# Combined DFT and NBO study on the electronic basis of Si···N-β-donor bond

**Bing Yin · YuanHe Huang · Guo Wang · Yang Wang**

**Abstract** Two groups of isoelectronic molecules with different SiXN (X=C, N, O ) units are analyzed by a combined DFT and NBO study to investigate the electronic basis of Si···N-β-donor bond. The influence of various energy components on the formation of Si···N-β-donor bond is explored. The importance of the electron delocalization from the lone pair of nitrogen atom into the acceptor-orbitals connected with Si atom is elicited by our calculations. The electron delocalization from the lone pair of nitrogen atom into the antibonding orbital of Si-X bond is quite different among the isoelectronic molecules with various types of SiXN units.

**Keywords** Antibonding orbital · Donor-acceptor interaction · DFT · Electron delocalization · NBO · Si···N-β-donor bond

## Introduction

The Si···N-β-donor bond, abbreviated as β-bond here after, is a weak secondary interaction between Si and N atoms in β-position within a SiXN unit (X=C, N, or O atom in this paper) [1]. Structurally, the existence of β-bond is evidenced by that ∠SiXN angle is smaller than the classical tetrahedral angle by ~10º, *i.e.*, about 100º or even smaller [2–12]. For

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the organosilicon compounds, this interaction is also related with α-effect [13–17]. It leads to the enhancement of reactivity and thus plays an important role in the applications, *e.g.*, polymer cross-linkers, surface-modification, and adhesion-mediating agents [13–20]. Several models, such as the dative bond [15], VSEPR concept [21] and Bartell's two bond radii model [22], have been adopted to search for a reasonable explanation, but the electronic basis of β-bond remains a matter of debate [2, 7, 11, 12].

Recent experimental and theoretical studies [2–12, 23–25] gave significant contributions to understanding the nature of β-bond. However, further studies are still necessary. For some aminomethylsilanes and hydroxyaminosilanes, the electron delocalization (ED), especially that from the lone pair (LP) of the N atom into the antibonding orbital at the *anti*-position relative to the N atoms, was proposed as the nature of β-bond [2, 7, 8]. However, β-bond might also arise mainly from the electrostatic and dipole interactions [11, 12].

In fact, the molecules with β-bond cover a wide range including representatives of different types of SiXN units [2, 7, 8, 11, 12]. Previous studies usually focused on the molecules containing a given type of SiXN unit. According to our best knowledge, the simultaneous treatment of molecules with different types of SiXN units, *i.e.*, SiCN SiNN and SiON units, is still infrequent, especially for the theoretical works. Therefore two groups of isoelectronic molecules with different types of SiXN units shown in Fig. 1 are studied here to explore the electronic basis of β-bond.

The molecules **A-C** are simple and elemental models since they exclude the complexity of multiple SiXN units and the back-bonding from substitution to the Si atoms. Therefore, our analysis on these molecules is expected to provide a basic explanation on β-bond. Moreover, it is found that ∠SiXN angle will reduce further when the H
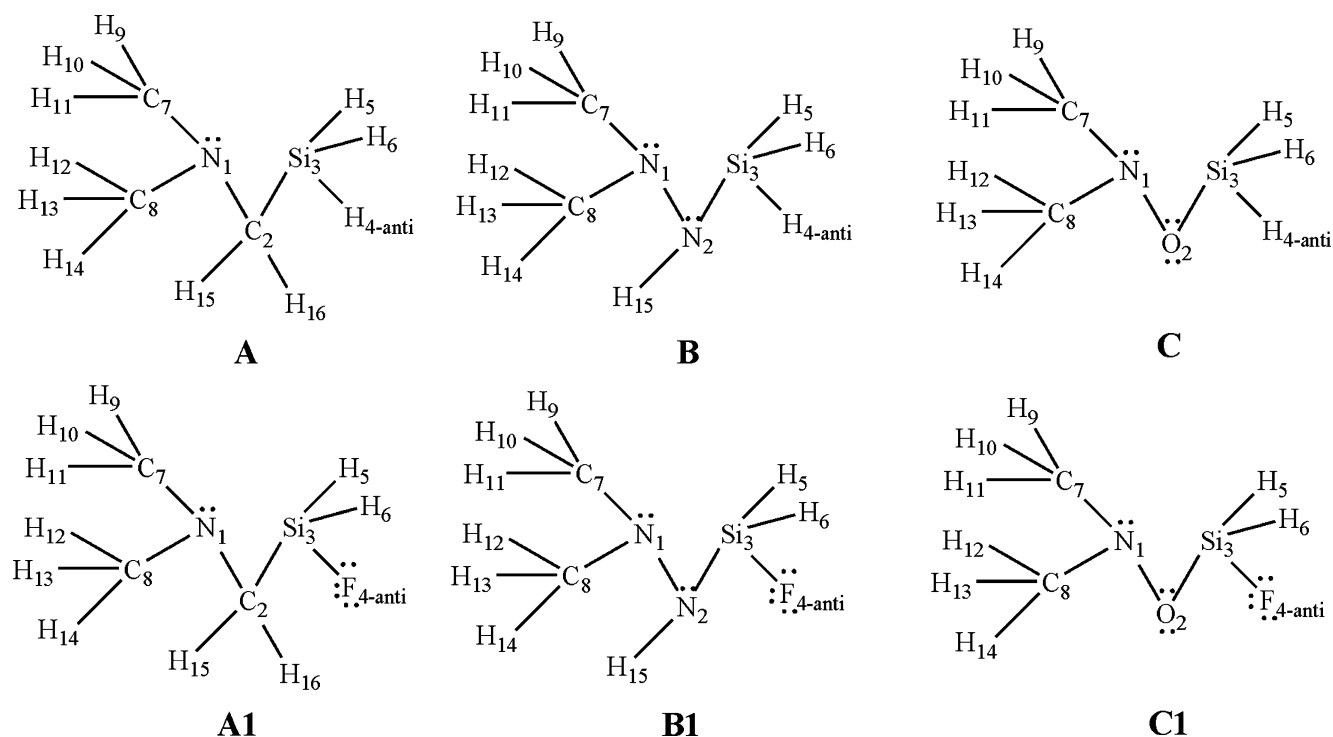
**Fig. 1** Schematic representation of the molecules under study

atom at the *anti*-position (H_anti) relative to N atom is substituted by atoms or groups of higher electronegativity [2, 6, 8]. Hence the molecules **A1**-**C1** are also selected here for further examination.

