

Supersilyl radicals from the dissociation of superdisilane observed by gas electron diffraction†

Sarah L. Masters (née Hinchley),*^a Duncan A. Grassie,^a Heather E. Robertson,^a Margit Hölbling^b and Karl Hassler^b

Received (in Cambridge, UK) 19th February 2007, Accepted 14th March 2007

First published as an Advance Article on the web 4th April 2007

DOI: 10.1039/b702599h

The vapour produced upon mild heating of hexa-*tert*-butyldisilane (superdisilane) has been studied by gas electron diffraction and *ab initio* molecular orbital calculations; the disilane is not observed in the vapour, and the observed radical structure is not the lowest energy structure predicted *ab initio*.

The loading of central Si–Si bonds using bulky ligands has produced some exciting structural observations. For example, the gas-phase investigation into the structure of 1,1,2-tri-*tert*-butyldisilane, Bu¹₂HSiSiH₂Bu¹, determined that an almost eclipsed structure was most favourable, with each *tert*-butyl group eclipsing an H atom at the opposite end of the molecule.¹ An eclipsed structure was also observed for 1,1,2,2-tetra-*tert*-butyldisilane, Bu¹₂HSiSiHBu¹₂, but in this case, two opposing *tert*-butyl groups almost eclipsed each other, leading to large distortions of angles around the silicon atoms.² In these molecules, a lengthening of the Si–Si bond up to ~240 pm was observed, compared to a Si–Si bond length of 233.1(3) pm, determined by gas electron diffraction (GED), for Si₂H₆.³

Loading more *tert*-butyl groups around the Si–Si core leads to further extension of this bond, and the solid-state structure of hexa-*tert*-butyldisilane, also known as superdisilane, Bu¹₃SiSiBu¹₃ (**1**), displays this phenomenon.⁴ The solid-state molecular structure is shown in Fig. 1, along with some important structural parameters, most notably the hyperextended Si–Si bond length of 269.7(3) pm. This bond length indicates a reduced Pauling bond order of only 0.26.⁴ Superdisilane is composed of two supersilyl groups, which have gained popularity as overloaded substituents in reactions. This is mainly due to their chemical inertness, saturation and ease of synthesis. The alkyl substituents tend not to migrate to the silicon centres of Si₂X₆ compounds so readily, and superdisilane is quite inactive at room temperature, despite the obvious strain placed on the central bond by the bulky substituents, showing no evidence of dissociation. However, structural studies have only been performed in the solid phase (crystallography), with no investigation of the gaseous structure.

The first synthesis of **1** was achieved by the dimerisation of [•]SiBu¹₃ (**2**), a byproduct of reaction of supersilyl alkaline metals,⁴ and previous investigations indicate that **1** dissociates reversibly

above 323 K back into these supersilyl radicals.⁴ Thus both the mode of preparation and the reversible dissociation both support the idea that [•]SiBu¹₃ is persistent and does not rearrange. We initiated our investigation of superdisilane with the aim of determining the gaseous structure, and comparing it to that obtained in the solid phase. Prior to our investigation, it was not known what temperature would be required to vaporise the sample using the Edinburgh gas electron diffraction apparatus, which requires a sample vapour pressure of 1–10 torr.

Ab initio molecular orbital calculations were performed at the MP2(fc) level with the 6-31G* basis set for **1**.⁵ These predicted that the central Si–Si bond length in the gaseous structure would be comparable to that observed for the solid-state structure, with a calculated value of 272.1 pm [269.7(3) pm solid]. The calculations also indicated that the overall distortion of the structure from the highest possible symmetry of D_{3d} to C₂ symmetry would be similar to that observed in the crystal, with a C(2)–Si(1)–Si(41)–C(68) dihedral angle of –165.8° [*cf.* –164.9(2)° solid].

