer than the Sn−Sn single bond distance of 2.824 Å in $H_3Sn{-}SnH_3$.[18] In this context, it is interesting that a recent X-ray crystal study of Ar*PbPbAr* shows that the Pb−Pb bond of 3.188 Å is much longer than those for diplumbanes such as $Ph_3PbPbPh_3$ (2.844 Å),[19] which has no π bonding.[20,21]

The energies required to cleave the Ge−Ge bond of RGe≡GeR (leading to two GeR units in the ground doublet state) are 54.7 kcal/mol (R = Tbt) and 33.8 kcal/mol (R = Ar*), the latter smaller value being ascribed to the higher twisting around the Ge−Ge bond. The energies are smaller for RSn≡SnR because of inherently weaker Sn−Sn bonds but are still as large as 37.4 kcal/mol (R = Tbt) and 25.9 kcal/mol (R = Ar*). These values suggest that RM≡MR does not dissociate into two MR fragments in solution. This is worthy of note, since the germanium and tin analogues of alkenes dissociate readily in solution and are best regarded as weak donor−acceptor complexes.[1]

The germanium and tin analogues of alkynes are interesting synthetic targets worthy of experimental testing, regardless of multiple or single bonding, when they are properly substituted. It is expected that these molecules will be soon synthesized in a stable form and open a new area of main-group chemistry.

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Note Added in Proof. The energies required to cleave the Pb−Pb bond of RPb≡PbR were 10.1 kcal/mol (R = Ar*) and 17.9 (R = Tbt) kcal/mol.

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(16) For the importance of the *i*-Pr groups on Ar* in synthesizing $Na_2[Ar^*GaGaAr^*]$ and making the Ga−Ga distance as short as triple bonds, see: (a) Robinson, G. H. *Acc. Chem. Res.* **1999**, *32*, 773. (b) Takagi, N.; Schmidt, M. W.; Nagase, S. *Organometallics* **2001**, *20*, 1646.

(17) This is consistent with the fact that mono- and dibridged structures become stable as the substituents become small.[4a]

(18) In addition, the singly bonded isomer Ar*S̈n−S̈nAr* (Sn−Sn = 3.087 Å, $\theta = 99.0°$, and $\omega = 172.8°$), in which the out-of-plane π bonding orbital is unoccupied, was calculated to be 4.8 kcal/mol more stable than Ar*Sn≡SnAr*, while TbtS̈n−S̈nTbt (Sn−Sn = 3.053 Å, $\theta = 97.3°$, and $\omega = 169.0°$) was 2.4 kcal/mol more stable than TbtSn≡SnTbt. On the other hand, Ar*G̈e−G̈eAr* (Ge−Ge = 2.636 Å, $\theta = 100.0°$, and $\omega = 148.7°$) was only 0.7 kcal/mol more stable than Ar*Ge≡GeAr*. In contrast, TbtG̈e−G̈eTbt as well as RS̈i−S̈iR (R = Tbt and Ar*) was not located as a mimimum. These are consistent with the fact that RM̈−M̈R becomes more stable than RM≡MR, as M becomes heavier;[1, 2e] the former structure corresponds to the transition state interconverting the doubly bridged isomer when R is small.

(19) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524.

(20) For the model calculation in which the *i*-Pr groups on Ar* are replaced by H atoms, see: Chen, Y.; Hartmann, M.; Diedenhofen, M.; Frenking, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2052. The calculation gives a structure that is close to the experimental structure of Ar*PbPbAr*. However, we have calculated that a highly twisted C_2 structure ($\omega = 53.9°$) is 2.2 kcal/mol more stable when the *i*-Pr groups are absent.

(21) In contrast to the model calculation omitting the *i*-Pr groups on Ar*,[20] Ar*Pb≡PbAr* (Pb−Pb = 2.853 Å, $\theta = 127.2$ and 127.3°, and $\omega = 179.7°$) was also located as a minimum, though it was 11.4 kcal/mol less stable than Ar*P̈b−P̈bAr* (Pb−Pb = 3.247 Å, $\theta = 99.2°$, and $\omega = 175.7°$). On the other hand, TbtPb≡PbTbt (Pb−Pb = 2.815 Å, $\theta = 130.7$ and 131.2°, and $\omega = 160.4°$) was 8.9 kcal/mol less stable than TbtP̈b−P̈bTbt (Pb−Pb = 3.208 Å, $\theta = 97.5$ and 97.6°, and $\omega = 170.5°$). These calculations were carried out at the B3LYP level (DZd for Pb, DZ for Si, and 3-21G for C and H).