Unusually Short Phantom Bonds Containing Si and P Atoms. A Theoretical Study of 2,4,5-Trioxa-1,3-disilabicyclo[1.1.1]pentane and its Phosphorus Dication Analogue

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By means of *ab initio* calculations, unusually short interatomic distances are predicted between the nonbonded atoms in the title compounds and interpreted in terms of small extent of back electron-donation from the linked oxygens and the accompanying orbital contraction around the nonbonded atoms.

In a recent theoretical study,[1] we have shown that the stretched Si–Si central bridge bond in pentasila[1.1.1]propellane can be shortened by oxygen substitution. We report here that oxygen substitution is also capable of decreasing greatly the interatomic distances between the nonbonded atoms in silicon and phosphorus compounds. In our present calculations geometries are fully optimized at the Hartree–Fock (HF) level with split-valence 3-21G[2] and d-polarized 6-31G*[3] basis sets and characterized as equilibrium structures by diagonalizing the HF/3-21G Hessian (force constant) matrices calculated on the HF/3-21G optimized geometries. Because of the importance of polarization functions and for uniform comparison, all geometrical values cited here are those at the HF/6-31G* level.

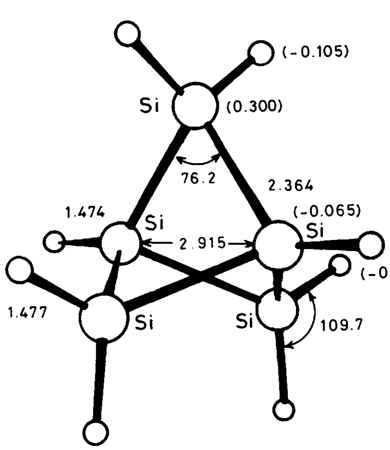
Figure 1 shows the optimized structure of pentasilabicyclo[1.1.1]pentane (**1**). The two central bridgehead silicon atoms in (**1**) are separated by a long interatomic distance of 2.915 Å, indicating the absence of an important bonding interaction. It is interesting that the replacement of the peripheral SiH_2 groups in (**1**) by electronegative oxygen atoms permits the bridgehead silicons to approach unusually close to each other. As a consequence, the distance between the bridgehead silicons becomes extremely short (2.060 Å) in 2,4,5-trioxa-1,3-disilabicyclo[1.1.1]pentane (**2**), as shown in Figure 2.

The Si–Si distance in (**2**) is much shorter than the Si–Si single bond distance (2.353 Å) in disilane.[3] It is 0.074 Å shorter than the Si–Si double bond distance (2.134 Å) in disilene:[4] the Si–Si double bond distances in the *X*-ray crystal structures of disilene derivatives[5,6] are in the range 2.14—2.16 Å.[7] No silicon–silicon triple bond has yet been isolated though the possible transient existence of *trans*-bent dimethyldisilyne has recently been suggested.[8,9] In this context, it is interesting that the nonbonded Si–Si separation in (**2**) compares favourably with the formal Si–Si triple bond distance (2.083 Å) in *trans*-bent disilyne.[10]

The extremely short distance in (**2**) implies the existence of a strong covalent bond between the silicons. However, the overlap population between the silicons was calculated to be −0.04. In addition, the detachment of two hydrogens from (**2**) to form 2,4,5-trioxa-1,3-disilatricyclo[1.1.1.0^{1,3}]pentane (**3**) results in a lengthening of the distance between the silicon atoms by 0.029 Å (see Figure 2), despite the possibility of some sort of bonding between these atoms.

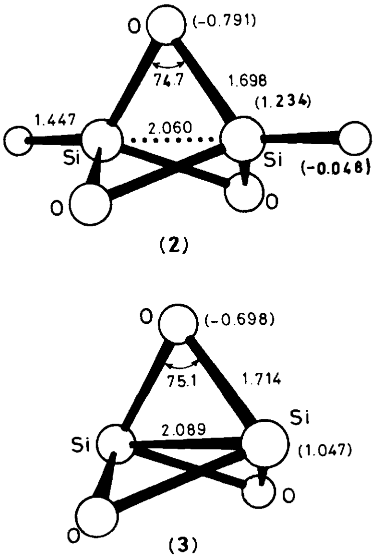
As Figure 3 shows, removal of the first hydrogen from (**2**) requires 87.2 kcal mol^{-1} (cal = 4.184 J), in good agreement with the generally accepted values for normal Si–H bond strengths.[11] In contrast, removal of the second hydrogen requires only 60.4 kcal mol^{-1}. This reduction in energy requirement (26.8 kcal mol^{-1}) suggests that (**3**) was able to recover part of the cost of the broken Si–H bond by forming an interbridgehead bond.

In an attempt to assess the strength of the interbridgehead bond in (**3**), we have calculated the energy released upon the addition of H_2 by means of Møller–Plesset perturbation theory up to full fourth order (MP4SDTQ)[12] with core-like oribitals doubly occupied. The reaction, (**3**) + H_2 → (**2**), was calculated to be 44.1 kcal mol^{-1} (49.7 kcal mol^{-1}



(**1**)

Figure 1. The HF/6-31G* optimized geometry (in Å and degrees) and charge densities (in parentheses) of (1) with D_{3h} symmetry. The total energy is −1449.20826 a.u.