Gas-phase data were collected for **1** at temperatures of 421 K for the sample and 444 K for the nozzle. The nozzle temperature is held slightly higher to prevent condensation of the sample, which would result in blockage of the inlet. The inlet tube (path length ~300 mm) is constructed from stainless steel, and the sample flows with a backing pressure of 2 × 10^{–6} torr. Analysis of the GED data revealed that no significant amount of **1** was present in the vapour. The fit of the theoretical model to the experimental data was poor and the initial R_G was 0.867 (R_D 0.706), which is far

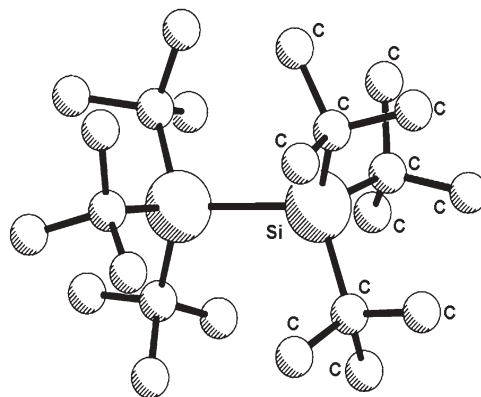


Fig. 1 Molecular structure of hexa-*tert*-butyldisilane in the crystalline phase.⁴ Hydrogen atoms have been removed for clarity. Selected bond lengths (pm), bond angles (°) and dihedral angles (°): rSi–Si 269.7, rSi–Cav 198.8, rC–Cav 153.8, ∠Si–Si–Cav 111.6, ∠Si–C–Cav 113.1, ϕC–Si–Si–C –164.8.

^aSchool of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ. E-mail: s.masters@ed.ac.uk

^bInstitut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 16, A-8010, Graz, Austria. E-mail: Hassler@anorg.tu-graz.ac.at

† Electronic Supplementary Information (ESI) available: Summary of GED experimental details and geometries from the *ab initio* molecular orbital calculations. See DOI: 10.1039/b702599h

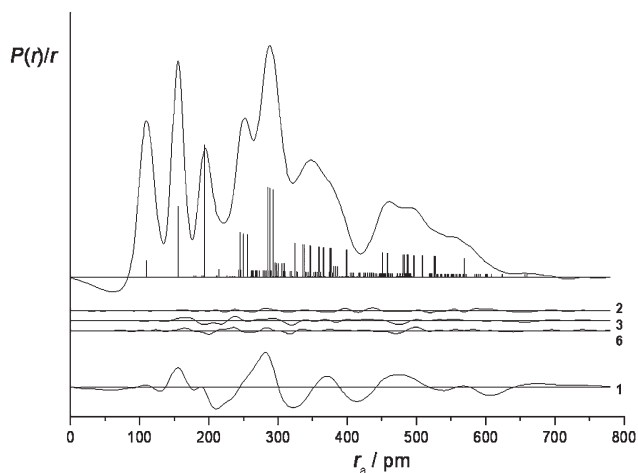


Fig. 2 Experimental radial distribution curve and interatomic distances for **2**. The difference curves show the differences between the experimental data and theoretical models for **1**, **2**, **3** and **6**. Note that the difference curve for **1** is from the initial fit, whilst the differences for **2**, **3**, and **6** arise from the final refined structures.

greater than normal. The radial distribution curve and difference curve for **1** (Fig. 2) shows that the fit of the model to the experimental data is wrong. There are discrepancies at 150 pm and 195 pm, indicating that intensity relating to the C–C and Si–C distances is missing. There is also a large difference at about 270 pm, where the Si–Si bond would be expected to be observed, indicating that there is no Si–Si bond of this length present in the vapour. The longer, non-bonded, experimental data do not generally agree with the postulated structure of **1**.

