carried out. Details on the design and performance of this home-made IR cell are given elsewhere.[15] For better thermal contact between the zeolite wafer and the cooled environment, helium (about 0.5 Torr) was admitted into the sample compartment before the background spectrum was recorded at 77 K (liquid nitrogen). Then CO was dosed to an equilibrium pressure of about 0.8 Torr, and IR spectra were measured at 77 K and on gradual heating of the IR cell after evaporation of liquid nitrogen. Reversibility of the IR spectra was checked by cooling again after the spectrum at 303 K was taken, thus proving that the observed spectral changes are due solely to temperature variation and not to any (unexpected) alteration of the system upon heating. The temperature was measured by means of a platinum resistance thermometer; the accuracy was about ±5 K. Transmission IR spectra were recorded at a resolution of 3 cm^{-1} with a Bruker IFS66 FTIR spectrometer. The spectrum of zeolite taken before dosage with CO was used as a background; this background spectrum was subtracted from all spectra shown in this work.

Received: May 6, 1998 [Z11825IE]
German version: *Angew. Chem.* **1998**, *110*, 3350–3353

Keywords: adsorption · carbon monoxide · heterogeneous catalysis · IR spectroscopy · zeolites

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Long-Range N →Si Interactions in Organosilicon Compounds with Hepta- and Octacoordinate Silicon Centers

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Dedicated to Professor Corriu

Si centers in organosilicon compounds exhibit coordination numbers between 1 and 10,[1] and the resulting distances vary over wide ranges as exemplified by the interaction N →Si in 1-amino-8-silylnaphthalene derivatives[2, 3] (Figure 1). The Cambridge Structural Database contains a total of 574 entries for d_{Si-N} distances greater than 200 pm (Figure 1 a). The range of shorter interactions are assigned to so-called "SiN single bonds" such as in sitrol (Figure 1 b). The compounds with SiN distances between 220 and 260 pm (Figure 1 c and d)[3c,d] have repeatedly been defined as intramolecular donor–acceptor complexes. What type of interaction is, however, represented by the numerous distances Si···N exceeding 275 pm? Two selected structures with Si coordination numbers of 7[4] and 8[5]

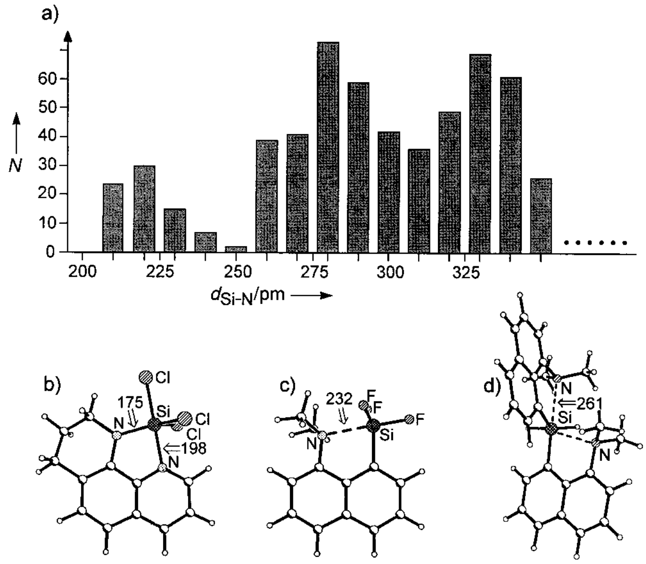

Figure 1. Differences in various Si–N bond lengths: a) histogram for the range between 200 and 350 pm, as revealed by a search in the Cambridge Structural Database, in which *N* is the number of hits within 10 pm ranges, and selected examples of Si–N interactions in 1-amino-8-silylnaphthalene derivatives (b, c), in which N···Si distances longer than 275 pm are also observed (d).

