Structure and Bonding in $(R_2SiX)_2$ Molecules (X = O, NH, CH_2, or S; R = H)†

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Analysis of the structure and bonding in $(R_2SiX)_2$ molecules (X = O, NH, CH_2, or S; R = H) by empirical, MNDO, and *ab initio* molecular orbital methods shows that: (*a*) the electronic structures of these systems are qualitatively similar, (*b*) short non-bonded 1,3-Si–Si distances are predominantly determined by the Si–X distance, and (*c*) the small antibonding Si–Si interactions increase with increasing Si–Si distance.

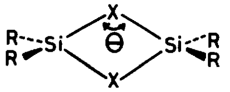
There has been considerable interest in the structure and bonding of the cyclic systems $(R_2SiX)_2$ [X = O (**1a**), NH (**1b**), CH_2 (**1c**), or S (**1d**)].[1–4] The discovery of an unusually short Si–Si non-bonded distance (shorter than Si–Si single bond) in (**1a**; R = mesityl) has increased these efforts recently.[1i] Other disilacycles, (**1b**)—(**1d**) have longer Si–Si distances.[2–4] Theoretical studies at various levels on (**1a**; R = H) showed differing Si–Si interactions. A CNDO calculation on (**1a**) indicated substantial Si–Si bonding,[5] but an MNDO calculation gave no Si–Si bonding interaction.‡ Recent *ab initio* calculations showed antibonding Si–Si interactions.[6] The short Si–Si distance in (**1a**) has been ascribed to O–O repulsions,[7] characteristic of silicon compounds,[6] and Si–Si attraction.[1] In the present study§ we find the following. (*a*) The bonding in (**1a**) is similar to that in (**1b**)—(**1d**) except for the trends expected from electronegativity changes. (*b*) The variation in the non-bonded Si–Si distances in (**1**) is a consequence of Si–X bond lengths. (*c*) The Si–Si antibonding interactions in (**1**) increase with increasing Si–Si distance. We also compare the electronic structure of (**1**) to those of the carbon analogues, (**2**).

Experimental

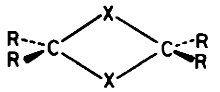
Methods of Calculation.—The molecular orbitals of (**1a**)—(**1d**) were analyzed using the fragment molecular orbital (f.m.o.) approach within the extended Hückel formalism.[8] Walsh diagrams were constructed using this method for the variation of θ and compared. The semiempirical MNDO[9] and the *ab initio* HF/3-21G level[10] calculations were used to find the geometric trends in (**1a**)—(**1d**). All calculations were carried out on the parent system (R = H).

Results and Discussion

The molecular orbitals of (**1a**; R = H) were constructed from the interaction of disilaethylene with O_2 (Figure). A cluster of eight valence m.o. energy levels, well separated from the vacant ones and the lower lying levels, appears. Two of these are fragment orbitals that do not find any orbital of the same symmetry in the other fragment (b_{2g} of Si_2H_4 and b_{3g} of O_2). They do not contribute to Si–O bonding. Another group arises where both the bonding and the antibonding combinations are occupied ($1b_{1u}$, $2b_{1u}$, $2b_{3u}$). A third group of m.o.s are such that only the bonding combinations of the f.m.o.s are occupied. The Si_2H_4–O_2 f.m.o. pairs involved here are the $\pi^* + \pi^*$ (b_{1g}), the $\pi + \sigma^*$ (b_{2u}), and the $\sigma + \sigma$ (a_g). The charges on the oxygens in these m.o.s (1.9 in b_{1g}, 1.8 in b_{2u}, and 1.6 in a_g as obtained from Mulliken overlap populations of the extended Hückel wave function) indicate charge transfer to oxygen and breaking of the Si–Si bond. These three m.o.s mainly contribute towards the Si–O bond. The interaction diagram and details of bonding remain qualitatively the same for X = NH, CH_2, or S with decreasing charge transfer. The increase in energy of the valence m.o.s of X_2 from O_2 to $(CH_2)_2$ justifies the decrease in the charge transfer.¶ Walsh diagrams for the variation of θ with X = O, NH, CH_2, or S were also similar. Values of θ from experiment were similar to those derived from extended Hückel calculations [86.0 and 90.5, (**1a**); 91.0 and 91.6, (**1b**); 91.0 and 85.8, (**1c**); 82.5 and 81.5°, (**1d**), respectively] and gave energy minima.



