

Covalency and ionicity do not oppose each other – Relationship between Si-O bond character and basicity of siloxanes

Simon Grabowsky^{*1}, Malte Fugel¹, Jens Beckmann¹, Graham S. Chandler², and Patrick Bultinck³

¹ *University of Bremen, Institute of Inorganic Chemistry and Crystallography, 28359 Bremen, Germany, E-Mail: simon.grabowsky@uni-bremen.de*

² *University of Western Australia, School of Molecular Sciences, Perth WA 6009, Australia*

³ *Ghent University, Department of Chemistry, 9000 Gent, Belgium*

Covalency and ionicity are orthogonal rather than antipodal concepts: We demonstrate for the case of siloxane systems $-(R_2Si-O)_n$ that both covalency and ionicity of the Si-O bonds impact on the basicity of the Si-O-Si linkage. The relationship between the siloxane basicity and the Si-O bond character has been under debate since previous studies have presented conflicting explanations. It has been shown by West and Weinhold with natural-bond-orbital methods that increased hyperconjugative interactions of $LP(O) \rightarrow \sigma^*(Si-R)$ type, i.e. increased orbital overlap and hence covalency, are responsible for the low siloxane basicity at large Si-O-Si angles.[1] On the other hand, increased ionicity towards larger Si-O-Si angles has been revealed with real-space bonding indicators by Gillespie and us in the past.[2]

To resolve this ostensible contradiction, we present a complementary bonding analysis that combines orbital-space, real-space and bond-index considerations. We analyze the isolated disiloxane molecule $H_3SiOSiH_3$ with varying Si-O-Si angles, and n-membered cyclic siloxane systems $Si_2H_4O(CH_2)_{n-3}$. All methods from quite different realms show that both covalent and ionic interactions increase simultaneously towards larger Si-O-Si angles.

In addition, we present highly accurate absolute hydrogen bond interaction energies of the investigated siloxane molecules with water and silanol as donors. It is found that intermolecular hydrogen bonding is significant at small Si-O-Si angles and weakens as the Si-O-Si angle increases until no stable hydrogen bond complexes are obtained beyond $\varphi(SiOSi)=168^\circ$, angles typically displayed by minerals or polymers.

Finally, we show that the properties of molecular siloxane systems with Si-O-Si linkages strained into five-membered rings as synthesized in our laboratory exhibit hydrophilic rather than hydrophobic properties in line with our theoretical predictions and in contrast to silicone polymorphs and silica minerals.

[1] (a) R. West, L. S. Wilson, D. L. Powell, *J. Organomet. Chem.* **1979**, *178*, 5–9. (b) F. Weinhold, R. West, *Organometallics* **2011**, *30*, 5815–5824. (c) F. Weinhold, R. West, *J. Am. Chem. Soc.* **2013**, *135*, 5762–5767.

[2] (a) S. Grabowsky, M. F. Hesse, C. Paulmann, P. Luger, J. Beckmann, *Inorg. Chem.* **2009**, *48*, 4384–4393. (b) R. J. Gillespie, S. A. Johnson, *Inorg. Chem.* **1997**, *36*, 3031–3039.