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[**] Molecular Interactions in Crystals, Part 145. This project was supported by the Hoechst AG, the Deutschen Forschungsgemeinschaft, the State of Hesse, the Fonds der Chemischen Industrie, and the Höchstleistungs-Rechenzentrum Stuttgart. Part 144: H. Bock, N. Nagel, *Z. Naturforsch. B.* **1998**, *53*, 805.

will be discussed here in detail, based on density functional theory (DFT) calculations.[6]

Tris[(2-dimethylaminomethyl)phenyl]silane, prepared by reaction of trichlorosilane with three equivalents of [(2-dimethylaminomethyl)phenyl]lithium, contains a formally sevenfold coordinated silicon center. Its structure determination[4] yields intramolecular Si–N distances of between 298.1(6) and 304.3(6) pm for both independent molecules in the crystal (Figure 2a). The energy of the Si–N interactions can be approximated as follows:[6] The vector of each nitrogen electron pair, which deviates by 23° from its idealized SiN bond axis (Figure 2a), is twisted perpendicular to this axis under continuous structure control to avoid additional severe overlap of the substituents within the molecule (Figure 2b). The energy difference due to the inevitably varied van der Waals contacts in the periphery of the molecule is calculated after removal of the central SiH group accompanied by H saturation of the ruptured bond of each phenyl substituent (Figures 2c and d) to be about 60 kJ mol^{-1}. The sum of all DFT-calculated energy contributions for a rotation of the three N vectors out of their SiN axis positions between the Si centers that are at first seven- and finally four-coordinate amounts to $\Delta\Delta H_f(\mathrm{Si-N}) = 42$ kJ mol^{-1} or to about 14 kJ mol^{-1} for a cooperation-free SiN interaction over a distance of about 300 pm (Figure 2).

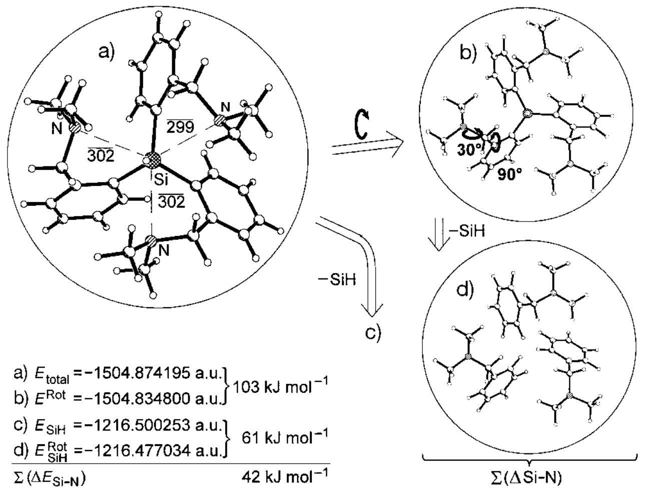


Figure 2. Density functional theory calculated[6] total energies for tris[(2-dimethylamino)methylphenyl]silane[4] a) based on its structural parameters, b) after twisting its three $H_4C_6-CH_2$ bonds by $\omega_1 = 90°$ as well as the H_2C-N bond by $\omega_2 = 30°$, and c) and d) after removal of the central SiH_2 subunit from the structures a) and b), respectively, accompanied by H saturation of the ruptured bonds of the phenyl substituents (see text).

Bis [2,6-bis(dimethylaminomethyl)phenyl]silane, the second selected "hypercoordinate" organosilicon compound, is prepared by treating 2,6-bis(dimethylaminomethyl)phenylsilane with an equimolar amount of 2,6-bis(dimethylaminomethyl)phenyllithium. Its structure determination[5] proves a formally eight-coordinate silicon center and exhibits intramolecular distances of 289.5(5) and 311.7(6) pm for the two different N →Si interactions between the two pairs of amino-N centers and the Si centers in the differently overcrowded halves (Figure 3a). The two types of N →Si interactions, which vary by 21 pm in length (Figure 3a) are approximated analogously to the ones in the seven-coordinate compound, but separately: altogether four rotations around the $H_3C_6-CH_2$ and $H_2C-N(CH_3)_2$ bonds (Figure 2b and c) turn the nitrogen electron pairs of the $(H_3C)_2N$ substituents perpendicular to the structurally characterized SiN connecting axes. The resulting van der Waals perturbations in the molecular periphery are approximated by two additional DFT calculations[6] after removal of the central SiH_2 group and H saturation of the phenyl substituents (Figures 2d and e). The energy contributions calculated for the interactions over the shorter and the longer SiN distances of 10 + 4 = 14 kJ mol^{-1} (limit of deviation ± 2 kJ mol^{-1} [6]) differ predominantly because of the individual van der Waals wrapping of the two molecular halves.