## Theoretical methods and computational details

Natural bond orbital (NBO) [26–29] theory is used in this study for the analysis of ED and electrostatic interactions. Both the ED and the electrostatic interactions have been proposed as the electronic basis of β-bond [2, 7, 8, 11, 12].

In the scheme of NBO, the ED arises from donor-acceptor interaction in which the electron density is transferred from the donor-orbitals into the acceptor-orbitals [30, 31]. The LP orbitals usually play the role of donor and antibonding orbitals such as σ* orbitals are acceptors [26–28]. The energetic effect of given ED is calculated with the NBO-deletion procedure [28] which is based on the variational method [32, 33]. Since the combined study of density functional theory (DFT) [34, 35] with NBO features certain advantages [27, 36–38], the NBO analysis is performed at the DFT level here.

Besides the energy minima, the structures with a 5 ° increment of ∠SiXN varying from 70 ° to 130 ° are also optimized and analyzed. The optimizations are performed at the MPWPW91 [39, 40] level with 6-311++G(3df,3pd) basis set. The NBO analysis is performed at the MPW1PW91 level [39, 40] with the same basis set. Gaussian 03 [41] and

NBO 5.0 codes [42] are used here. The local-minimum character of optimized structures is confirmed by the frequency analysis [43].

The reliability of selected exchange-correlation functionals is examined by comparing the MPWPW91 structures with those from the experiments and the optimizations at MP2/6-311++G** level.

As shown in Table 1, only the ∠SiON (about 102 °) of **C** attains the structural proof of β-bond and is consistent with the previous result [11], because it is substantially smaller than the classical 109.5 ° of tetrahedral angle. Generally, the differences of the structural parameters with various methods are less than 1.5 ° and 0.01 Å respectively for the bond angles and the bond lengths. For the length of O-N bond, the DFT value is 0.02 Å longer than that of MP2 and the experimental value is just between them. For the Si-H bond lengths, there is a systematic deviation between DFT and MP2 calculations, but quite small (~ 0.015 Å ). Therefore the selected functionals is appropriate to the study here.

## Results and discussions

Analysis on the molecules A-C

*Analysis on various energy components*

Because there are multiple LP and σ* orbitals in these molecules [44] and the small ∠SiXN is the structural

**Table 1** Optimized structural parameters of **A-C** (bond lengths in Å and bond angles in °)

| Molecule | A (SiCN) | | | B (SiNN) | | C (SiON) | | |
|---|---|---|---|---|---|---|---|---|
| Method | MP2 | DFT | GED [a] | MP2 | DFT | MP2 | DFT | XRD [b] |
| $Si_3$-$X_2$ | 1.895 | 1.902 | 1.879(2) | 1.738 | 1.734 | 1.688 | 1.684 | 1.668 |
| $X_2$-$N_1$ | 1.464 | 1.463 | 1.471(3) | 1.420 | 1.422 | 1.458 | 1.481 | 1.471 |
| ∠SiXN | 114.22 | 115.19 | 114.7(3) | 114.46 | 116.41 | 103.48 | 101.78 | 102.63(5) |
| $C_7$-$N_1$ | 1.458 | 1.459 | 1.463(5) | 1.459 | 1.460 | 1.458 | 1.459 | 1.455 |
| $C_8$-$N_1$ | 1.457 | 1.457 | 1.456(5) | 1.459 | 1.460 | 1.458 | 1.459 | 1.455 |
| ∠$X_2N_1C_7$ | 111.13 | 112.37 | 110.9(4) | 110.64 | 111.50 | 105.50 | 105.78 | 105.5(1) |
| ∠$X_2N_1C_8$ | 110.35 | 111.46 | 110.9(5) | 109.41 | 110.35 | 105.50 | 105.78 | 105.5(1) |
| ∠$C_7N_1C_8$ | 109.59 | 110.88 | 111.1(5) | 111.05 | 112.12 | 111.02 | 112.11 | |
| Si-$H_{4\text{-}anti}$ | 1.480 | 1.494 | | 1.478 | 1.493 | 1.475 | 1.492 | |
| Si-$H_5$ | 1.476 | 1.492 | | 1.474 | 1.490 | 1.475 | 1.491 | |
| Si-$H_6$ | 1.478 | 1.493 | | 1.482 | 1.499 | 1.475 | 1.491 | |

