

Factors contributing to phantom bonds in inorganic molecules: interpretations and predictions

A RATHNA and JAYARAMAN CHANDRASEKHAR*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

Abstract. The validity of various qualitative proposals for interpreting and predicting the existence of short contacts between formally non-bonded atoms, as in cyclodisiloxane and related inorganic ring systems, is critically evaluated. The models range from simple considerations of geometric constraints, lone pair repulsions and π -complex formation to proposals such as the unsupported π -bond model and the σ -bridged- π bond concept. It is pointed out that a unified description based on a combination of closed and open 3-centre 2-electron bonds is possible. The role of hybridisation is emphasized in the short phantom bond computed in an earlier model system. These insights are used to predict structures with exceptionally short Si..Si and B..B phantom bonds. The proposals are confirmed by *ab initio* calculations.

Keywords. Phantom bond; 3-centre 2-electron bond; inorganic rings; silicon; boron; MO calculations.

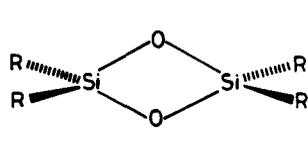
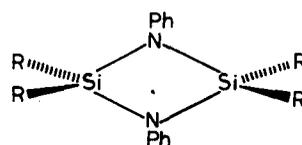
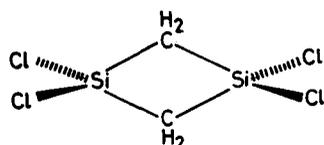
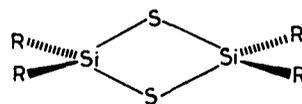
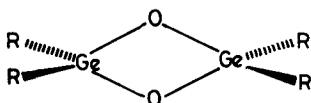
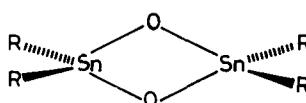
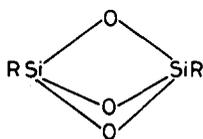
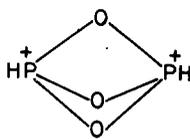
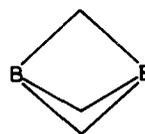
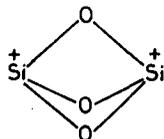
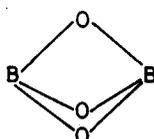
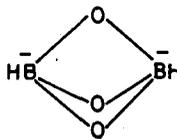
1. Introduction

The crystal structure of the cyclodisiloxane, **1a**, revealed a remarkable structural feature (Fink *et al* 1984). The Si..Si distance (2.31 Å) in **1a** was found to be shorter than the Si–Si single bond length (2.34 Å). Formally, non-bonded atoms in a molecule, making a contact comparable to a covalent linkage, may be considered to be connected by a *phantom* bond. The electronic origin of the phantom bond in the disiloxane ring and the generality of the structural feature in other inorganic rings have been the subject of several experimental and theoretical investigations.

Experimentally determined structures of a number of other four-membered rings related to cyclodisiloxanes do not show the existence of abnormally short Si..Si contacts. These include rings containing nitrogen, **2**: 2.59 Å (Parkanyi *et al* 1980), carbon, **3**: 2.70 Å (Vilkov *et al* 1968), and sulphur, **4**: 2.84 Å (Yokoi *et al* 1955; Yokoi 1957). Thus, oxygen appears to be unique in inducing a phantom bond, among the structures studied. Interestingly, the germanium analogue, **5**, of cyclodisiloxane exhibits a Ge..Ge distance (2.62 Å) which is longer than the normal Ge–Ge covalent bond length of 2.46 Å (Masamune *et al* 1989). Crystal structure of a di-stanna derivative, **6**, also has a non-bonded Sn..Sn contact (2.94 Å) which is marginally longer than the single bond distance of 2.81 Å (Edelman *et al* 1990).