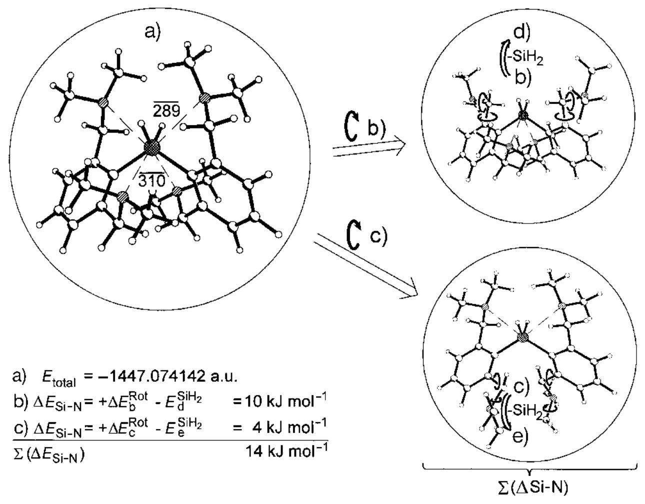
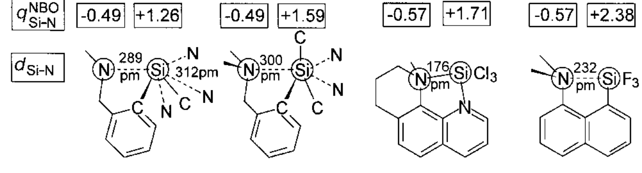


Figure 3. Density functional theory calculated[6] total energies for bis[2,6-bis(dimethylamino)methylphenyl]silane[5] a) based on its structural parameters, b) after twisting of the 289 pm distant or c) the 310 pm distant $(H_3C)_2N$ substituent groups by angles $\omega(H_3C_6-CH_2) = 120°$ as well as $\omega(H_2C-N(CH_3)_2) = 30°$, and d,e) after removal of the central SiH_2 unit accompanied by H saturation of the phenyl substituents starting from the structures in (b) and (c), respectively (see text).

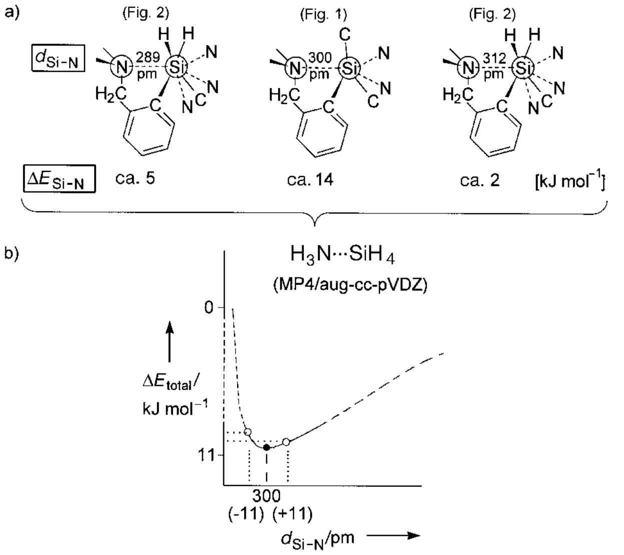
Altogether three different long-range N →Si interactions in two organosilicon molecules containing seven- or eight-coordinate Si centers have been approximated by density functional theory calculations [6] (Schemes 1 and 2). The DFT charge densities q^{NBO}_{Si-N} resulting from "Natural Bond Orbital" analysis are complemented by those for 1-dimethylamino-8-trichlorosilylnaphthalene (sitrol, Figure 1b) and -trifluorosilylnaphthalene (Scheme 1). As can be seen from the data, the calculated DFT/NBO charge densities do not correlate with the experimental bond distances d_{Si-N}. Details such as the



Scheme 1. DFT/NBO charge densities for N →Si interactions at distances of 176 and 300 pm in amino-organosilyl compounds with Si coordination numbers between 5 and 8.

increase in positive charge at the Si center especially on substitution of F for Cl (Figure 1b and c) can be rationalized by the sequence of effective nuclear charges: Si < Cl < N < F. In the aminosilyl compounds with higher coordination numbers for Si (Figures 2 and 3), the charge density at the Si centers is lowered slightly as the number of SiN interactions increase, whereas that of the N centers remains constant.