[a] from gas-phase electron diffraction shown in ref [2] [b] from X-ray diffraction shown in ref [7]

evidence of β-bond [2–8, 10–12], the orbitals adjacent to Si atom may be of great importance. Therefore ED from certain LP is mainly categorized into two types: ED into the σ* orbitals related to the Si atoms and ED into the other σ*. In the following, certain ED is denoted in the form of "donor-orbitals/acceptor-orbitals". For instance, "LP(N)/ σ* (Si-$H_{anti}$)" means the ED from the lone pair of N atom into the σ* antibonding orbital between Si and $H_{anti}$ atoms. Besides, the Geminal ED [28, 29] may not be ignored since the N-X and X-Si bonds constitute the SiXN units. Another factor, Lewis energy (LE) [45, 46], in which the effect of electrostatic interactions is included, needs to be analyzed too. Based on these considerations, the total energies of molecules **A-C** could be mainly decomposed into the following components: LP(N)/Si-related, LP(N)/other σ*, LP(X)/Si-related, LP(X)/other σ*, Geminal ED and LE. "Si-related" means the sum of all the acceptor-orbitals connected with the Si atom. "Other σ*" is the sum of all the σ* acceptors which are not connected with the Si atom. The ED components are calculated with the NBO-deletion procedure [28, 32, 33]. In this procedure, the off-diagonal element of Fock matrix corresponding to a given ED is deleted and the modified Fock matrix is used to calculate the new energy. The difference between the original and the new energy represents the energetic effect of the deleted ED. As to the LE, it is calculated by deleting all the acceptor orbitals using NOSTAR option in the NBO program [28, 42].

The variations of these energy components with the change of ∠SiXN are shown in Fig. 2. The energies in Fig. 2 are all related to those at ∠SiXN=130 °. The total energy minima are at 115.19 °, 116.41 °, and 101.78 ° respectively for **A**, **B**, and **C**.

From Fig. 2, it is shown that the change tendencies of a given component with the variation of ∠SiXN are similar for **A-C**, though the magnitudes are somewhat different from the different SiXN units. It can be shown by Fig. 2c

that the energies of LP(N)/Si-related decrease with the reducing of ∠SiXN, but the energies of LP(N)/other σ* shown in Fig. 2d increase with the decrease of ∠SiXN, as well as those of LP(X)/Si-related and LP(X)/other σ* (Fig. 2f). For Geminal ED, it is nearly invariant with the change of ∠SiXN except for smaller ∠SiXN (Fig. 2e).

Therefore the LP(N)/Si-related is always favorable to small ∠SiXN. In contrast, the LP(N)/other σ* together with the LP(X)/ Si-related and the LP(X)/other σ* are always unfavorable to small ∠SiXN. The influence of Geminal ED on ∠SiXN is negligible. As shown in Fig. 2b, the LE favors small ∠SiXN when ∠SiXN has larger values, but turns to be disfavoring when ∠SiXN is smaller than certain values.

Although the change tendency of the same components in Fig. 2 is similar with the variations of ∠SiXN for molecules **A-C**, β-bond exists only in **C** molecule. It would be important to further discuss the change details of the components with the variation of ∠SiXN for understanding the formation of the β-bond in these systems. Therefore the contributions of the different components to the variation of energies are explored.

Since small ∠SiXN corresponds to the existence of β-bond [2, 5, 6, 8, 11, 12], the components which favor small ∠SiXN should be the favoring factors of β-bond. Likewise, the components which disfavor small ∠SiXN are the disfavoring factors of β-bond.

From Fig. 2, obviously the LP(N)/Si-related is the favoring factor due to always going down with the decrease of ∠SiXN. The LP(N)/other σ*, the LP(X)/Si-related and the LP(X)/ other σ* are the disfavoring factors, their change direction is just opposite to that of the LP(N)/Si-related. However, the change degree of these factors is quite different for molecules **A-C** with the variation of ∠SiXN. The calculations show that from 115 ° to 100 °, LP(N)/Si-related decreases by about 31 kJ mol$^{-1}$ for **C**, but less than 18 kJ mol$^{-1}$ for **A** and **B**. 115 ° of ∠SiXN is the point corresponding to the minima of total energies for **A** and **B**,

**Fig. 2** Variations of the energies of different components with the changes of ∠SiXN (**a**) total energy (**b**) Lewis energy (**c**) LP(N)/Si-related (**d**) LP(N)/ other σ* (**e**) Geminal ED (**f**) ED from LP(X), the sum of LP(X)/ Si-related and LP(X)/other σ*



(a)

(b)

(c)

(d)

(e)

