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Exceptional Steric Congestion in an *in,in*-Bis(hydrosilane)

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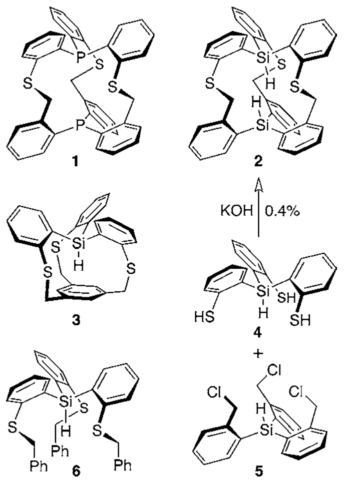
Supporting Information

ABSTRACT: The synthesis and characterization of a macrobicyclic *in,in*-bis(hydrosilane) is described. A combination of crystallographic and computational data indicate that the central hydrogen−hydrogen nonbonded contact distance is the shortest for any crystallographically characterized compound.

We recently reported the synthesis of the macrobicyclic *in,in*-bisphosphine **1** (Scheme 1), a molecule in which the two bridgehead phosphines are in van der Waals contact, show strong spin−spin coupling, and resist reaction with reagents larger than protons (and even protonation is slow).[1] The corresponding *in,in*-bis(hydrosilane) **2**, with its clashing internal hydrogen atoms, would be an even more unusual structure if it could be prepared. The *in,in* geometry of **1** is strongly favored over a possible *in,out* isomer[2] [by 18 kcal/mol at the B3PW91/6-31G(d) level[3]], but for compound **2**, the preference is much reduced (to 6 kcal/mol). However, our prior work with triarylelement-containing *in*-cyclophanes,[4] including silane **3**,[5] left us with reasonable precursors of compound **2** and every reason to attempt the synthesis.

Scheme 1



Condensation of tris(2-mercaptophenyl)silane[5] (**4**) and tris[2-(chloromethyl)phenyl]silane (**5**) at high dilution in benzene/ethanol in the presence of KOH gave compound **2** in 0.4% yield after extensive purification (Scheme 1). Although formed in exceptionally low yield, the desired **2** was easily located in the reaction mixture (composed mostly of oligomeric and polymeric byproducts) because of the similarity of its chromatographic mobility to that of diphosphine **1**. Two spectroscopic signatures suggested that compound **2** possesses the desired *in,in* configuration. First, the two Si−H resonances in the ^{1}H NMR spectrum of **2** were shifted ~2 ppm downfield (to δ 8.24 and δ 8.57) from the silane proton resonance in the nonmacrocyclic model compound **6** (δ 6.21),[5] an example of steric deshielding of proton resonances.[6] Second, the Si−H stretch[7] observed in the IR spectrum of **2** appeared at 2325 cm^{-1}, roughly 150 cm^{-1} higher in frequency than the Si−H stretch in model **6** (2177 cm^{-1}).[5] This is a clear case of compressional frequency enhancement, although less than the 200−400 cm^{-1} shifts observed for C−H and Si−H stretches in a number of congested *in*-cyclophanes.[5,8,9]

Compound **2** crystallized in space group $P\overline{3}$, with the molecule lying on a special position possessing crystallographic C_3 symmetry, a fortunate occurrence that facilitated comparison with the calculated structures of **2**, which are also C_3-symmetric.[10,11] The molecular structure of **2** is illustrated in Figure 1. The *in,in* geometry is confirmed, as is the unique "head-on collision" of the two *in*-hydrogen atoms.

Table 1 summarizes the salient interatomic distances for atoms on the central axis of **2**. Most significantly, the two Si atoms, whose positions were well-determined, are only 4.43 Å apart,[12] a distance ($d_{\mathrm{Si-Si}}$) that must accommodate two Si−H bonds as well as the H−H nonbonded contact ($d_{\mathrm{H-H}}$). The H atom positions were refined, but foreshortening of the Si−H

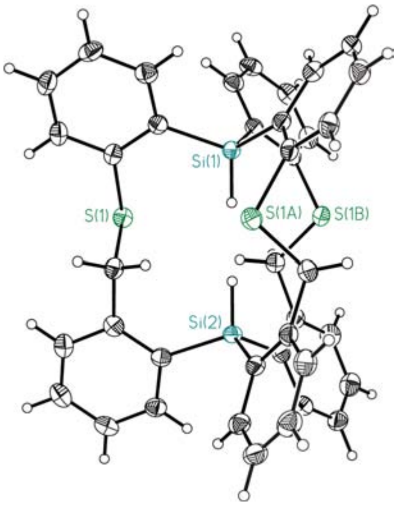


Figure 1. Molecular structure of compound **2**; 50% thermal ellipsoids have been employed.