The energy differences $\Delta E_{\text{Si–N}}$ estimated by DFT calculations (Figures 2 and 3) also cannot be correlated (directly) with the bond lengths $d_{\text{Si–N}}$ (Scheme 2a). To test nonlinear correlation and also to further support the relatively small DFT energy differences $\Delta E_{\text{Si–N}}$ (Scheme 2a), correlated calculations with large double-zeta basis sets at MP2 as well as MP4 levels have been performed for the simplest model adduct $H_3N \rightarrow SiH_4$.[7] The resulting geometry-optimized potential curve shows a minimum of $-11\,\text{kJ}\,\text{mol}^{-1}$ at 300 pm (Scheme 2b), which corresponds to the $\Delta E_{\text{Si–N}} \approx 14\,\text{kJ}\,\text{mol}^{-1}$ contribution estimated for the N →Si interaction at a distance of 300 pm (Scheme 2a). Remarkably, both the higher ($\Delta E_{\text{Si–N}} \approx 5\,\text{kJ}\,\text{mol}^{-1}$ for $d_{\text{Si–N}} = 289$ pm) as well as the lower value ($\Delta E_{\text{Si–N}} \approx 5\,\text{kJ}\,\text{mol}^{-1}$ for $d_{\text{Si–N}} = 312$ pm) follow the prediction of the potential curve: the first is shifted by 11 pm from the minimum towards the steeper slope (→repulsive interaction) and the other 11 pm towards the flatter part (→dissociative interaction) of the potential curve. The rather small DFT energy differences (estimated deviation limit $\pm 2\,\text{kJ}\,\text{mol}^{-1}$)[6] are, therefore, convincingly confirmed by the nonlinear correlation (Scheme 2b).



Scheme 2. Energies of N →Si interactions: a) DFT-estimated contributions based on the crystal structures of the amino.organosilyl compounds investigated with seven- and eight-coordinate Si centers; b) total energy potential curve for the model adduct $H_3N \rightarrow SiH_4$, calculated with basis sets aug-cc-pVDZ using MP2 correlation for the geometry optimization and MP4 correlation for all single point calculations.[7]

The following comments on SiN bond lengths, discussed over a range of $312 - 176 = 126$ pm (!), are based on additional assumptions: The shortest bond length of 176 pm in the trichlorosilyl compound sitrol (Figure 1b) might be favored for steric reasons by the undulated perhydropyridine ring, whereas for the longest bond lengths between 289 and 312 pm the minimum on the distance-dependent potential curve (Scheme 2b) can explain the DFT-calculated results for the experimentally determined structures. Again, however, we draw attention to the spatial overcrowding in the hypercoordinate aminosilyl compounds investigated (Figures 2 and 3), which causes numerous van der Waals contacts in the molecular periphery that are presumably bonding because of the considerable positive charge at their Si centers (Scheme 1). For a tentative answer concerning the possible origin of bonding in long range N ··· Si interactions, the pure electrostatic attraction between charges q_{Si} of $+1.6$ and q_{N} of -0.5 at 300 pm distance has been estimated to be about $60\,\text{kJ}\,\text{mol}^{-1}$. Accordingly, a proposal of Coulomb-dominated donor–acceptor bonding is forwarded for these special hypercoordinate N ··· Si compounds.

In conclusion the importance of long-range interactions for the chemist is emphasized—from the crystal growth[10, 11] to protein structures.[12] Therefore, an extension of the DFT calculations presented to other systems and especially those with Si ··· O interactions, which differ even more in their effective nuclear charges, is envisaged.

Received: February 13, 1998
Supplemented version: May 18, 1998 [Z11477IE]
German version: *Angew. Chem.* **1998**, *110*, 3305–3307

Keywords: density functional calculations • donor–acceptor systems • hypercoordinate compounds • silicon