As already discussed, superdisilane begins to dissociate at 323 K under normal pressure conditions. This helps to explain the lack of superdisilane in the vapour. However, no vapour was detected for diffraction at lower temperatures under the pressure conditions required for the experiment. Therefore the observation that **1** breaks apart at elevated temperatures is corroborated. With no superdisilane present, the observed vapour could result from either dissociation of **1** into supersilyl radicals, or from further reaction of the radicals to form rearrangement products.

Four possible radical products of dissociation of **1** have been considered (Fig. 3). The first of these is the supersilyl radical (**2**), which is the product of dissociation with no further rearrangement. We also considered the possibility of migration of a H-atom to the silicon, giving HSiBu^t₂CMe₂·CH₂ (**3**), or the migration of a methyl group to the silicon, giving MeSiBu^t₂·CMe₂ (**4**). Finally, following the migration of the methyl group there is the possibility of H-atom migration to the resultant C radical centre, giving MeSiBu^t₂CHMe·CH₂ (**5**). Supersilane HSiBu^t₃ (**6**) has also been investigated as a possible product for observation, although this would result in two products of reaction in the vapour.

The initial fits of **4** and **5** to the GED data suggest that these structures are not present in the vapour. Initial R_G values of ~0.500 show minimal agreement between the theoretical and experimental data. An especially poor fit was observed in the region of the C–C and Si–C bond lengths, indicating that C–C bonds are not being broken and extra Si–C bonds are not being formed.

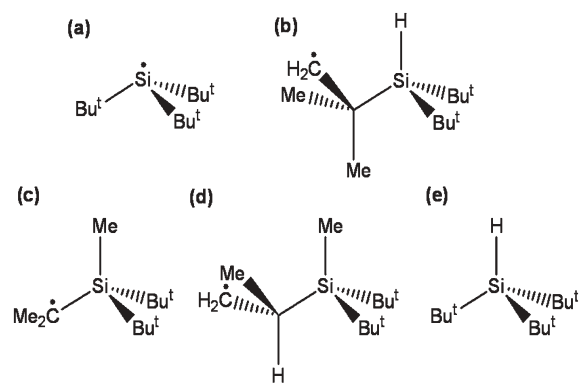


Fig. 3 Four possible dissociation products of superdisilane: (a) SiBu^t₃ (**2**), (b) HSiBu^t₂CMe₂·CH₂ (**3**), (c) MeSiBu^t₂·CMe₂ (**4**) and (d) MeSiBu^t₂CHMe·CH₂ (**5**). The fifth possibility, HSiBu^t₃ (**6**), is shown in (e).

The initial fits of **2**, **3** and **6** to the data were much better, with R_G values of ~0.250. Full models describing the structures were written and refinements performed using the ed@ed structure refinement program.⁶ A summary of the refinements, including the number of parameters required to describe the structures and number of refining amplitudes, is given in Table 1.

From Table 1 it can be seen that **2** provides the best fit to the experimental data and requires the lowest number of parameters to describe the structure fully. The radial distribution curve and difference curves for **2**, **3** and **6** can be seen in Fig. 2. While there is not much difference between the quality of the fit at longer distances, the difference curves are noticeably worse for **3** and **6** between 150 and 350 pm and around 480 pm. The discrepancy around 150 pm corresponds to the Si–H distance, which required a restraint to be applied during the refinements of both **3** and **6** using the SARACEN method,⁷ and it can be inferred that there is no Si–H bond present in the compound. Fitting the data with a mixture of compounds would therefore also be expected to be worse, as Si–H bonds would be present in these mixtures as well. Thus we conclude that only **2**, SiBu^t₃ radicals, are present in the vapour under the conditions of the experiment, and that Si₂Bu^t₆ cannot be observed in the gas phase.

