

Reply to: “A double bond with weak σ - and strong π -interactions is still a double bond”

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REPLYING TO C. Foroutan-Nejad *Nature Communications* <https://doi.org/10.1038/s41467-021-24238-x> (2021)

In our original paper¹, we reported synthesis of 1,2,2,3,4,4-hexa-*tert*-butylbicyclo[1.1.0]tetrasilane (**2**, Fig. 1). The X-ray crystallography of **2** showed a planar geometry around the bridgehead silicon atom (angle sums except for the inter-bridgehead bond = 359.79°). On the basis of experimental results of X-ray crystallography, electron paramagnetic resonance, magnetic susceptibility, UV/Vis and ²⁹Si NMR spectra, and theoretical calculations including natural bond orbital analysis, we concluded that **2** has a silicon–silicon π single bond between the bridgehead silicon atoms. We have been aware that the HOMO–6 and HOMO–1 represent in-phase and out-of-phase orbital interactions between the linearly arranged two $\sigma(\text{Si}_{\text{bridgehead}}-\text{C}_{\text{tert-butyl}})$ orbitals, respectively. We did not discuss them in the original paper because (i) we considered that the σ -type bonding interaction between the bridgehead silicon atoms due to the in-phase interaction (HOMO–6) should be canceled out by the corresponding out-of-phase interaction (HOMO–1) and (ii) we did not find σ -type interaction between the bridgehead silicon atoms within the above-mentioned our theoretical investigation (output threshold > 2.1 kJ mol^{–1}).

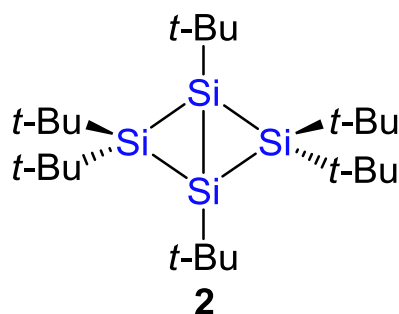


Fig. 1 Chemical structure of **2**.

In their commentary, Dr. Foroutan-Nejad took a different approach to characterize **2**. The author analyzed electron density of **2** theoretically and concluded that the silicon–silicon π bond is accompanied by a weak but non-negligible σ bond. We welcome discussion about the unusual bonding situation in the isolable compound **2** from diverse viewpoints to obtain deeper understanding of this chemical bond.

Received: 9 December 2020; Accepted: 9 June 2021;
Published online: 29 June 2021

Reference

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

Author contributions

S.K., S.I. and H.M. discussed the content of this reply and wrote the manuscript. Y.K., K.O., H.I., T.K. and M.H. read and agreed to this reply.

Competing interests

The authors declare no competing interests.

Additional information

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Peer review information *Nature Communications* thanks Chérif F. Matta and the other anonymous reviewer(s) for their contribution to the peer review of this work.

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