Numerous theoretical calculations have been carried out on the parent cyclodisiloxane, **1b**, to probe the nature of the non-bonded interaction (Fink *et al* 1984; Bachrach and Streitwieser 1985; Kudo and Nagase 1985; Grev and Schaefer 1987;

*For correspondence

1a, R = Mesityl c, R = Fb, R = H234567a, R = Hb, R = F89101112

Jemmis *et al* 1987; Somogyi and Tamas 1990; Gordon *et al* 1991). MNDO type semiempirical methods fail to reproduce the unusual geometrical feature of 1 (Fink *et al* 1984; Jemmis *et al* 1987). However, *ab initio* calculations are quite successful, especially if the geometry optimisation is carried out with the 6-31G* basis set. Such calculations have therefore been used to provide various qualitative interpretations and also to predict new structures, 1c, 7-9, with exceptionally short phantom bonds (table 1). In particular, the bicyclic system, 7, with two silicon atoms at the bridgehead positions has been predicted to have Si..Si contacts as short as around 2 Å (Nagase

Table 1. Computed structural parameters in inorganic rings.

Molecule	Geometric parameter	MNDO	3-21G	6-31G*
<u>1b</u>	Si..Si	2.612	2.540	2.394
<u>1c</u>	Si..Si	2.582	2.474	2.341
<u>7a</u>	Si..Si	2.286	2.179	2.060
<u>7b</u>	Si..Si	2.238	2.140	2.033
<u>8</u>	P..P	—	—	2.038
<u>9</u>	B..B	—	—	1.606

et al 1988). Related compounds, 8 and 9, with phantom P..P and B..B bonds, respectively, have also been predicted (Nagase *et al* 1988; Liang and Allen 1991).

In this paper, various proposals for interpreting phantom bonds are critically evaluated. A unified bonding description is provided to account for the phantom bonds in cyclodisiloxane and related derivatives. Finally, additional systems with phantom bonds are proposed and evaluated using *ab initio* MO calculations.

2. Models for interpreting phantom bonds

The simplest explanation for the short Si..Si contact in cyclodisiloxane is that the distance is a direct consequence of geometric constraints in the four-membered ring. Assuming planar square geometries for $(R_2SiX)_2$ ring systems, the Si..Si distance directly depends on the Si-X bond length. If the Si-O bonds have normal lengths, the corresponding Si..Si contact necessarily has to be unusually small (Jemmis *et al* 1987; Masamune *et al* 1989; Schmidt *et al* 1991). A similar suggestion has been made to estimate non-bonded Si..Si distances in several ring systems (Kabe *et al* 1990). The ratio of the non-bonded distance to normal bond lengths is roughly constant for a given type of ring (say, four-membered or bicyclo [1.1.1] pentyl), irrespective of the nature of the atoms involved. Using the well-known lengths from hydrocarbon structures, Si..Si distances can be estimated. Since the bond angles in the highly constrained rings do not vary over a wide range, such structural homology rules are approximately valid. Nevertheless, emphasis on geometric factors alone cannot provide a satisfactory explanation for several structural details. For example, the very fact that cyclodisiloxane adopts a nearly square geometry is surprising, since the Si-O-Si angle is generally much greater than the O-Si-O angle in unconstrained systems. Other subtle effects seen in the computed structures in table 1 cannot also be interpreted using exclusively geometric arguments. Hence, a more detailed analysis of electronic factors is essential.

The relative contraction of the Si-O-Si angles in cyclodisiloxane and the consequent reduction in Si..Si distance have been attributed to the large repulsions between the oxygen lone pairs (Fink *et al* 1984; Bachrach and Streitwieser 1985). This interpretation has been questioned on the basis of the smaller Si-O-Si angle computed in disilene oxide and the smaller Si-S-Si angle in the sulphur analogue of cyclodisiloxane (Kudo and Nagase 1985). While these structures lack O-O repulsions, the

smaller angles are not entirely unexpected. Disilene oxide being a three-membered ring includes smaller bond angles. Further, the natural bond angle involving sulphur is consistently shorter than that subtended at oxygen. Hence the above comparisons do not rule out the role of lone pair repulsions in leading to a short Si..Si distance in cyclodisiloxane. In fact, a similar electrostatic interpretation has been proposed to account for the short Si..Si contact computed for 2,4,5-trioxa-1,3-disilabicyclo [1.1.1]-pentane, **7** (Streitwieser 1989).

Alternative bonding models have also been proposed to account for the phantom bond in cyclodisiloxane, especially since related compounds with one or more carbon atoms seem to have normal geometries. The suggestion that the silicon atoms may be connected by a formal σ bond while the ring is characterised by a delocalised four-centre six-electron bond (Fink *et al* 1984) has not been supported by calculations. Canonical and localised MO's as well as electron density analyses do not reveal the presence of an electron deficient ring periphery (Bachrach and Streitwieser 1985; Kudo and Nagase 1985). Further, no bond critical point along the Si..Si internuclear axis could be found, ruling out a σ bond between the two atoms (Gordon *et al* 1991).

