A Double Bond with Weak σ- and Strong π-Interactions Is Still a Double Bond

Cina Foroutan-Nejad*

Department of Chemistry, Faculty of Science, Masaryk University & National Centre for Biomolecular Research, Faculty of Science, Masaryk University, 625 00 Brno, Czech Republic

canyslopus@yahoo.co.uk
Synthesis of 1,3 singlet diradicals in cyclic organic molecules has been the main route toward formation of single π-bonds, i.e. π-bonded atoms without σ-bonding.\textsuperscript{1–4} The unpaired electrons of the radicals occupy $p$ atomic orbitals that can ideally form a long-range π-bond without formation of a σ-bond. Most of the studies on the single π-bonds rely on the experimental data, which confirm formation of a singlet diradical, but a thorough bonding analysis on 1,3 singlet diradicals has not been performed yet. In a recent study Kyushin et al. reported synthesis and characterization of a four-membered singlet diradical silicon ring with a 1,3 silicon-silicon single π-bond. The bond was identified by analyses on the basis of canonical molecular orbitals (CMOs) and natural bond orbitals\textsuperscript{5} (NBOs), which confirms that two $sp^3$ hybridized silicon atoms are connected to each other via a π-MO that is the HOMO of the molecule.\textsuperscript{4} Here, I studied this system in more details and show that this bond is not a single π-bond, but rather a double bond with weak σ-bond.

The first evidence against the hypothetical single π-bond can be found in CMOs, where HOMO –6 of the molecule represents a σ-interaction between two $sp^3$ hybridized silicon atoms, Fig. 1. This orbital with HOMO –1, HOMO –2, and HOMO –3 constitute the sigma framework of the silicon ring. However, MO-based analyses do not provide a quantitative picture of bonding.\textsuperscript{6} To obtain a more quantitative picture of the bonding, the molecule was analyzed within the context of Bader’s theory.\textsuperscript{7} Topological analysis of the electron density identifies no bond critical point (BCP) between two $sp^3$ hybridized silicon atoms. Nevertheless, presence or absence of (BCPs) is not a reliable measure of bonding; therefore, other parameters were studied.\textsuperscript{8} Ideally a pure π-bond should have 2 BCPs above and below the nodal plane of the π-MO; however, this feature is visible only if the σ-electron density is removed.\textsuperscript{9,10} In ordinary molecules with double bonds, the core and σ-electrons mask the fingerprint of π-electron density. In order to visually search for a potential
single $\pi$-bond, the derivatives of the electron density, namely the Laplacian of the electron density, $\nabla^2 \rho(r)$ and energy density were probed.

**Fig1.** Occupied molecular orbitals of the molecule; HOMO–6 corresponds to a $\sigma$-bond across the ring.

The plot of $\nabla^2 \rho(r)$ shows regions of electron density concentration on Si atoms corresponding to their atomic $p$ orbitals, **Fig 2a.** This feature becomes more pronounced after removing electrons from the $\sigma$-skeleton but the region in between two Si atoms has a positive Laplacian that is a feature of noncovalent interactions or that of charge-shift bonds. These features become more pronounced in the central region of the ring after removing electrons from the $\sigma$-
framework of the Si$_4$ ring, Fig 1b and c. Although no BCP between two Si atoms is found, some of properties of the ring critical point (RCP) in the middle of the Si$_4$ ring are interesting. The electron density of this point is 0.0311 au. The contribution of HOMO –6, the bonding σ-MO, to the local electron density to is 0.0086 au, comparable with that of a weak hydrogen bond.$^{12}$ The rest of MOs sum up to 0.0225 au of electron density that is the sum of core electrons of the Si atoms and valance electrons of the other atoms. It is worth emphasizing that at the RCP the π-electron density and contributions of the other σ-MOs equals zero because the RCP falls on the nodal plane of these orbitals. Removing electrons from HOMO –6 shifts $\nabla^2 \rho(r)$ of the RCP from 0.0654 au to a more positive value, 0.0735 au. This is because the negative eigenvalue of the Hessian of the electron density, $\lambda_1$, which reflects the out-of-plane curvature of the local electron density, changes from $-0.0111$ au to $-0.0036$ au when electrons of HOMO –6 are removed from the total electron density.

The contour plots of the energy density are consistent with covalent-type interaction between the Si atoms because the energy density remains negative in the mid-ring region, Fig 2d-f. Removing the σ-electrons from HOMO –6 changes the distribution of the energy density and reduces its absolute value at the center of the ring from $-0.0028$ au to $-0.0008$ au, suggesting a bonding contribution from HOMO –6. Removing the rest of σ-electrons does not change the energy density at the RCP but intensifies the features of π bond by forming some local maxima at the position of $p$ atomic orbitals corresponding to the negative region of Laplacian on the Si atoms as it is evident in Fig 2e and f.
Fig 2. Contour plots of the Laplacian of electron density (a to c) and energy density (d to f) in the molecule. CH$_3$ groups are removed for more clarity in the plot. Positive and negative values are represented by blue and red lines, respectively. (a) The central region between 1,3 atoms has a positive Laplacian that is a sign of closed-shell interaction. (b) By removing electrons from the σ-bonding HOMO –6 the electron density concentrations, corresponding to p atomic orbitals on Si atoms intensifies. (d) Removing all electrons from the σ-framework of Si$_4$ intensifies the p-electron density concentration. (d) Contour plot of energy density that shows a covalent-type interaction.
between Si atoms. (h) Contour plot of energy density after removing electrons from HOMO –6, and (f) after removing electrons from all σ-MOs of Si₄ moiety. The p-atomic orbital-shaped feature appears on the Si atoms by removing the σ-electrons in the contour plot of energy density too.