(f)
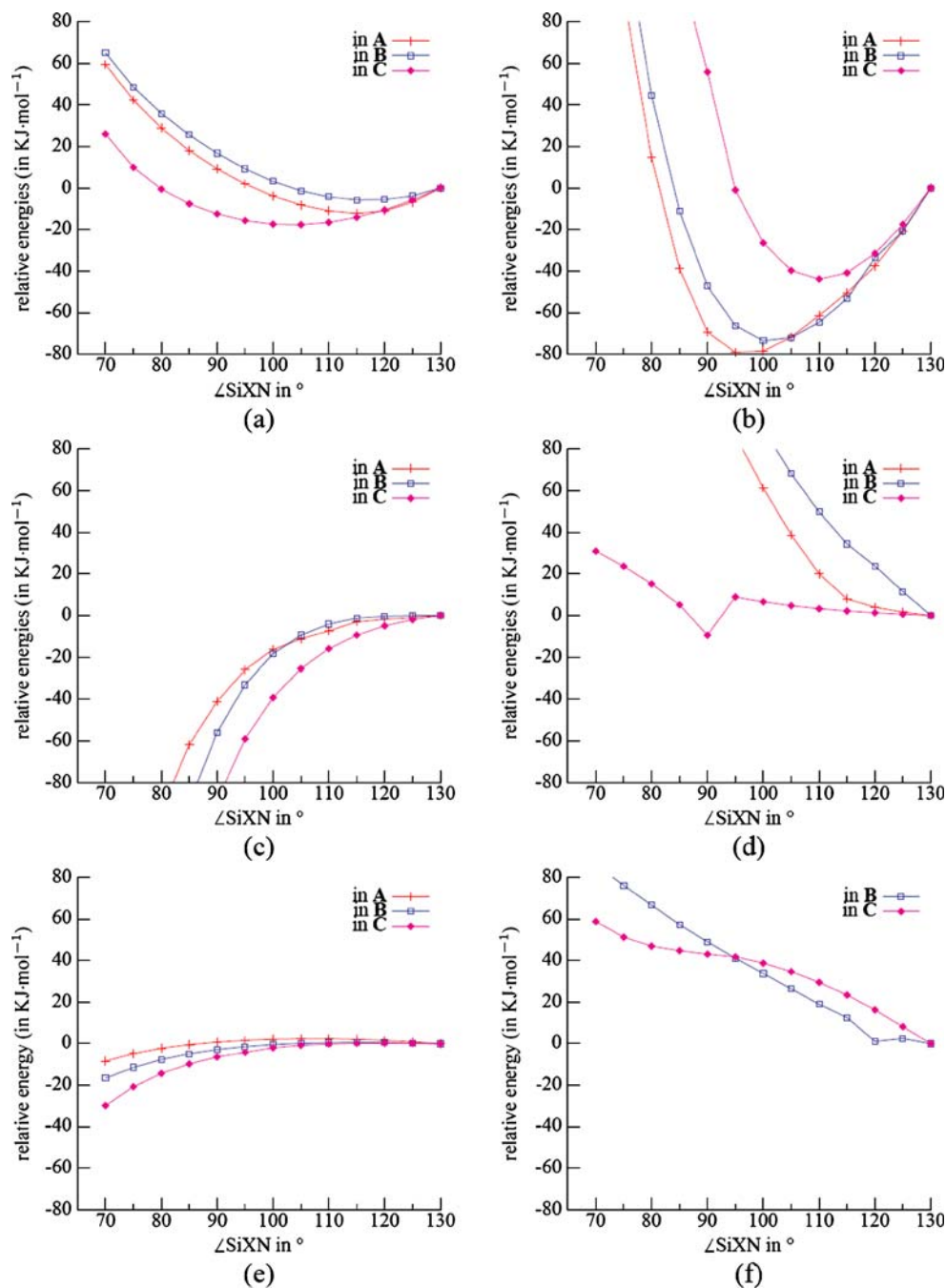
whereas 100 º can be considered to be in the angle range of β-bond. Thus the LP(N)/Si-related is much more favorable to β-bond in **C** than in **A** and **B**.

On the other hand, the LP(N)/other σ* and the ED from LP(X), *i.e.*, the sum of LP(X)/Si-related and LP(X)/ other σ*, increase quickly with the decrease of ∠SiXN, more than 53 kJ mol$^{-1}$ from 115 º to 100 º for **A**, even as high as 77 kJ mol$^{-1}$ for **B**. This indicates that the two disfavoring factors are very strong to suppress the formation of β-bond in **A** and **B**. However the suppression is weaker for **C**, lifting of the two factors is less than 14 kJ mol$^{-1}$ from 115 º to 100 º.

As to the LE, it seems to be favorable to β-bond for **A** and **B**, because the LE falls about 20~28 kJ mol$^{-1}$ from 115 º to 100 º. However, as shown in Fig. 2b, the minimum of LE for **C** is at 110 º of ∠SiON and deviated from the minimum point 102 º of the total energy. In addition, the LE increases quite quickly when ∠SiON is less than 110 º for **C**. Therefore the LE should not be a favorable factor of β-bond for molecule **C**. Figure 2b shows that the curve of LE of **C** is always higher than those of **A** and **B**. This means that the ability of LE to favor small ∠SiXN is not enhanced but weakened from the molecules without β-bond to the molecule with β-bond.

We would like to point that, from 115 º to 100 º of ∠SiXN, the fall magnitudes of the LP(N)/Si-related together with the LE are 41.46 and 37.46 kJ mol$^{-1}$ respectively for molecules **A** and **B**. The increases of those disfavoring factors are 53.32 and 75.87 kJ mol$^{-1}$ respectively. So in the case of molecules **A** and **B**, LP(N)/Si-related cannot counteract the effects of the disfavoring factors and thus β-bond cannot be allowed to exist. While in the case of **C**, from 115 º to 100 º of ∠SiXN, LP(N)/Si-related decreases by 31.08 kJ mol$^{-1}$ and the increase of those disfavoring factors is only 28.40 kJ mol$^{-1}$. That is to say LP(N)/Si-related alone is capable of dominating those β-bond disfavoring factors in molecule **C**, thus β-bond is allowed to exist.

In order to pinpoint the importance of each factor sharply, the reoptimizations of molecule **A-C** with selected factors absent are performed. The reoptimizations are carried out by removing the off-diagonal element of Fock matrix for the given ED with the NBO-deletion procedure. Table 2 lists the results from the reoptimizations. The change of ∠SiXN provides the direct evidence of the functions of various components [47, 48].

With the disfavoring factors absent, the ∠SiXN tends to reduce. For instance, with the absence of LP(N)/other σ* , the ∠SiXN reduces to 103 º, 82 º, and 84 º respectively for **A**, **B**, and **C**. It is demonstrated by Table 2 that the ∠SiXN relaxes to 120 º or larger without the consideration of LP(N)/Si-related. LP(N)/Si-related thus is indeed a favorable factor of β-bond. Therefore the functions of the various factors analyzed above are supported by these reoptimizations.

Besides, it should also be noticed that the factors influencing β-bond are interrelated. The influence would also be changed with the absence of certain factors. For instance, although the reoptimizations based on the LE solely lead to smaller ∠SiXN, the ∠SiXN are still outside the angle range of β-bond and quite larger than the minima in Fig. 2b for **A** and **B** molecules. In the case of **C**, the ∠SiON increases to 109.60 º considering the LE only, it is close to the result in Fig. 2b. The results of reoptimizations show that the LE alone is unable to result in β-bond in these molecules. Moreover, the LP(N)/other σ* goes up much faster in **A** and **B** than in **C** with the decrease of ∠SiXN, but the reoptimized structures show that both **B** and **C** have almost the same ∠SiXN without considering this factor, ∠SiON is even smaller than ∠SiCN. The ∠SiXN angles of reoptimized structures with Geminal ED absent are nearly the same as those before the reoptimization. So the effect of Geminal ED on β-bond is negligible indeed.