	X
(**1a**)	O
(**1b**)	NH
(**1c**)	CH_2
(**1d**)	S



	X
(**2a**)	O
(**2b**)	S

If the bonding in (**1a**)—(**1d**) is similar, then why is the Si–Si distance short in (**1a**) alone? The Table gives the Si–Si distances in (**1**; R = H) estimated by (*a*) MNDO, (*b*) 3-21G, (*c*) variation of the sum of eight valence m.o. energies using extended Hückel, and (*d*) assuming a square Si_2X_2 geometry with standard Si–X distances. In the last case Si–X distances found for the H_3SiXH_n molecules by the *ab initio* 3-21G method are used.[11] These Si–X distances are close to those found by experimental methods and at higher theoretical levels.[11] Comparisons in the Table reveal an unexpected result. The best estimate of the Si–Si non-bonded distance is obtained by assuming a fixed Si–X distance and a square geometry (except for X = S which is discussed later). Even though better agreement with the experimental geometries

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† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

‡ See footnote 11 in ref. 1(*i*).

§ Taken in part from N. R. Sreenivaskumar, M.Sc. Thesis, University of Hyderabad, 1984.

¶ Parameters involved in these extended Hückel calculations were as follows: Si–O 1.69, Si–N 1.75, Si–C 1.895, Si–S 2.18, Si–H 1.48, N–H 1.00, and C–H 1.09 Å; HSiH 116 (**1a**), 110 (**1b**), 104 (**1c**), or 110° (**1d**); HCH = 109.5°. Calculations were carried out over the θ range 60—110°. The H_{ii} values and exponents used were from A. R. Pinhas and R. Hoffmann, *Inorg. Chem.*, 1979, **18**, 654, except for Si. The H_{ii} and exponents for Si were 3*s* (−17.3 eV, 1.383), 3*p* (−9.2 eV, 1.383). These were repeated with *d* orbitals on Si (3*d*, H_{ii} = −6.0 eV, exponent 1.383) but the results were little different.

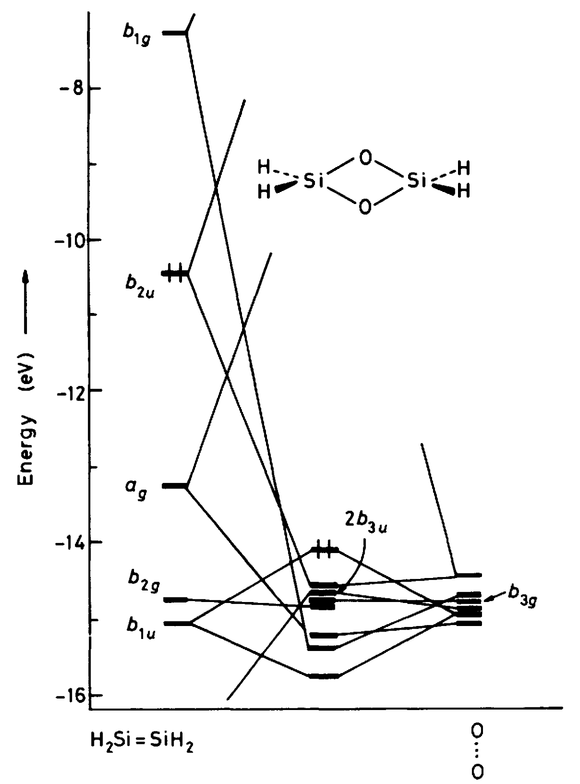
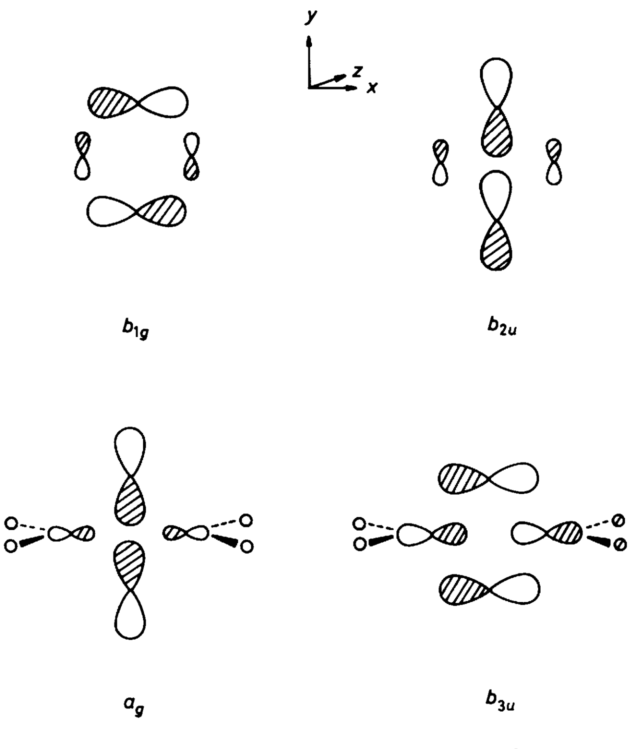


Figure. The interaction diagram between Si_2H_4 and O_2 at distances found in (**1a**; R = H). The symmetry labels are given assuming D_{2h} symmetry for all species



of (**1**) may be obtained at higher theoretical levels[6] the current results obtained by a square model with standard distances suggests an operating criterion to find short (⩽ twice the covalent radii) 1,3-non-bonded interactions in four-membered rings. The ratio of covalent radii required for close 1,3-non-bonded interactions (A–A ⩽ the single bond distance) in four-membered A_2X_2 rings is $r_X/r_A \leqslant \sqrt{2} - 1$. In $(R_2SiX)_2$ systems this is possible only for the smallest X, oxygen, where the radius ratio r_O/r_{Si} is roughly 0.4.[12] For any other X in (**1**), the ratio is considerably larger.

