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Stabilisation of planar tetracoordinate silicon: a new building block for conjugated Si -containing systems

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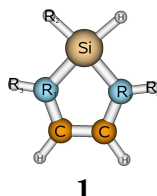
Introduction

Although the synthesis of planar tetracoordinate carbon-containing molecules received considerable attention over the last decades, only a few attempts to construct systems containing its silicon counterpart was made. Although the preparation of a compound featuring planar tetracoordinated silicon was reported in 1979 [1], this claim was later questioned [2], [3], and later attempts to synthesize this type of compounds were unsuccessful [4].

The aim of this work was to conduct a systematic study of the electronic and steric factors that might influence the stability of planar tetracoordinate silicon (PTSi), and use the gained information to find possible synthetic goals containing this unusual bond structure.

Early QC calculations [3] indicated that contrary to carbon, planar tetracoordinated silicon has a σ type HOMO and a vacant p-orbital thus favouring electronegative, π donor substituents. Since planar geometry allows PTSi to be incorporated into and possibly stabilized by π -conjugation, five-membered 6π electron rings are attractive targets for the investigation of the PTSi structure.

Results and Discussion



Calculating the energy difference between the planar and tetrahedral Si forms of **1** with various R groups allows us to estimate the stabilizing effect of different substituents on PTSi. In the case of substitution inside the five-membered ring R_1 the data in **Table 1** gives us the conclusion that indeed π donor substituents stabilize the planar bond arrangement around the Si atom over the tetrahedral one. In the case of $R_1 = O, N$ or S the possibility of a 6π electron delocalization arises which might contribute to the stabilizing effect. Since the N containing ring **1b** showed the largest stabilization, further substitution (R_2, R_3) was carried out on this ring. Substitution on the Si atom (R_2 position) showed significant stabilization of the planar form only in the **1i**, **1l** and **1m** cases, but even these substituent combinations were not able to produce a planar energy minimum. Substitution on the R_3 position was not able to provide significant energy gain.

| | 1a | 1b | 1c | 1d | 1e | 1f | 1g | 1h | 1i | 1j | 1k | 1l | 1m |
|------------|------|------|------|------|------|--------|------|--------|--------|------|------|--------|------|
| R_1 | O | N | S | C | C=O | N | N | N | N | N | N | N | N |
| R_2 | H | H | H | H | H | CH_3 | F | NH_2 | NO_2 | OH | Ph | CF_3 | CHO |
| ΔE | 37.5 | 20.8 | 38.7 | 81.1 | 76.7 | 22.5 | 23.0 | 23.0 | 14.1 | 21.5 | 24.1 | 18.3 | 17.9 |

Table 1: Energy differences (kcal/mol) of the planar and tetrahedral forms of **1**
Calculated at the $mp2/6-31+G^*$ level of theory

In order to gain a deeper understanding of how the different substituents achieve the stabilisation of PTSi, the bond lengths, NBO charges, Wiberg and AIM -derived bond indices and bond ellipticities were calculated for both the planar and tetrahedral forms of 1a-1m. Interestingly, although

neither of these parameters correlate well with the calculated ΔE -s when considered only to the planar form, the *differences* between the planar and tetragonal forms, e.g. the difference of the charges on the Si atom show an excellent correlation with ΔE (**Figure 1**), allowing the conclusion that inductive effects play a major role in the stabilization.

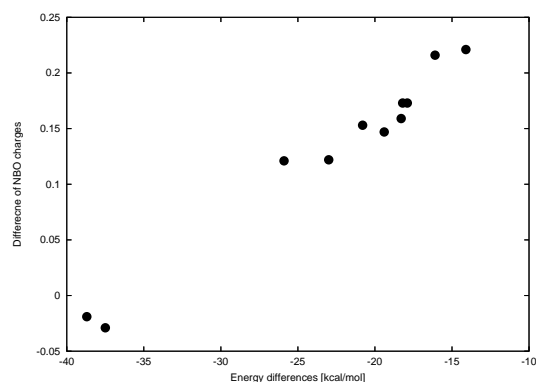
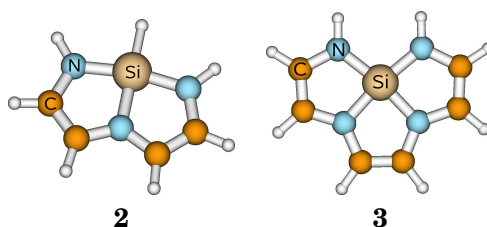


Figure 1

In order to investigate the possible contribution of aromaticity to the stability of PTSi species, calculations for **1a** - **1c** were repeated after saturating the C-C double bond. The energy differences severely increased in favour of the non-planar form, indicating the importance of conjugation in the five-membered ring. NICS1 values were also computed for **1a** - **1m**, again giving good correlation with the energy differences. The NICS1 value of **1i**, **1l** and **1m** was approximately -7, less but comparable to the -10 of pyrrole, a well known aromatic five membered heterocycle (calculated at the same level of theory).

Since the stabilization of the planar form of tetravalent Si over the tetragonal one could not be achieved via electronic effects only, we considered the introduction of steric hindrance in PTSi containing structures. **2** and **3**, the ring-fused derivatives of **1b** both proved to be minima on the potential energy surface.



The kinetic stability of **2** and **3** was also investigated by mapping the reaction route toward dimerisation. Since dimerisation over the Si-N bond is energetically favourable, a suitably high kinetic barrier is an imperative factor in the chemical stability of these compounds. The barrier towards dimerisation of **2** is calculated to be only 6 kcal/mol. This value is however increased by the inclusion of a tBu (steric hindrance) or CHO (electronic stabilization) group on the silicon atom, thus providing feasible targets for synthesis. Inclusion of a CF_3 group resulted in another minimum on the dimerization route possessing two pentavalent silicon atoms.

References

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