Rationalization of the Short Si–Si Bond Length in 2,4,5-Trioxa-1,3-disilabicyclo[1.1.1]pentane by an Ionic Model

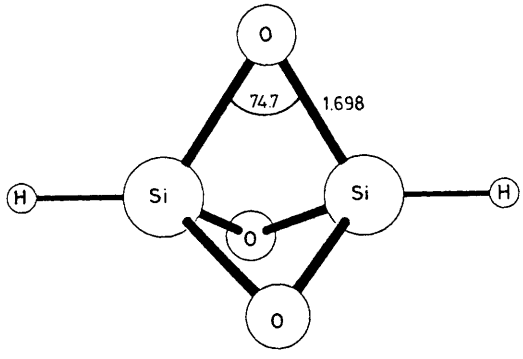
Andrew Streitwieser

Department of Chemistry, University of California, Berkeley CA 94720, U.S.A.

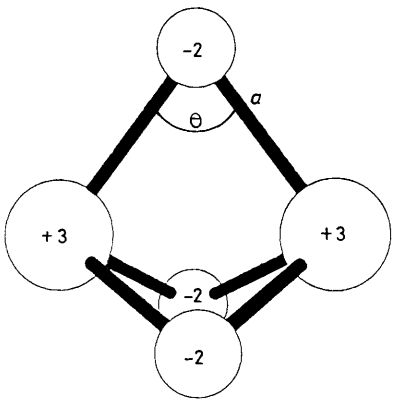
The short Si–Si bond length in the title compound, discovered in a recent theoretical study, is readily rationalized by an ionic model.

In a recent theoretical study, Nagase *et al.* have found that 2,4,5-trioxa-1,3-disilabicyclo[1.1.1]pentane, (**1**), has an unusually short Si–Si bond length of 2.06 Å, which they claim 'implies the existence of a strong covalent bond between the silicons.' The structure was then rationalized in terms of a π-complex model. Another recent study[2] has shown that many aspects of silicon chemistry can be rationalized in terms of an ionic model, in particular with high Si(+) O(−) bond polarity for Si–O compounds. Thus, it is instructive to see how well the unusual Si–Si bond length in (**1**) can be rationalized in terms of a purely ionic model, one in which the Si–H groups are represented by point charges of +3 and the oxygens as point charges of −2.

The electrostatic energy, E, of a D_{3h} collection of charges arranged as in (**2**) is considered, with the Si–O bond length, a and the Si–O–Si angle, θ. Application of Coulomb's Law takes the form given in equation (1). Trigonometry gives r(Si–Si) = $2a\sin(\theta)$ and r(O–O) = $2a\cos(\theta/2)\cos(30°)$. Equation (2) expresses the electrostatic energy in unitless form. The electrostatic energy is negative over a wide range of θ from 18 to 154°. Over this range the single +3, +3 repulsion and the



(**1**)



(2)

three −2, −2 repulsions are less than the six −2, +3 attractions between negative oxygens and positive silicons. The energy minimum is found at about 80°, a value fortuitously close to the Si–O–Si angle of 74.7° found for (**1**).

$$E = -(2\cdot3)/r(\text{Si–O}) + (3\cdot3)/r(\text{Si–Si}) + 3(2\cdot2)/r(\text{O–O})$$

$$aE = -36 + 4.5/\sin(\theta/2) + 6/\cos(\theta/2)\cos(30°) \quad (2)$$

Of course, the bonds between oxygen and silicon in their compounds are not wholly ionic and their replacement by point charges is a gross approximation. Note that although full charges were used in deriving the electrostatic result above, fractional but proportional charges (*e.g.*, +0.3 and −0.2 for Si and O, respectively) would give an identical result if no other bonding forces are considered significant. The important point is that ionic models can be useful as models and that they may be more useful in rationalizing structures than purely covalent models.

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