One thing worth noting is that, besides NBO-deletion analysis, there is also the structural evidence supporting our results on the variation of ED with ∠SiXN. Both MPWPW91 and MP2 optimizations show that the average length of C-H bonds in **A-C** is shortening when ∠SiXN is reducing. A previous study [49] has pointed out that the ED into σ*(C-H) could lead to the lengthening of C-H bond. Therefore the shortening of C-H bonds in **A-C** implies the weakening of the ED into the σ*(C-H). Since the C-H bonds are not related to the Si atom, this change corresponds to the weakening of LP(N)/other σ* and its energy increasing for small ∠SiXN.

### Analysis on LP(N)/Si-related

The above analysis shows that LP(N)/Si-related is the main factor resulting in β-bond. In order to understand more details, this ED is further decomposed into four components: LP(N)/σ*(Si-H$_{anti}$), LP(N)/σ*(Si-H$_{other}$), LP(N)/σ* (Si-X) and LP(N)/Si-Ryd*. LP(N)/σ*(Si-H$_{other}$) is the sum of the effects of 2 σ* acceptors which are not at the anti-position relative to N atom. H$_{other}$ means the 2 hydrogen atoms which are not at anti-position relative to N atom. LP(N)/Si-Ryd* is the ED from the LP of N atom into the extra-valence orbitals [47, 50] of Si atom.

From Fig. 3 it can be found that the four components all fall monotonously with the decrease of ∠SiXN in **C**. As for **A** and **B**, the change of LP(N)/σ*(Si-X) is not monotonous. At the point of ∠SiXN=100 º, the energies of LP(N)/σ*(Si-X) are even higher than those at 130 º in **A** and **B**.

LP(N)/σ*(Si-H$_{anti}$) has been proposed as the electronic basis of β-bond [2, 7, 8]. This ED is indeed a favoring factor of β-bond as shown by that its energy continues decreasing with the decrease of ∠SiXN (Fig. 3a). However, for the molecules with different types of SiXN units, the contributions of LP(N)/σ*(Si-H$_{anti}$) are quite same to each other. For example, they decrease by 9.37, 9.68, 10.29 kJ mol$^{-1}$ for **A-C** respectively from 115 º to 100 º of ∠SiXN. The curves of LP(N)/σ*(Si-H$_{anti}$) in Fig. 3a are very close to each other for the molecules with and without

**Table 2** ∠SiXN (in º) of the reoptimized structures with selected factors absent[a]

| Absent factors | ∠SiCN (A) | ∠SiNN (B) | ∠SiON (C) |
|---|---|---|---|
| Except LE | 107.30 (-7.89) | 111.63 (-4.78) | 109.60 (8.12) |
| LP(N)/Si-related | 119.79 (4.60) | 129.77 (13.36) | 126.38 (24.60) |
| LP(N)/other σ* | 103.37 (-11.82) | 82.17 (-34.24) | 83.69 (-18.09) |
| Geminal ED | 115.03 (-0.16) | 116.72 (0.31) | 101.31 (-0.47) |
| ED from LP(X) | | 104.37 (-12.04) | 80.03 (-21.75) |

[a] The relative change values of ∠SiXN are shown in parenthesis for the reoptimizations

**Fig. 3** Variations of the energies of components of the LP(N)/Si-related with the changes of ∠SiXN (**a**) LP(N)/σ*(Si-H$_{anti}$) (**b**) LP(N)/σ* (Si-H$_{other}$) (**c**) LP(N)/ σ*(Si-X) (**d**) LP(N)/Si-Ryd*
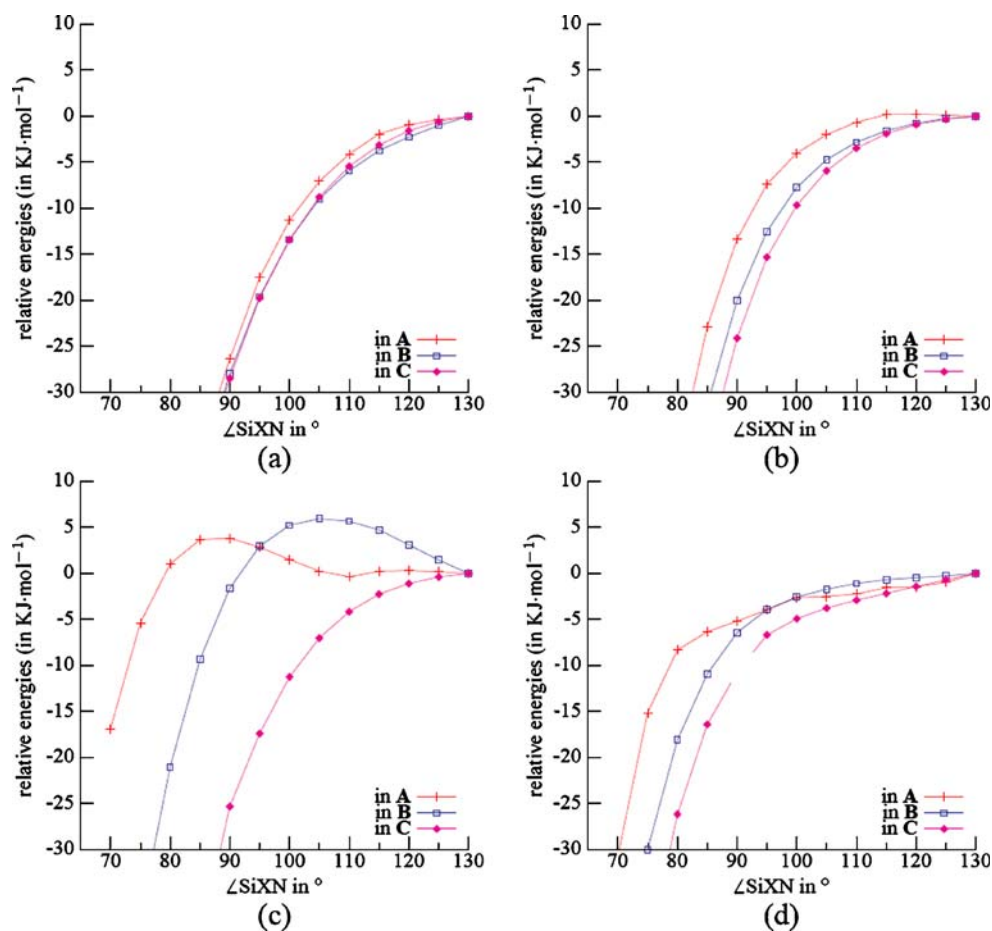
β-bond. Therefore LP(N)/σ*(Si-H$_{anti}$) should not be the key factor resulting in the difference for the formation of β-bond for the molecules with different types of SiXN units.