(**2**)

(**3**)

Figure 2. The HF/6-31G* optimized geometries (in Å and degrees) and charge densities (in parentheses) of (2) and (3) with D_{3h} symmetry. The total energies are −803.69150 (2) and −802.40867 (3) a.u.

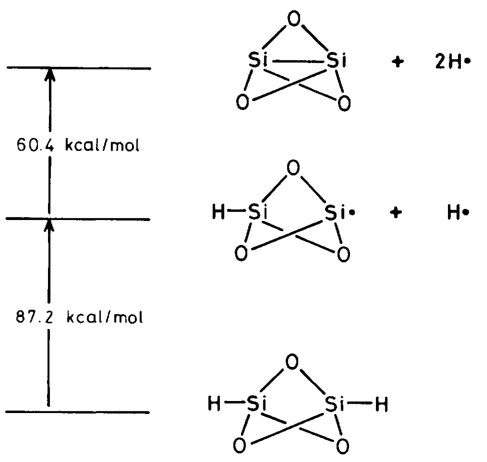


Figure 3. The MP2/6-31G* relative energies calculated at the HF/6-31G* optimized geometry of (**3**).

before zero-point correction) exothermic at the MP4SDTQ/6-31G*//HF/6-31G* level. In terms of bond energies (E), the hydrogenation process may be written as equation (1). As far as the transferability of Si–O bonds is valid, one obtains equation (2). If one uses the values of E(Si–H) = 90[11] and E(H–H) = 109[13] kcal mol^{-1}, one deduces that E(Si–Si) is 27 kcal mol^{-1} larger than E(Si · · · Si) despite the somewhat longer distance in (**3**).

$$E(\text{Si–Si}) + 6E(\text{Si–O}) + E(\text{H–H}) = E(\text{Si}\cdots\text{Si}) + 6E(\text{Si–O}) + 2E(\text{Si–H}) - 44.1\ \text{kcal mol}^{-1} \quad (1)$$

$$E(\text{Si–Si}) - E(\text{Si}\cdots\text{Si}) = 2E(\text{Si–H}) - E(\text{H–H}) - 44.1\ \text{kcal mol}^{-1} \quad (2)$$

The unusual distance in (**2**) may be explained in terms of a π-complex model.[14,15] Compound (**2**) can be considered as resulting from a donor–acceptor interaction between HSiSiH and three O atoms. The great electronegativity of oxygen, compared to silicon, leads to the predominance of a π(HSiSiH) → O electron-donation over a O → π*(HSiSiH) back electron-donation, forming a π complex between HSiSiH and O with a T structure.[15] Thus, the unusual distance is a result of the high π complex character and small extent of back donation into the antibonding π* orbital of the original HSi≡SiH fragment. Furthermore, the predominance of the donation from HSiSiH to three O atoms makes the silicons very positively charged, as shown in Figure 2, the accompanying orbital contraction around the bridgehead silicons being suitable for the proximity of the silicons.† In this view, it is instructive to note that the replacement of two hydrogens in (**2**) by two fluorines, which makes the silicons more positively charged, leads to further shortening of the interbridgehead silicon distance: Si–Si = 2.033 Å, Si–O = 1.688 Å, Si–F = 1.541 Å, and ∠Si–O–Si = 74.1°. The Si–Si distance of 2.033 Å is the shortest that has ever been reported; a relatively short distance (2.341 Å) is seen between the nonbonded silicons in tetrafluorocyclodisiloxane.[16]

As Figure 4 shows, a similar trend holds also for the isoelectronic phosphorus dication analogues (**4**) and (**5**): the P–P distance of 2.308 Å in (**4**) is significantly shorter than a P–P single bond (2.214 Å in diphosphane)[3] and only 0.034 Å longer than a P–P double bond distance (2.004 Å in diphosphene).[17]

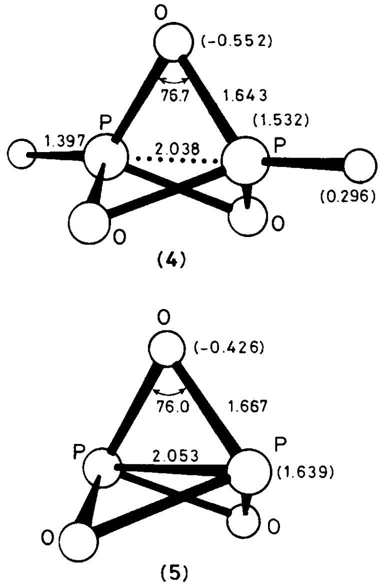


Figure 4. The HF/6-31G* optimized geometries (in Å and degrees) and charge densities (in parentheses) of the dication phosphorus compounds (**4**) and (**5**) with D_{3h} symmetry. The total energies are −906.30137 (**4**) and −904.99374 (**5**) a.u.

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† The somewhat longer distance in (**3**) is due to the increased back donation and the less positively charged silicons (see Figure 2): the π* level of SiSi is lower than that of HSiSiH.