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Pople, *J. Chem. Phys.* **1972**, *56*, 2257; M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163) were carried out on the super-computer NEC-SX4 of the Höchstleistungs-Rechenzentrum Stuttgart. The starting point was the structure coordinates of the two compounds (Figure 1a and 2a), in which the vectors of the electron pairs on N were turned perpendicular to the connecting axes SiN while controlling the interatomic distances on-line to minimize additional structural changes (Figures 1b and 2b, c). Removal of the molecular Si centers (SiH or SiH_2) by H saturation of the ruptured bonds of the substituent groups (Figures 1c, d and 2d, e) allows an estimate of the van der Waals energy changes in the periphery of the molecule. After subtraction of the total energy from these estimations (Figures 1a and 2a), approximate sums of the energy contributions due to the long-range SiN interactions result. The accuracy of the B3LYP procedure has been statistically evaluated for relative energies to be about 0.4 kcal mol^{-1} (J. B. Foresmanm, A. Frisch in "Exploring Chemistry with Electronic Structure Methods", 2nd ed., GAUSSIAN Inc., Pittsburg, **1996**), and, therefore, deviations of only 1–2 kJ mol^{-1} are assumed for the basis sets used. In addition, substantial changes in the Si tetahedral geometry due to $N \rightarrow Si$ hyperconjugation can be excluded by comparison with the average bond angle $\varphi(CSiC) = 111°$ in triphenylsilane (J. Allemand, R. Gerdi, *Cryst. Struct. Commun.* **1979**, *8*, 927): both the smaller average angle of 108° in the compound with the seven-coordinate Si center (Figure 2) as well as the larger one of 113° for eightfold coordination (Figure 3) can be straightforwardly rationalized by the different central SiH or SiH_2 units and the phenyl group substituents of considerably different bulk.

[7] The total energy potential curve for the model adduct chosen, H_3NA, has been calculated using fourth-order Møller-Plesset perturbation theory (MP4) and a correlation consistent basis set with polarized valence "double-zeta" functions(aug-cc-pVDZ) (D. E. Woon, T. H. Dunning, Jr., *J. Chem. Phys.* **1993**, *98*, 1358; R. A. Kendall, T. H. Dunning Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796). The same basis set also was employed in the geometry optimization at the MP2 level.

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Synthesis of Immobilized CMP-Sialic Acids and Their Enzymatic Transfer with Sialyltransferase[**]

Yasuhiro Kajihara,[*] Takashi Ebata, and Hisashi Kodama

The enzymatic synthesis of oligosaccharides and their analogues with glycosyltransferases (GTases) has progressed remarkably as a result of the ability to synthesize the donor substrates.[1] Sialyltransferase (STase)[2] and fucosyltransferase[3] reactions have also been used to study the structure and function of oligosaccharides on glycoproteins and on cell surfaces by use of modified sugar nucleotides. We have developed a concise synthetic method for the preparation of CMP-sialic acid (CMP-*N*-acetylneuraminic acid, CMP-NeuAc; CMP = cytidinmonophosphate) and its analogues.[4] Since then we have begun investigating possible applications of STase reactions with use of synthetic CMP-NeuAc analogues (Figure 1).

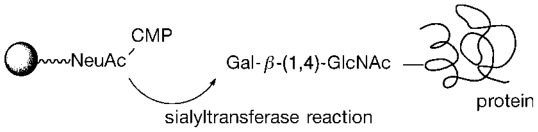

Figure 1. Schematic representation of the novel immobilization method for glycoproteins.

Many enzymes and lectins are glycoproteins containing N- or O-linked oligosaccharides. When these proteins have several oligosaccharides on their surfaces, this layer of oligosaccharides exhibits dynamic fluctuation.[5] Therefore, increasing the number of oligosaccharide chains also increases the surface area covered. With most immobilization methods[6] used for such glycoproteins, this carbohydrate layer hinders the approach to the amino or carboxyl groups on the surface of the protein. Unfortunately, if the reagent attaches to amino acids located close to the catalytic site, the immobilized enzyme may lose its activity. Therefore, we wanted to synthesize a CMP-NeuAc derivative in which the 9''-position is attached to the solid phase, and examine its sialyltransfer ability as part of a novel immobilization procedure. The nonreducing end of oligosaccharides are frequently galactosides which serve as acceptors in STase

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[**] We are grateful to Dr. James C. Paulson (Cytel corporation) for a generous gift of α-(2→3)-sialyltransferase. We thank Dr. Hajime Matsushita and Dr. Koshi Koseki (Life Science Research Laboratory, Japan Tobacco Inc.) for helpful discussions and encouragement. We also thank Mr.Masayosi Kusama for the mass spectroscopic analyses (Japan Tobacco Inc.).

1433-7851/98/3722-3166 $ 17.50+.50/0