LP(N)/σ*(Si-H$_{other}$) and LP(N)/Si-Ryd* work in a way similar to LP(N)/σ*(Si-H$_{anti}$). The tendencies of their variations with the changes of ∠SiXN are the same and the change curves of Fig. 3c and d are close to each other for the different molecules. So these two factors are also not responsible for the difference of β-bond formation in **A-C**. It should be stressed that the effect of σ*(Si-H$_{anti}$) is even larger than the sum of two σ*(Si-H$_{other}$). This corresponds to the conformational sensitivity of substitutions on Si atom as shown in previous studies [2, 8].

Figure 3c demonstrates that the variations of LP(N)/σ* (Si-X) in **A-C** are distinctly different from each other. From 130 º to 100 º, the contribution of LP(N)/σ*(Si-C) to the energy change of **A** is small, only 1.51 kJ mol$^{-1}$. For **B**, its LP(N)/σ*(Si-N) increases by 5.26 kJ mol$^{-1}$. That is to say, the LP(N)/σ*(Si-N) is a disfavoring factor in **B**. However in the case of **C**, the LP(N)/σ*(Si-O) becomes a factor favorable to β-bond since its energy is always decreasing with the reducing of ∠SiON. Moreover, its contribution is even comparable to that of the LP(N)/σ*(Si-H$_{anti}$). For

example, the LP(N)/σ*(Si-O) contributes to energy lowering of **C** by 8.98 kJ mol$^{-1}$ while the corresponding value of LP(N)/σ*(Si-H$_{anti}$) is 10.29 kJ mol$^{-1}$ from 115 º to 100 º. Therefore the ED from the lone pair of N atom into the antibonding orbital of Si-X bond is the main reason causing the differences for the formation of β-bond among the isoelectronic molecules **A-C**. Reoptimizations of **C** with the LP(N)/σ*(Si-O) excluded also supports this conclusion, since the reoptimized ∠SiON increases by 8.9 º, but the corresponding angle changes of **A** and **B** are less than 2.8 º.

The change of the Si-X bond lengths and the populations on the antibonding orbitals is shown in Fig. 4. For the Si-N and Si-O bonds, their lengths and antibonding orbital populations almost continue increasing as ∠SiXN is reducing. This result implies that the strength of these two bonds is weakening for small ∠SiXN. Moreover, the change for the Si-O bond is larger than that for the Si-N bond. In other words, the molecules with β-bond possess a weakened Si-X bond. Therefore the reactions are easy to take place [14, 18, 51], especially for the substitutions of Si atom [6]. The change of the Si-C bond with ∠SiCN is not monotonic, the length and antibonding orbital populations of the Si-C bond decrease when ∠SiCN varies from 110 º to 90 º.

**Fig. 4** Change of the lengths and the populations on the anti-bonding orbitals with ∠SiXN for the Si-X bonds (**a**) Bond lengths (**b**) Antibonding orbital populations
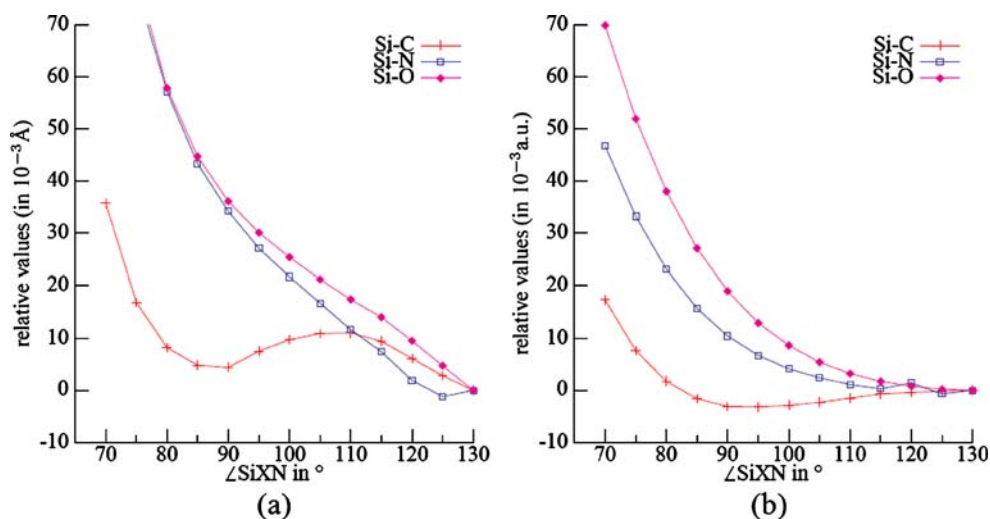
Discussions on the molecules A1-C1

The obtained ∠SiXN of **A1** and **C1** are 101.23 ° and 86.64 ° respectively by DFT optimizations. We found two minima 107.56 ° and 119.18 ° for **B1** using the same DFT method. However, at MP2/6-311++G** level, only one minimum with ∠SiXN of 107.58 ° was located and thus only the structure with ∠SiNN of 107.56 ° is considered for **B1**.