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Table 1. Experimental and Calculated Interatomic Distances for the Core Atoms of Compound 2

method	$d_{\mathrm{Si-Si}}$ (Å)	$d_{\mathrm{H-H}}$ (Å)
X-ray	4.433(2)	1.89(10)
B3LYP/6-31G(d)	4.535	1.623
B3LYP/6-311+G(2d,p)	4.518	1.618
B3PW91/6-31G(d)	4.501	1.576
B3PW91/6-311+G(2d,p)	4.484	1.570
M062X/6-31G(d)	4.474	1.568
M062X/6-311+G(2d,p)	4.449	1.560
MP2(FC)/6-31G(d)	4.458	1.556

distances[13] made the observed $d_{\mathrm{H-H}}$ far too long. If a standard Si−H bond distance of 1.48 Å[14] were employed, then $d_{\mathrm{H-H}}$ would be only 1.47 Å, but there must be some compression of the Si−H bond in this environment. The computational methods listed in Table 1 gave Si−H bond distances ranging from 1.44 to 1.46 Å and $d_{\mathrm{H-H}}$ values ranging from 1.56 to 1.62 Å. However, all of these methods significantly overestimated $d_{\mathrm{Si-Si}}$,[15] so the actual $d_{\mathrm{H-H}}$ (or, alternatively, the Si−H bond distances) must be shorter still.

The "world record" for the shortest experimentally determined H−H nonbonded contact is 1.617(3) Å via neutron diffraction for a cage pentacyclodecane.[16,17] This distance is in almost perfect agreement with the results of modern calculations [e.g., B3PW91/6-31G(d), 1.616 Å; MP2/6-31G(d), 1.622 Å]. There can be little doubt that $d_{\mathrm{H-H}}$ in **2** is significantly shorter, on the order of 1.56 Å, but direct experimental confirmation awaits a large enough crystal for a neutron diffraction experiment.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectra for **2**, atomic coordinates of the calculated structures of **2**; and a CIF for the structure determination of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(7) Two Si−H stretching modes must exist. An HF/6-31G(d) frequency calculation gave these as essentially "symmetric" and "antisymmetric" stretches that are 80 cm^{-1} apart, with the former only 4% as intense as the latter. In contrast, a B3LYP/6-31G(d) calculation gave two modes of comparable intensity that are 44 cm^{-1} apart. The IR spectrum of **2** shows only one strong band in the Si−H region, but candidates for the weaker "symmetric" stretch are marked on the spectrum in the Supporting Information.

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(10) From a computational perspective, several other conformations of compound **2** exist, possessing both C_3 and C_1 symmetry, but all are substantially higher in energy than the observed C_3-symmetric conformation and possess even *shorter* H−H nonbonded contacts ($d_{\mathrm{H-H}}$). Thus, at the B3PW91/6-31G(d) level with zero-point energy corrections, the C_3-symmetric ground state (ΔE = 0 kcal/mol) has $d_{\mathrm{H-H}}$ = 1.58 Å (see Table 1), but other conformational minima include the following: C_1-A, ΔE = +6.9 kcal/mol, $d_{\mathrm{H-H}}$ = 1.56 Å; C_1-B, ΔE = +12.6 kcal/mol, $d_{\mathrm{H-H}}$ = 1.54 Å; C_3-C, ΔE = +31.7 kcal/mol, $d_{\mathrm{H-H}}$ = 1.43 Å; and C_3-D, ΔE = +30.9 kcal/mol, $d_{\mathrm{H-H}}$ = 1.35 Å. In the ground state and the two C_1-symmetric conformations, the two triarylsilane caps possess the same configuration; this permits the linking arms to adopt nearly extended conformations. In the high-energy C_3-symmetric conformations, the two triarylsilanes possess opposite configurations; this forces the links into gauche-like conformations and significantly shrinks the internal cavity. (The atomic coordinates of these alternative conformations are found in the Supporting Information.) None of these conformations is close enough in energy to that of the C_3-symmetric ground state to have any significant concentration in solution.

(11) A referee suggested that the observed C_3 symmetry may be imposed by the crystal lattice, but in addition to the fact that the computed lowest-energy conformation possesses C_3 symmetry, the reoptimization of structures with small distortions from ideal C_3 symmetry invariably returned to the C_3-symmetric minimum in gas-phase calculations.

(12) The separation of the silicon atoms in **2** (4.43 Å) is 0.8 Å greater than the observed separation of the phosphorus atoms in the two crystallographically independent molecules in the X-ray structure of **1** (3.58 and 3.71 Å).[1]

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(17) Extensive searches of the Cambridge Structural Database (CSD) failed to find any molecule with a short H−H contact distance for which the B3PW91/6-31G(d)-optimized geometry of the molecule

supports a contact shorter than that of Ermer et al.[16] Besides the Ermer pentacyclodecane and very closely related compounds, the only other molecule with a comparably short contact distance is a bisadamantyl-containing cyclophane,[18] with a B3PW91/6-31G(d)-calculated H−H contact of 1.637 Å.

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