The investigation would appear to end satisfactorily at this point with the observation of **2** in the vapour. However, examination of the UB3LYP/6-31G* energies of **2**, **3**, **4** and **5** indicate that **2** is not the lowest-energy structure calculated at this level (Table 2; **6** cannot be included in the assessment as it has an extra proton and the relative energy is not comparable). In fact **4**, in which a methyl group has migrated from one *tert*-butyl group to the silicon centre, resulting in a planar CMe₂ group, is significantly lower in energy. The initial fit of **4** to the GED data was not good, and this was

Table 1 Summary of refinements for the possible dissociation products of superdisilane

Compound	Symmetry	Number of refining parameters	Groups of refining amplitudes	Final R_G
2	C_3	16	11	0.0683
3	C_1	35	11	0.0904
6	C_3	17	10	0.0968

Table 2 Gibbs free energies (G) in hartrees of **1**, **2**, **3**, **4** and **5** calculated at the (U)B3LYP/6-31G* level, corrected for zero-point energy (ZPE). For **2**, **3**, **4** and **5**, the relative energies (in kJ mol^{-1}) from the lowest energy structure are also recorded

Molecule	Energy/hartree ^a	Relative energy/ kJ mol^{-1}
1 ^b	-1525.3720	—
2	-762.6957	+74.1
3	-762.6875	+95.6
4	-762.7239	0.0
5	-762.7060	+47.0

^a All energies include correction to thermal free energies computed at 421.0 K. ^b Basis set superposition error (BSSE) has been accounted for in this calculation.

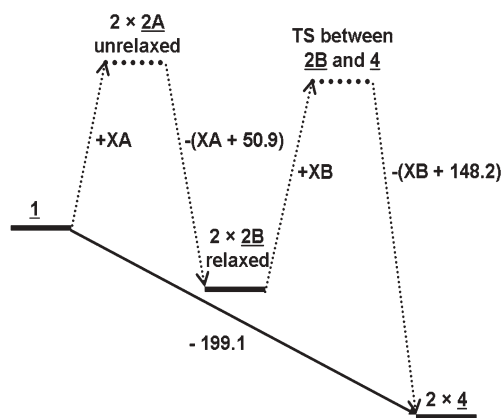


Fig. 4 Summary of the DFT results for superdisilane, **1**, in the solid-state geometry; the supersilyl radicals with solid-state geometries, **2A**; the supersilyl radicals in the gas phase, **2B**; and the lowest-energy structure, **4**, via an unknown transition state. All energy differences in kJ mol^{-1} .

attributed to the presence of the Me group on silicon. Therefore there must be an initial dissociation of superdisilane to give supersilyl radicals, which we observe by gas electron diffraction, followed by a further rearrangement process, which we do not observe under the conditions of the experiment. The energy diagram for this process (Fig. 4) can be examined in more detail using information from Table 2.

The Gibbs free energy of reaction to break superdisilane into supersilyl radicals at 298 K [$\Delta G^0(298)$] is $+6.8 \text{ kJ mol}^{-1}$, whilst [$\Delta G^0(421)$] is $-50.9 \text{ kJ mol}^{-1}$. This compares to $\Delta G^0(298)$ of $247.5 \text{ kJ mol}^{-1}$ for the dissociation of Si_2H_6 to $^{\bullet}\text{SiH}_3$ radicals (calculated at the B3LYP/6-31G* level, Si-Si bond length 235.0 pm). The energy pathway for the dissociation of superdisilane, via **2A** (Fig. 4), has not yet been investigated. The Si-Si bond is significantly weakened by the presence of the bulky alkyl groups, and the overall process of dissociation is exothermic. The relative stability of the seemingly impossibly strained superdisilane at room temperature can be explained by the intramolecular interactions between the methyl groups at each end of the molecule. The subsequent rearrangement of the supersilyl radicals (**2**) to the lowest-energy structure (**4**) would release a further $148.2 \text{ kJ mol}^{-1}$,

thus the overall energy change from **1** to **4** at 421 K is $-199.1 \text{ kJ mol}^{-1}$; in principle a highly exothermic process.

