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Preliminary communication

THE MOLECULAR STRUCTURE OF A GERMENE GeR_2 (R = $CH(SiMe_3)_2$) BY GAS ELECTRON DIFFRACTION; SELF-CONSISTENT-FIELD MOLECULAR ORBITAL CALCULATIONS ON STANNENE, SnH_2, AND DISTANNENE, Sn_2H_4

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Summary

$Ge[CH(SiMe_3)_2]_2$ is a V-shaped monomer in the gas phase at ca. 430 K, with Ge—C 204(2) pm and angle CGeC = 107(2)°; ab initio MO calculations on Sn_2H_4, with better than double ζ basis, indicate that (i) a non-planar *trans*-folded conformation is more stable than a planar structure by 26 kJ mol^{-1}, and (ii) the optimal angle between the Sn—Sn vector and an SnH_2 plane is 46°.

The Group IV metal(II) alkyls $(MR_2)_n$ (M = Ge or Sn, R = $CH(SiMe_3)_2$) at present represent a unique class of compounds, which exist as monomers (n = 1, the carbene analogues) or dimers (n = 2, the alkene analogues) depending on phase. Points of interest for each of MR_2 and M_2R_4 include (i) the equilibrium geometry; (ii) M—C angles and CMC bond lengths and angles; (iii) trends as between M = C, (Si), Ge, and Sn; and (iv) for MR_2, comparisons with related MX_2 molecules. The present communication addresses these problems, and provides (a) experimental results on the gas phase structure of GeR_2 and (b) computational data on SnH_2 and Sn_2H_4 (as models for SnR_2 and Sn_2R_4).

The compounds GeR_2 and SnR_2 (R = $CH(SiMe_3)_2$) are monomeric in hydrocarbon solution and in the gas phase (by mass spectrometry or photoelectron spectroscopy) [1]. The molecular structure of gaseous SnR_2 (by gas electron dif-

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fraction (GED)) is V-shaped, with Sn—C 224(1) pm and angle CSnC 96(1)° [2].

The electron diffraction pattern of GeR_2 was recorded with reservoir and nozzle temperatures of about 430 K corresponding to a vapour pressure of about 1 torr. Structure refinements were based on a model of C_2 symmetry defined by three bond distances (Ge—C, Si—C, and C—H), five valence angles, and three torsional angles. Least-squares refinements gave Ge—C 204(2) and Si—C(mean) 189(1) pm; angles CGeC 107(2)°, GeCSi 111(1)°, and SiCSi 113(1)°. The other structure parameters are unexceptional, Fig. 1.

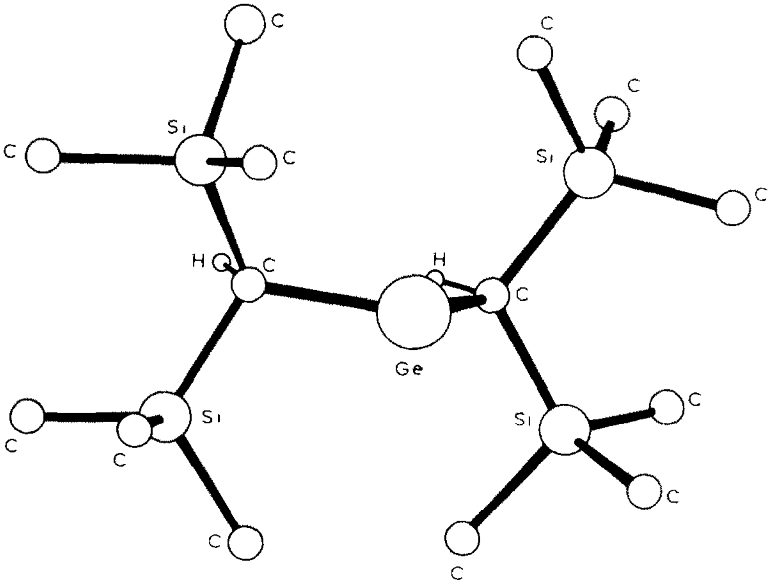
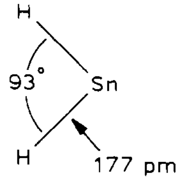


Fig. 1. Molecular structure of $Ge[CH(SiMe_3)_2]_2$, as determined by gas-phase electron diffraction.

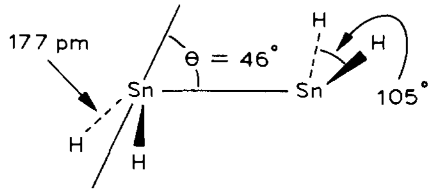
The Ge—C bond distance is about 10 pm larger than in $GeMe_4$, 194.5(3) pm [3]. A similar $M^{II} \rightarrow M^{IV}$ SnC bond-shortening was noted in SnR_2 vs. $SnMe_4$ [2]. Surprisingly, the CGeC valence angle is now found to be ca. 10° larger than CSnC in SnR_2. Previously we noted (i) a similar, but somewhat less marked, monotonic decrease in the angle at M of the isoelectronic amides $M[N(SiMe_3)_2]_2$ (NMN 101(1.5) (M = Ge), 96 (M = Sn), or 91(2)° (M = Pb)), attributed to Bent's rule; and (ii) a similar M^{IV}—N → M^{II}—N bond-lengthening [4]. A further manifestation of Bent's rule is that $CM^{II}C > NM^{II}N > OM^{II}O$ (from X-ray data on $M(OAr)_2$, Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4) [5]; however, the large CGeC angle is probably due to steric effects.