The ∠SiXN in the minima of **A1-C1** are reduced by at least 9 ° compared with those in **A-C**. Therefore further reducing of the ∠SiXN angle takes place when the $H_{anti}$ atom is substituted by the strong electronegative fluorine atom (denoted as $F_{anti}$). Since ∠SiCN of **A1** is 101.23 °, **A1** can be considered becoming a molecule with β-bond. ∠SiNN of **B1** also reduces to 107.56 °, though it is still outside the angle range of β-bond.

In order to know more details, the changes of the energy components analyzed above are also calculated for **A1** and **B1** with the variation of ∠SiXN. The energy changes are similar to those in **A** and **B**. This indicates that the influence on the β-bond is similar to the case in **A** and **B** for the same energy components in **A1** and **B1**. However, there is not the lone pair of fluorine $LP(F_{anti})$ in **A** and **B** molecules. Related to the values at ∠SiXN=130 °, the calculations show that electron delocalization from the lone pair of fluorine, *i.e.*, ED from $LP(F_{anti})$, falls by 7.7 kJ mol$^{-1}$ in **A1**, but increases by 7.7 kJ mol$^{-1}$ in **B1** at 100 °of ∠SiXN. The different behavior of the ED from $LP(F_{anti})$ may be one of the factors resulting in that the ∠SCN is smaller than the ∠SiNN after the substitution of $F_{anti}$.

An explanation from quantum superposition

Quantum superposition [29, 52] shows that the energy lowering of certain donor-acceptor interaction depends mainly on the magnitude of the interaction matrix element between the two donor and acceptor orbitals [52]. In NBO

theory, this matrix element is approximately proportional to the overlap of the corresponding orbitals [29, 50, 53, 54].

As the ∠SiXN is reducing, the N···Si distance is shortening and thus the overlap between the LP(N) and the acceptor-orbitals related to Si atom is increasing. This is why the LP(N)/Si-related is always favoring small ∠SiXN. Since the Si-related acceptors compete with the other σ* orbitals to get electrons from the LP(N), it is not surprising that the LP(N)/other σ* functions in the opposite direction of the LP(N)/Si-related. As shown in Fig. 4, smaller ∠SiXN leads to longer Si-X bonds for **B** and **C** molecules, therefore the overlap between the LP(X) and the Si-related acceptor orbitals is weakened at small ∠SiNN and ∠SiON, the LP(X)/Si-related is thus against small ∠SiXN. In NBO theory, bonding σ and antibonding σ* orbitals between *a* and *b* atoms are expressed as the linear combination of hybrid orbitals of these two atoms [26, 55]:

$$\sigma(a-b) = c_a h_a + c_b h_b \qquad (1)$$

$$\sigma^*(a-b) = c_b h_a - c_a h_b \qquad (2)$$

where $h_a$ and $h_b$ are the hybrid orbitals of *a* and *b* atoms, $c_a$ and $c_b$ are the coefficients of linear combination.

Figure 5 shows the relationship of position between LP (N) and σ*(Si-H,X). The overlap between the LP(N) and σ*(Si-H) consists of two components: one is the positive overlap between the LP(N) and the hybrid orbital of Si atom $h_{Si}$; the other is the minus overlap between the LP(N) and the 1s orbital of H atom $h_H$. Hence, the total overlap is determined by the difference between their magnitudes of absolute values [50]. The calculations show that the distance between $H_{anti}$ and N atoms is about 0.6∼0.8 Å longer than that between the N and the two $H_{other}$ atoms. That is to say, the absolute value of minus part $(-h_H)$ of the overlap of the $LP(N)/\sigma^*(Si-H_{anti})$ is smaller than those of the $LP(N)/\sigma^*(Si-H_{other})$. Moreover, it is found that the

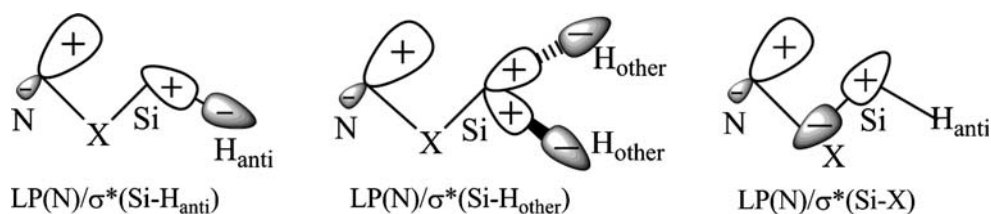**Fig. 5** Schematic representation of relative positions between LP(N) and σ*(Si-H,X) (antibonding orbital shown as linear combination of hybrid orbital, "+" and "-" symbol represent orbital phase)

positive overlap of the LP(N)/σ*(Si-H$_{anti}$) is larger than that of the LP(N)/σ*(Si-H$_{other}$). Therefore the overlap of LP(N)/σ*(Si-H$_{anti}$) is larger than that of the LP(N)/σ*(Si-H$_{other}$). In fact, our calculations confirm that the interaction matrix element of the LP(N)/σ*(Si-H$_{anti}$) is larger than that of the LP(N)/σ*(Si-H$_{other}$). At the minima of **A-C**, the magnitude of the interaction matrix element of the LP(N)/σ*(Si-H$_{anti}$) is larger than that of the LP(N)/σ*(Si-H$_{other}$) by 0.0081, 0.0111 and 0.0141 a.u. respectively. The σ*(Si-H$_{anti}$) thus is the strongest acceptor among the three σ*(Si-H) orbitals.