The transition state between the observed experimental structure (**2**) and the lowest energy structure calculated *ab initio* (**4**) is the subject of intensive ongoing investigation. We believe this barrier must be large to prevent instant conversion. Silicon-centered radicals are experimentally more stable than the carbon-centered radicals, and it has been shown experimentally that the 1,2 H-shift for $\text{Me}_2\text{HSi}^{\bullet}\text{CH}_2 \rightarrow ^{\bullet}\text{SiMe}_3$ has an activation barrier of $\sim 171.5 \text{ kJ mol}^{-1}$.⁸ It is also known that 1,2 Me-shifts are generally harder to initiate than 1,2 H-shifts,⁹ and the reverse shift of a methyl group from a stable carbon centre to the silicon centre, as is proposed to be the lowest energy structure in this case, can be expected to have an even higher activation barrier. Probing the potential-energy surface computationally will provide information about the barrier height to interconversion. We believe this knowledge will move us further towards explaining the observation of $^{\bullet}\text{SiBu}^{\dagger}_3$ radicals, rather than the calculated lowest-energy structure, in the vapour.

SLM thanks the Royal Society of Edinburgh for a BP/RSE Personal Research Fellowship, the EPSRC for funding the electron diffraction research (EP/D057167/1) and the EPSRC National Service for Computational Chemistry Software (NSCCS) for computing time. This work has also made use of the resources provided by the EaStCHEM Research Computing Facility. (<http://www.eastchem.ac.uk/rcf>.) This facility is partially supported by the eDIKT initiative. (<http://www.edikt.org>.) KH and MH thank the 'Fonds zur Förderung der wissenschaftlichen Forschung, FWF, Vienna' for funding of project P-17435. The authors thank the referees for their very helpful suggestions and comments.

Notes and references

- S. L. Hinchley, B. A. Smart, C. A. Morrison, H. E. Robertson, D. W. H. Rankin, R. Zink and K. Hassler, *J. Chem. Soc., Dalton Trans.*, 1999, 2303.
- S. L. Hinchley, H. E. Robertson, A. Parkin, D. W. H. Rankin, G. Tekautz and K. Hassler, *Dalton Trans.*, 2004, 759.
- B. Beagley, A. R. Conrad, J. M. Freeman, J. J. Monaghan, B. G. Norton and G. C. Holywell, *J. Mol. Struct.*, 1972, **11**, 371.
- N. Wiberg, H. Schuster, A. Simon and K. Peters, *Angew. Chem.*, 1986, **98**, 100; N. Wiberg, H. Schuster, A. Simon and K. Peters, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 79.
- HF and MP2 calculations were performed using the resources of the National Service for Computational Chemistry Software (<http://www.nscs.ac.uk>). DFT calculations were performed using the resources of the EaStCHEM Research Computing Facility (<http://www.eastchem.ac.uk/rcf>). Calculations were performed using the Gaussian 03 suite of programs. See the ESI for full reference (reference S5).
- S. L. Hinchley, H. E. Robertson, K. B. Borisenko, A. R. Turner, B. F. Johnston, D. W. H. Rankin, M. Ahmadian, J. N. Jones and A. H. Cowley, *Dalton Trans.*, 2004, 2469.
- A. J. Blake, P. T. Brain, H. McNab, J. Miller, C. A. Morrison, S. Parsons, D. W. H. Rankin, H. E. Robertson and B. A. Smart, *J. Phys. Chem.*, 1996, **100**, 12280; P. T. Brain, C. A. Morrison, S. Parsons and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1996, 4589; N. W. Mitzel and D. W. H. Rankin, *Dalton Trans.*, 2003, 3650.
- T. J. Barton, A. Revis, I. M. T. Davidson, S. Ijadi-Maghsoodi, K. J. Hughes and M. S. Gordon, *J. Am. Chem. Soc.*, 1986, **108**, 4022.
- I. M. T. Davidson and S. Ijadi-Maghsoodi, *Organometallics*, 1986, **5**, 2086.