Another unusual proposal is that the Si..Si interactions in **1b** become more antibonding with increasing separation (Jemmis *et al* 1987). This counter-intuitive suggestion was based on the variation of overlap integral with distance for silicon *p* orbitals with the chosen orbital exponents near the length of interest. This model, even if it is theoretically justified, is of limited appeal as it goes against commonly used qualitative rules of MO theory. A further complicating factor is that the Si..Si interaction in **1** is computed to be antibonding using Mulliken population analysis, but is weakly bonding using Mayer's scheme at the *ab initio* level (Somogyi and Tamas 1990).

After initially suggesting that the phantom bond in cyclodisiloxane is due to the large affinity of silicon for oxygen (Kudo and Nagase 1985), π -complex formation has been held responsible for the short contact (Nagase *et al* 1988). In the latter model, the oxygen atoms in **1** and **7** form π -complexes with the central Si-Si unit. In another proposal, the silicon atoms of **1** are suggested to be held together by a π -bond, but without an intervening σ -bond. The Si..Si linkage is thus an *unsupported* π -bond (Grev and Schaefer 1987). Previously, it had also been pointed out that in strained ring systems, such as propellanes, the bridgehead atoms are held by σ -bridged- π bonds (Jackson and Allen 1984). The same proposal was extended to molecules such as **1**, especially since the model is relevant in rings made of atoms with widely differing electronegativities (Liang and Allen 1991).

The above three models, although proposed independently, have a remarkably similar basis. The different bonding proposals can all be understood from a unified point of view. Consider a sequence X-Y-X where X and Y are atoms or groups connected by formal single bonds. The conventional localised bonding model is shown in figure 1a. The canonical version can be obtained by forming symmetric and antisymmetric combination of the two X-Y bond orbitals (figure 1b). These orbitals (ϕ_S and ϕ_A) can also be visualised as combinations of atomic or hybrid orbitals as in figure 1c. While the two MO's principally contribute to X-Y bonding, there is an important difference in their effect on X..X bonding. Even if the X atoms are formally non-bonded, the ϕ_S combination would lead to attractive interaction between the two atoms. On the other hand, the ϕ_A combination is X..X antibonding in nature. Depending on the relative coefficients and sizes of the constituent orbitals, which in

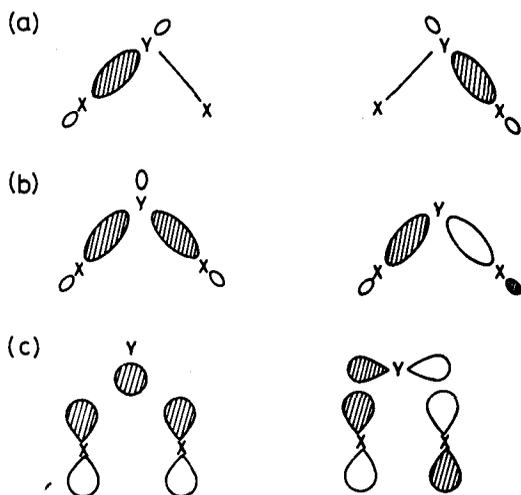


Figure 1. Schematic representation of MO's in a bent X-Y-X unit: (a) Localised orbitals, (b) their symmetric (ϕ_s) and antisymmetric (ϕ_a) combinations and (c) the latter as linear combinations of constituent atomic or hybrid orbitals.

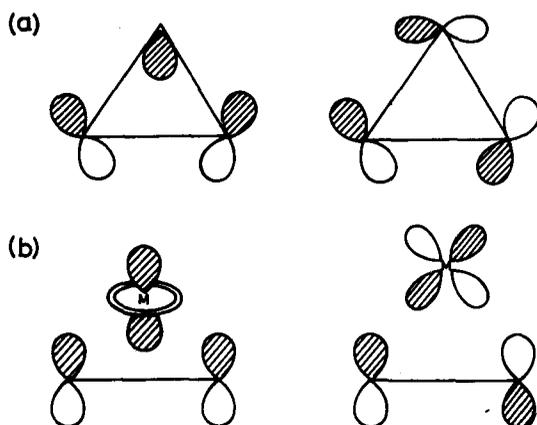


Figure 2. (a) Walsh orbitals of cyclopropane; (b) MO's representing σ -donation and π -back donation in metal complexes.

turn are predominantly governed by the electronegativities of X and Y, the two MO's will affect X..X bonding to different extents.