Table. Si–Si distances (Å) in (**1**) and (**2**) (R = H) from various methods. Other geometric parameters of (**1**) and (**2**) at MNDO and 3-21G levels are available from the authors

	Method				
Compd.	Exptl.	Assuming square geometry[a]	MNDO	3-21G	Extended Hückel valence m.o. energies
(**1a**)	2.31[b]	2.36	2.61	2.54[c]	2.40
(**1b**)	2.49[d]	2.46	2.63	2.62	2.51
(**1c**)	2.70[e]	2.71	2.56	2.74	2.58
(**1d**)	2.84[f]	3.18	2.88	3.13[c]	2.72
(**2a**)		2.04	2.02	2.05[c]	
(**2b**)		2.68	2.37	2.55	

[a] Si–X or C–X single bond lengths taken from $SiH_3X(H)$ and $CH_3X(H)$ calculated at the 3-21G level (ref. 11). [b] Ref. 1*i*. [c] Ref. 6. [d] Ref. 2*h*. [e] Ref. 3*e*. [f] Ref. 4*f*.

The simple model failed to predict the Si–Si distance in (**1d**) because it is substantially distorted from a square geometry. The reason is also not difficult to find. The bond angles around X in saturated compounds XH_n (*e.g.* CH_4, NH_3,[13] OH_2,[14] or SiH_4) are in the range of 105—110°. Natural bond angles around sulphur on the other hand are close to 90° (HXH = 92° in H_2S). A square geometry for (**1d**) would mean a deviation of only 2° of the SiSSi angle from the unconstrained value in H_2S, but a 20° deviation in the SSiS angle in relation to that in SiH_4. The bending potential increases non-linearly as a function of the displacement. Assuming comparable bending force constants the strain can be decreased by distributing the displacement evenly to the bond angles and thus leading to the experimental SiSSi angle of 82.5°.[4f]

With radius ratios of 0.535 and 0.737 for (**2a**) and (**2b**) respectively, we cannot expect short C–C distances. The Table shows the estimated distances by various methods, none showing an unusual 1,3-C–C distance. For short distances greater differences in atomic radii are required.[15] $(R_2GeX)_2$ for example, should provide a short 1,3-Ge–Ge distance.

There are several instances in the literature where interactions between atoms at normal bonding distances are found to be non-bonding or antibonding.[16] Isolobal analogy[17] relates (**1a**)—(**1d**) to $L_4M(\mu\text{-}X)_2ML_4$ (M = d^8 transition metal, L = unidentate ligand, X = bridging CO, NO, *etc.*) where long and short M–M distances are observed without much change in metal–metal bonding.[18] What is unusual about (**1**; R = H) is that the antibonding Si–Si interaction increases with increasing Si–Si distance. This is contrary to expected behaviour. One of the contributions to this is the increase in the overlap $\langle p_x(Si)|p_x(Si)\rangle$ with distance [−0.377 at Si–Si = 2.11 Å, and −0.385 at Si–Si = 2.31 Å for (**1a**; R = H) using the exponents specified*]. The overlap between atomic orbitals increases in magnitude with decreasing interatomic distance, reaches a maximum and decreases again. This is reflected in the contribution to total overlap population from individual m.o.s. Thus the overlap population corresponding to the b_{3u} m.o. in the total Si–Si overlap population increases in magnitude from −0.011 at 2.11 Å to −0.031 at 2.41 Å.

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* See footnote ¶ on p. 271.

Conclusions

The 1,3-non-bonded Si–Si distances in (**1a**)—(**1d**) are mainly controlled by Si–X bond lengths. Four-membered ring compounds with short 1,3-distances may be expected in A_2B_2 systems with $r_A/r_B \leqslant 0.414$. Fragment molecular orbital calculations based on the extended Hückel method, MNDO calculations, and *ab initio* m.o. calculations at the 3-21G level on (**1**; R = H) support these results. Mulliken overlap population analysis of (**1**) at various levels indicates that the Si–Si interaction is slightly antibonding and that the antibonding interaction increases in magnitude with increasing Si–Si distance. This is traced to the behaviour of the atomic orbital overlap with distance.

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