The Quest of Stable Silanones: Substituent Effects

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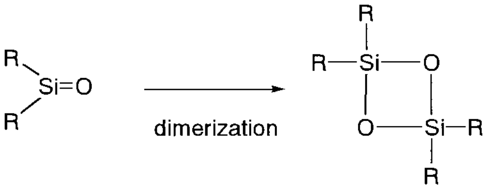
In quest of isolable silanones ($R_2Si=O$), substituent effects are theoretically investigated. Substituent groups worthy of experimental testing are predicted, which make silanones kinetically stable toward dimerization and isomerization.

The synthesis and isolation of stable compounds with multiple bonds to silicon have attracted constant interest in silicon chemistry.[1] Recent remarkable progress in the heavier analogues of ketones[2] is marked by the isolation of a stable silanethione ($R_2Si=S$)[3] and silaneselone ($R_2Si=Se$).[4] As the member of this family, stable silanones ($R_2Si=O$) are the focus of interest. Despite many attempts,[2,5] they are still unknown[6] except for the transient intermediates and spectroscopic detection.[7] The major obstacle to the isolation of $R_2Si=O$ is the high reactivity due to the polarized $Si^{\delta+}=O^{\delta-}$ bond, especially toward dimerization leading to cyclosiloxane $(R_2Si=O)_2$; when R = H, the head-to-tail dimerization is highly exothermic and proceeds with no barrier.[8a] It is an important subject whether silanones are isolable when they are properly substituted. Thus, substituent effects were theoretically investigated.[9]



We first tested the effects of Me and Ph groups using hybrid density functional theory at the B3LYP/6-31G* level.[10] The dimerization of $R_2Si=O$ was highly exothermic by 103 (R = Me) and 96 (R = Ph) kcal mol^{-1}, as in the parent $H_2Si=O$ case (106 kcal mol^{-1}). In an attempt to reduce the polarity of the Si–O bond, electropositive silyl groups such as SiH_3, $SiMe_3$ and $Si(SiH_3)_3$ were introduced as substituents.[11] The exothermic energies decreased, but were still as large as 93 (R = SiH_3), 85 (R = $SiMe_3$), and 80 (R = $Si(SiH_3)_3$) kcal mol^{-1}, suggesting that electronic effects only are not enough to prevent dimerization.

Therefore, we next considered bulky aryl groups. Because of the size of molecules, calculations were carried out with the two-layered ONIOM (B3LYP/6-31G*:PM3) method.[12] This method can well reproduce the full B3LYP/6-31G* calculations. For example, the Si=O distances of $Me_2Si=O$ and $Ph_2Si=O$ are reproduced within 0.003 Å, while the Si–O and Si–C distances and Si–O–Si angle in the four-membered rings of cyclic dimers $(Me_2Si=O)_2$ and $(Ph_2Si=O)_2$ are reproduced within 0.005 Å, 0.018 Å, and 0.3°, respectively. The exothermic energies for the dimerizations of $Me_2Si=O$ and $Ph_2Si=O$ are underestimated only by 7 and 3 kcal mol^{-1}, respectively. The results below are based on the ONIOM method.

As an example of representative bulky groups, Tip ($-C_6H_2$-2,4,6-*i*-Pr_3) was tested. However, the dimerization of $Tip_2Si=O$ was 84 kcal mol^{-1} exothermic. Here, it is instructive to note that the successful isolation of a silanethione (TipTbtSi=S) is realized with the help of not only Tip but also a bulkier Tbt ($-C_6H_2$-2,4,6-$\{CH(SiMe_3)_2\}_3$) group[3,13]; note also that, when the Tip group is replaced by a smaller Mes ($-C_6H_2$-2,4,6-Me_3) group, the isolation is not successful because of the facile head-to-tail dimerization.[3] In fact, it was calculated that the dimerization of TipTbtSi=S is only 7 kcal mol^{-1} exothermic. In contrast, the dimerization of TipTbtSi=O was highly exothermic by 72 kcal mol^{-1}, owing to the more polarized Si=O bond.[14]

To increase the crowding of substituents, a bulkier Mes* (C_6H_2-2,4,6-*t*-Bu_3) group was introduced instead of Tip. The dimerization of Mes*TbtSi=O was 10 kcal mol^{-1} exothermic. In order to search for more stable silanones, the Mes* group was replaced by a still bulkier *m*-terphenyl group (Ar = $-C_6H_3$-2,6-$(C_6H_2$-2,4,6-$Me_3)_2$) that can cover the O-part of the Si–O bond. It is noteworthy that the dimerization of ArTbtSi=O (Figure 1) is 48 kcal mol^{-1} endothermic. When two Tbt groups are available on the Si atom, the dimerization of $Tbt_2Si=O$ (Figure 2) is 46 kcal mol^{-1} endothermic.[15] These high endothermicity suggests that ArTbtSi=O and $Tbt_2Si=O$ are very stable to dimerization.[16]

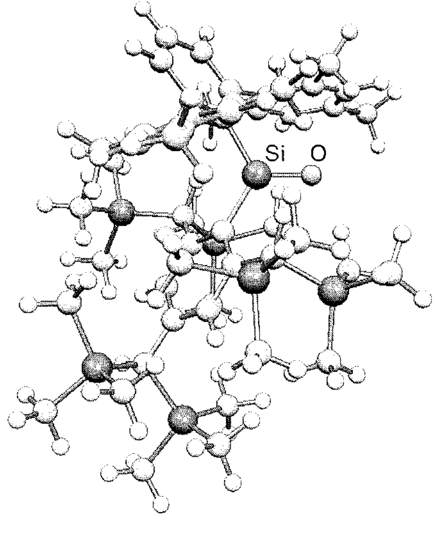


Figure 1. Optimized structure of ArTbtSi=O.