Similar to the σ*(Si-H), the overlap between the LP(N) and the σ*(Si-X) is also determined by the difference between the two components with opposite contributions. Higher electronegativity of X will lead to σ*(Si-X) of higher polarization toward Si atom [26]. The polarization is obtained as the square of the coefficient of $h_{Si}$ in Eq. (2). This gives rise to the increase of the overlap between the LP(N) and the $h_{Si}$ [26, 50]. As predicted by Bent's rule [56], the increased electronegativity of X atom may also reduce the p-character of $h_x$, i.e., reduce the contribution of p-type atomic orbitals to the hybrid orbital of X atoms. This effect will increase the overlap between the LP(N) and the $h_X$ due to the reduced diffuseness of the hybrid orbital [50].

As shown in Table 3, the calculated polarization and p-character are nearly invariant from 115 ° to 110 ° of ∠SiXN. From **A** to **B**, the polarization of σ*(Si-X) toward Si atom increases from ~70% to~80%, which is in accordance with the order of electronegativity of X (C < N < O). Simultaneously, the p-character of $h_X$ decreases from ~72% to ~60%. These indicate that the overlap between the LP(N) and the $h_{Si}$ increase from **A** to

**B**, as well as that between the LP(N) and the $h_X$. It is shown that the polarization of σ*(Si-X) also increases by ~5% from **B** to **C**. This enhanced polarization indicates increased overlaps between the LP(N) and the $h_{Si}$ of σ*(Si-O) with the increase of electronegativity of O atom. However, the calculated p-characters of $h_X$ of molecules **B** and **C** are all around 61%, i.e., the diffuseness degree of $h_X$ is almost the same for **B** and **C**. Therefore, compared with **A** and **B**, **C** has a larger difference between the positive and minus overlaps for the LP(N) and σ*(Si-X). These finally lead to increased total overlap of the LP(N)/σ*(Si-X) in the case of **C**. The different overlap between LP(N) and σ*(Si-X) causes different changes of LP(N)/σ*(Si-X) with variation of ∠SiXN. This may be the important factor causing the differences of β-bond formation among the isoelectronic molecules with different SiXN units.

It has been pointed out that the orientation of LP(N) may be an important factor influencing its donor ability [2]. From the optimized equilibrium structures of **A-C**, the LP (N) of molecule **C** lies within the SiXN plane due to the near-zero torsion angle (<0.04º) of LP(N)-N-O-Si, but the LP(N) of **A** and **B** deviate from the SiXN plane by about 50 ºand 19.0 °, respectively. It seems that smaller deviation of LP(N) from the SiXN plane may be favorable to β-bond. From a view of quantum superposition, the orientation of LP(N) will influence its overlap with a given acceptor orbital and does have effect on the related ED. The energy changes of the ED from LP(N) discussed above should partially reflect the influence of the orientation of LP(N).

### Conclusions

Combined DFT and NBO study is performed on the two groups of the isoelectronic molecules with different types of SXN units. LP(N)/Si-related, the ED from the lone pair of nitrogen atom into acceptor orbitals connected with Si atom, is the main factor favorable to β-bond. As in the case of molecule **C**, β-bond is allowed to exist because the LP(N)/Si-related is capable of dominating those unfavorable factors. Lewis energy alone is shown unable to result in β-bond and thus electrostatic interaction, included in the Lewis energy, is not the decisive factor for the formation of β-bond.

**Table 3** Polarization of the σ*(Si-X) toward Si atom and the p-character of the $h_x$

| ∠SiXN | Polarization toward Si (%) | | | p-character of h$_x$ (%) | | |
|---|---|---|---|---|---|---|
| | A | B | C | A | B | C |
| 115 ° | 69.62 | 79.90 | 84.10 | 71.52 | 58.89 | 60.71 |
| 110 ° | 69.61 | 79.84 | 84.10 | 72.02 | 60.23 | 61.56 |
| 105 ° | 69.71 | 79.82 | 84.15 | 72.34 | 61.51 | 62.27 |
| 100 ° | 69.89 | 79.85 | 84.24 | 72.56 | 62.61 | 62.28 |

Analysis on the components of LP(N)/Si-related demonstrates that the changes of the electron delocalization from the LP of N atom into the antibonding orbital of Si-X bond are distinctly different from each other for the isoelectronic molecules with different types of SiXN units. Therefore it may be the key factor causing the differences for the formation of β-bond among the isoelectronic molecules. LP (N)/σ*(Si-H$_{anti}$), which functions nearly indistinguishably in molecules with various SiXN units, should not be the key factor resulting in the difference. Compared with the antibonding orbitals of the other two Si-H bonds, our calculations show that σ*(Si-H$_{anti}$) is the strongest acceptor-orbital among the three antibonding orbitals.

It is shown that the LP(N) of molecule **C** lies within the SiXN plane, but those of A and B deviate quite larger from the plane. Hence smaller deviation of LP(N) from the SiXN plane may be favorable to β-bond.

The Si-X bonds in **B** and **C** is weakening as ∠SiXN is reducing due to the increasing of its bond lengths and populations on the antibonding orbital. The weakened Si-X bond resulting from small ∠SiXN may enhance the reactivity of molecules containing β-bond, especially for the substitution reactions at Si atom.

Substitution of H$_{anti}$ by F atom will lead to further reducing of the ∠SiXN. The different behavior of the ED from LP(F$_{anti}$) may be one of the factors resulting in β-bond.

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