Studies by X-ray crystallography show that GeR_2 [6] and SnR_2 [1] are dimeric in the solid phase. The C_2MMC_2 fragments are *trans*-folded, the angle between the M—M vectors and MC_2 plane being θ 32° (M = Ge) and 41° (M = Sn). Ab initio MO calculations on Ge_2H_4 [7] (see also refs. 2 and 8) have yielded *trans*-folded equilibrium structures with θ ranging from 34 to 40°.

We now report the results of similar calculations on SnH_2 and Sn_2H_4, with better than double-ζ basis [9]; the calculated equilibrium structures are summarised in I and II [10].



(I)



(II)

The optimal Sn—Sn bond distance in Sn_2H_4, 271 pm, is slightly shorter than the experimental value for Sn_2R_4, 276 pm [1]. The experimental CSnC angle in SnR_2 is 97° [2]; in Sn_2R_4 it has increased to 112° [1]. A similar difference is now found between the optimal HSnH angles in SnH_2 (93°) and Sn_2H_4 (105°). The larger angles in the alkyl derivatives may be due to steric factors.

The equilibrium conformation of Sn_2H_4 is *trans*-folded with θ 46°; the experimental values [6] for θ in Ge_2R_4 and Sn_2R_4 are 32 and 42°, respectively. The energy of the equilibrium conformation of Sn_2H_4 is 26 kJ mol^{-1} below the optimum planar model (where Sn—Sn 255 pm). The stability of a *trans*-folded relative to a planar structure increases along the series C_2H_4, Si_2H_4, Ge_2H_4, and Sn_2H_4 (as was previously shown diagrammatically for the first three members [2]). In Sn_2H_4, θ is calculated to be only 6° larger than in Ge_2H_4, but stabilisation by *trans*-folding is 26 vs. 12 kJ mol^{-1}.

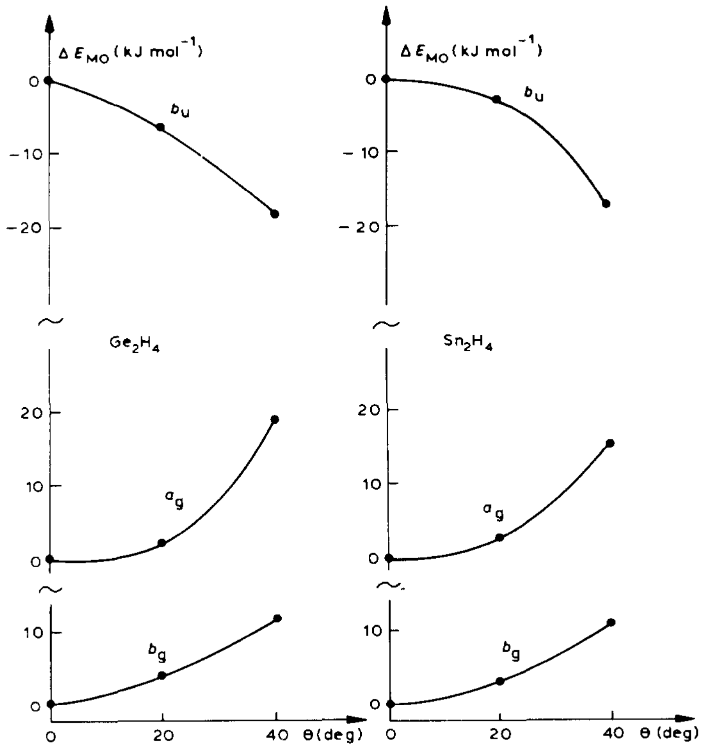


Fig. 2. Variation of energies of the three highest occupied molecular orbitals of Ge_2H_4 and Sn_2H_4 with the fold angle θ.

In Fig. 2 we show the variation of the orbital energies of the HOMO's of Ge_2H_4 and Sn_2H_4 as functions of θ. In both molecules the energy of the b_u (M—M π-bonding) orbital drops when θ is increased from zero. (The effect is due to mixing with the M—M σ-antibonding orbital.) The energy of the a_g (M—M σ-bonding) orbital increases with θ. The non-planar equilibrium structures of these molecules may thus be attributed to the "inertness" of the b_u electrons. In the equilibrium conformation, these electrons constitute a delocalised lone-pair in metal-centred (*sp*)-hybrid orbitals; the stabilisation by π-bonding in the planar form does not apparently compensate for the $sp \rightarrow p$ promotion energy.

If Ge_2H_4 and Sn_2H_4 were *cis*-folded, mixing of the b_u HOMO with the σ antibonding orbital is forbidden by symmetry. The SCF energy is therefore found to increase with θ, and internal rotation about the M—M bonds is restricted.

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