In ArTbtSi=O and $Tbt_2Si=O$, two bulky groups crowd around the Si-end of the Si–O bond. Therefore, it may be argued that, for example, ArTbtSi=O undergoes facile isomerization that leads to a silylene, TbtSi-OAr or ArSi-OTbt. To make this point clear, the transition states for the 1,2-Ar and 1,2-Tbt shifts were located, which were identified by vibrational frequency analysis. The barriers for the 1,2-Ar and 1,2-

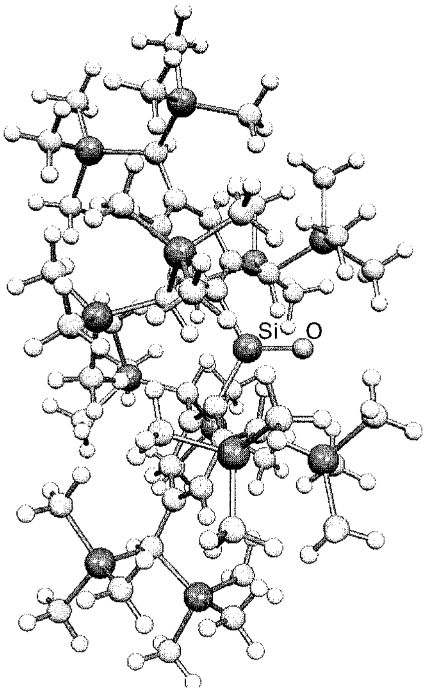


Figure 2. Optimized structure of $Tbt_2Si{=}O$.

Tbt shifts in ArTbtSi=O are 56 and 60 kcal mol^{-1}, respectively.[17] On the other hand, the barrier for the 1,2-Tbt shift in $Tbt_2Si{=}O$ to TbtSi-OTbt is 51 kcal mol^{-1}.[18] As is evident from these large barrier heights, ArTbtSi=O and $Tbt_2Si{=}O$ are highly stable to isomerization.

As Figures 1 and 2 show, the two bulky groups on Si help to protect the Si=O bond from reactive reagents. It is interesting that the two bulky groups make the π^* level of the Si=O bond significantly higher than that of $H_2Si{=}O$.[19] Owing to the bulk of substituents, the C–Si–C angles of 121.4° for ArTbtSi=O and 128.8° for $Tbt_2Si{=}O$ are larger than the H–Si–H angle of 111.6° for $H_2Si{=}O$. However, it is worthy of remark that ArTbtSi=O and $Tbt_2Si{=}O$ have a planar trigonal structure around the Si atom, as do ketones: the sum of bond angles around the Si atom is 359.9° for ArTbtSi=O and $Tbt_2Si{=}O$. The Si=O distances of 1.548 Å for ArTbtSi=O and 1.553 Å for $Tbt_2Si{=}O$ lengthen only by ca. 0.02 Å from that of 1.532 Å for $H_2Si{=}O$.

It is expected that the present work will be of help in designing stable silanones and stimulate the successful synthesis and isolation.[20]

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Dedicated to Professor Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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11 According to the natural population analysis of $R_2Si{=}O$, the charges on Si and O are +1.13 and –1.01 for R = SiH_3, +1.07 and –1.04 for R = $SiMe_3$, and +1.24 and –1.03 for R = $Si(SiH_3)_3$, respectively, while they are +1.94 and –1.05 for R = Me and +1.96 and –1.06 for R = Ph.

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14 Therefore, the isolation of silanones is more difficult than that of silanethiones,[8c] as is also apparent from the bond polarization in the parent compounds: $H_2Si^{+1.48} = O^{-1.01}$ vs $H_2Si^{+0.93} = S^{-0.57}$ at B3LYP/6-31G*.

15 According to preliminary calculations, the dimerization of $Ar^*_2Si{=}O$ ($Ar^* = \text{-}C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3)_2$) is highly endothermic. Ar* as well as Tbt is known as a representative bulky group in main group chemistry. For recent reviews on Ar* and Tbt, see: B. Twamley, S. T. Haubrich, and P. P. Power, *Adv. Organomet. Chem.*, **44**, 1 (1999) and ref 2.

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17 The 1,2-Ar and 1,2-Tbt shifts are 11 and 8 kcal mol^{-1} exothermic, respectively.

18 The 1,2-Tbt shift is 12 kcal mol^{-1} exothermic.

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20 The same is more expected for the isolation of silynes (RSi≡CR) because the Si≡C bonds are less polarized than the Si=O bonds in silanones and can be protected by substituents on both sides, which attract considerable interest as another important target in silicon chemistry.