In an extreme possibility, the two types of interactions are equally effective. Such a situation is indeed found in symmetric three-membered rings. The connection between ϕ_s and ϕ_a shown in figure 1c and the well-known degenerate Walsh orbitals of cyclopropane shown in figure 2a (Jorgensen and Salem 1973) is obvious. Molecules in which the symmetric and antisymmetric MO's are highly non-equivalent are more common. A familiar example is provided by the nature of the metal-ligand bond in organometallic system (figure 2b). The symmetric combination ϕ_s is the same as the MO which corresponds to the interaction of the ligand donor and metal $d(\sigma)$ acceptor orbitals. The antisymmetric combination corresponds to π -back donation, i.e., metal

$d(\pi)$ to ligand π^* orbital interaction. In metal complexes, the two sets of interactions are not equally effective. Molecules characterised by such bonding can be generally termed π -complexes. Thus the π -complex model for organometallic systems (Dewar 1951; Chatt and Duncanson 1953) essentially involves the ϕ_S and ϕ_A type MO's shown in figure 1c.

The above bonding description is valid even for an entirely different combination, viz., that of two metal atoms sharing a bridging ligand atom. A typical example is a dinuclear copper cluster with a sulphide bridge. The bonding involves two lone pairs on sulphur interacting with the metal acceptor orbitals. While the direction of electron flow is different from the previous examples, the nature and symmetry of the MO's are similar. The MO's correspond to the symmetric and antisymmetric combinations as shown in figure 1c, involving d orbitals on X and σ and π type lone pairs in Y. The relative importance of the two MO's for metal-ligand as well as metal-metal bonding depends on the participating elements and also on the precise geometry of the bridge (Knotter *et al* 1991, 1992; Alemany and Alvarez 1992; Abraham *et al* 1993).

The combination of ϕ_S and ϕ_A orbitals can also be readily recognised as the closed and open three-centre two-electron bonds ubiquitously employed in describing structures of boron compounds. The analysis has also been used for rationalising wide structural variations in elemental clusters.

From the above discussion it is evident that the ϕ_S and ϕ_A MO's provide a common basis for understanding bonding in a variety of chemical systems. In particular, the remarkable geometrical features in cyclodisiloxane as well as in bicyclic derivatives, **7**, can be rationalised. In view of the large difference in electronegativities of Si and O, the ϕ_S and ϕ_A MO's are highly non-equivalent in these systems. The Si-O interaction is more effective in the former. As an important consequence, the two silicon atoms attain some mutually bonding character. This argument is equivalent to a π -complex model in which σ -donation is more effective than π -back donation (Nagase *et al* 1988). By noting that the silicon atoms do not share a σ -bond, the description is identical to the unsupported π -bond model (Grev and Schaefer 1987). The key MO ϕ_S which contributes to the reduction in Si..Si distance corresponds to a closed three-centre two-electron bond or a σ -bridged- π -bond (Liang and Allen 1991). Thus, the different bonding models for explaining phantom bonds in **1** and related systems utilise essentially the same bonding scheme and emphasize the same orbital interaction.

While the above analysis provides a pleasing interpretation for the phantom bonds in cyclodisiloxanes and related derivatives, some questions remain. It has recently been argued on the basis of computed electron density variations that there is no evidence for the presence of unsupported π -bonds in **1** (Gordon *et al* 1991). The authors have correctly ruled out direct Si..Si σ -type bonding in view of the lack of any bond critical point along the internuclear axis. However, evidence for the unsupported π -bond has been sought by analysing electron densities *above* the ring plane. As would be clear from the previous discussion, the corresponding bond (or the equivalent σ -bridged- π -bond) is to be found in the ring plane. The computed results are therefore not inconsistent with the important role of the closed 3-centre 2-electron bond in **1** and related rings.