The most reliable information regarding the contribution of the π- and σ-frameworks to the bonding can be obtained from computing the delocalization index between 1,3 Si atoms. Delocalization index is a direct measure of electron sharing that is covalency between homonuclear bonds and is directly related to the bond dissociation energy.$^{13,14}$ The total electron delocalization between the atoms is 0.73 e that is comparable with the delocalization index of a single bond (~1.0) in a homonuclear species. The individual contributions of π- and σ-electrons in the delocalization index are 0.51 e and 0.22 e, respectively. These values suggest that although a weak π-interaction forms between 1,3 silicon atoms, a weaker but nonnegligible σ-interaction is present between the same pair of atoms.

In a nutshell, this species is a special system in which π-bond is stronger than the σ-bond but sadly it still is a double bonded system.

**Methods**

The structure of the molecule was taken from the supporting information of the original paper by Kyushin et al.$^4$ and reoptimized at two levels of theory, B3LYP/6-31g(d) as the original paper, and B3LYP/def2-TZVP for more accuracy by Gaussian 09.$^{15}$ No symmetry was imposed during optimization. A local minimum with lower energy compared to the previously reported structure was found and confirmed via frequency computations. CMOs of the molecule were analyzed at both levels of theory and no difference were found. The wavefunctions were analyzed and visualized by AIMAll at both levels of theory.$^{16}$ The values reported here are from B3LYP/6-31g(d) akin to those reported in the original paper.
References

1. Abe, M. & Akisaka, R. Is π-Single Bonding (C–π–C) Possible? A Challenge in Organic Chemistry. *Chem. Lett.* **46**, 1586–1592 (2017).

2. Akisaka, R. & Abe, M. Bulky Substituent Effect on Reactivity of Localized Singlet Cyclopentane-1,3-diyls with π-Single Bonding (C-π-C) Character. *Chem. – Asian J.* **14**, 4223–4228 (2019).

3. Nakagaki, T., Sakai, T., Mizuta, T., Fujiwara, Y. & Abe, M. Kinetic Stabilization and Reactivity of π Single-Bonded Species: Effect of the Alkoxy Group on the Lifetime of Singlet 2,2-Dialkoxy-1,3-diphenyloctahydropentalene-1,3-diyls. *Chem. – Eur. J.* **19**, 10395–10404 (2013).

4. Kyushin, S. *et al.* Silicon–silicon π single bond. *Nat. Commun.* **11**, 4009 (2020).

5. Landis, C. R. & Weinhold, F. The NBO View of Chemical Bonding. in *The Chemical Bond* 91–120 (John Wiley & Sons, Ltd, 2014). doi:10.1002/9783527664696.ch3.

6. Foroutan-Nejad, C. Na…B Bond in NaBH3–; A Bond Like No Other. *Angew. Chem. Int. Ed.* doi:10.1002/anie.202010024.

7. Bader, R. F. W. *Atoms in molecules: a quantum theory*. (Clarendon Press, 1990).

8. Foroutan-Nejad, C., Shahbazian, S. & Marek, R. Toward a Consistent Interpretation of the QTAIM: Tortuous Link between Chemical Bonds, Interactions, and Bond/Line Paths. *Chem. – Eur. J.* **20**, 10140–10152 (2014).

9. Azami, S. M. Electron Density Based Characterization of π Bonds in Planar Molecules. *J. Phys. Chem. A* **114**, 11794–11797 (2010).

10. Foroutan-Nejad, C., Shahbazian, S., Feixas, F., Rashidi-Ranjbar, P. & Solà, M. A dissected ring current model for assessing magnetic aromaticity: A general approach for both organic and inorganic rings. *J. Comput. Chem.* **32**, 2422–2431 (2011).
11. Shaik, S., Danovich, D., Wu, W. & Hiberty, P. C. Charge-shift bonding and its manifestations in chemistry. *Nat. Chem.* **1**, 443–449 (2009).

12. Badri, Z., Bouzková, K., Foroutan-Nejad, C. & Marek, R. Origin of the Thermodynamic Stability of the Polymorph IV of Crystalline Barbituric Acid: Evidence from Solid-State NMR and Electron Density Analyses. *Cryst. Growth Des.* **14**, 2763–2772 (2014).

13. Badri, Z. & Foroutan-Nejad, C. Unification of ground-state aromaticity criteria – structure, electron delocalization, and energy – in light of the quantum chemical topology. *Phys. Chem. Chem. Phys.* **18**, 11693–11699 (2016).

14. Francisco, E., Menéndez Crespo, D., Costales, A. & Martín Pendás, Á. A multipolar approach to the interatomic covalent interaction energy. *J. Comput. Chem.* **38**, 816–829 (2017).

15. M. J. Frisch, *et al.* *Gaussian 09*. (Gaussian, Inc., Wallingford CT, 2013).

16. Keith, T. A. *AIMAll*. (Gristmill Software, 2017).