A point which remains to be clarified is the relative importance of lone-pair repulsions and 3-centre bonding in leading to phantom bonds. In many of the systems

found or calculated to have such short non-bonded contacts, both factors can operate. In order to unravel the individual contributions, studies on other model systems are needed. In one such effort (Jackson and Allen 1984; Liang and Allen 1991), 1,3-diborabicyclo [1.1.1] pentane has been calculated to have a short B..B distance, comparable to that found in carboranes. This result has been interpreted as highlighting the importance of σ -bridged- π -bonding interaction in 9, primarily resulting from the variation in electronegativities of carbon and boron. However, this claim overlooks another important contribution to the phantom B..B bond. Tricoordinate boron prefers to be planar. This factor necessarily brings the bridgehead atoms closer. The short contact in 9 is predominantly governed by hybridisation at boron, and only partly by multi-centred bonding.

In order to evaluate the validity of the above critical interpretations, additional systems with potentially short phantom bonds are proposed and confirmed using *ab initio* MO calculations.

3. Predictions of molecules with phantom bonds

Lone pair repulsions, dominance of closed 3-centre 2-electron bonding and hybridisation effects are indicated to be the factors which are crucial to the design of molecules with phantom bonds. These features can be readily incorporated in additional systems by modifying the silicon and boron derivatives already calculated to have short non-bonded contacts. Thus, the bridgehead dication, 10, derived from 7 is expected to have a short Si..Si distance due to further contributions from rehybridisation. Similarly, the tri-oxa derivative, 11, should have a short B..B distance due to additional lone pair repulsions as compared to 9 as well as from more effective σ -bridged- π -bonding. The role of hybridisation at the bridgehead atoms can be discerned by examining the corresponding dihydride, 12.

MNDO (Dewar and Thiel 1977) and *ab initio* calculations (Hehre *et al* 1986) with the 3-21G and 6-31G* basis sets were carried out on 10–12. The optimised geometric parameters are shown in table 2. As in earlier calculations (table 1) the Si..Si contact

Table 2. Computed structural parameters in inorganic compounds predicted to have phantom bonds on qualitative grounds.

Molecule	Geometric parameter	MNDO	3-21G	6-31G*
<u>10</u>	Si..Si	2.230	2.139	1.987
	Si–O	1.770	1.753	1.686
	Si–O–Si	78.11	75.21	72.18
<u>11</u>	B..B	1.560	1.525	1.460
	B–O	1.488	1.483	1.441
	B–O–B	63.25	61.86	60.88
<u>12</u>	B..B	1.738	1.682	1.623
	B–O	1.508	1.536	1.507
	B–H	1.186	1.242	1.257
	B–O–B	70.38	66.41	65.17

is overestimated by the MNDO procedure as well as by 3-21G calculations. The values optimised at the 6-31G* level are likely to be the most reliable. It is clear that the phantom bond becomes shorter in 10 compared to 7a or 7b due to rehybridisation at the bridgehead atoms. Similarly, 11 is calculated to have a B..B contact as short as 1.46 Å. The presence of tetracoordinate boron in 12 increases the distance to 1.62 Å. The latter still represents a phantom bond, since the normal B–B single bond length varies from 1.6–1.9 Å in boranes and carboranes (Beaudet 1988). The short contact can be attributed to lone-pair repulsions and σ -bridged- π bonding. Nevertheless, the importance of hybridisation at the bridgehead atoms is also clearly revealed. Part of the increased B..B contact in 12 relative to 11 may also result from repulsions involving the formally negatively charged boron atoms. It is remarkable that in spite of a similar repulsion in the dication, 10, the Si..Si contact is less than 2 Å. Interestingly, 10 and 11 represent the compounds with the shortest known (or predicted) Si..Si and B..B non-bonded contacts, respectively.

4. Conclusions

Various proposals for rationalising the short non-bonded contacts in cyclodisiloxane and related derivatives are summarised and critically evaluated. There is no direct σ -type bonding between the atoms concerned. Lone pair repulsions contribute significantly to the short contact. Attractive interactions between the non-bonded atoms are also induced by closed 3-centre 2-electron bonds. This proposal is equivalent to the π -complex, σ -bridged- π bond and the unsupported π bond models. The relative importance of lone-pair repulsions and multi-centred bonding remains to be resolved. Hybridisation effects at the bridgehead atom are also crucial in contributing to the short contacts in some bicyclic systems. These insights have been used to predict structures with the shortest known Si..Si and B..B phantom bonds.

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