ENHANCED LONG-RANGE Si⋯N INTERACTIONS IN ORGANOSILICON CATIONS. A THEORETICAL STUDY[+]

Zeněk HAVLAS[a],* and Hans BOCK[b]

[a] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic,*
   and Center for Complex Molecular Systems and Biomolecules, Flemingovo nám. 2,
   166 10 Prague 6, Czech Republic; e-mail: havlas@uochb.cas.cz
[b] *Chemistry Department, University of Frankfurt, Marie-Curie-Str. 11, D-60439 Frankfurt/Main,*
   Germany; e-mail: bock@risc.anorg.chemie.uni-frankfurt.de

Dedicated to Professor Pavel Hobza on the occasion of his 55th birthday.

For the model organosilicon cation $H_3N\cdots SiH_3^+$, potential curves have been calculated by density functional theory at the B3LYP level, by both MP2 and MP4 perturbation procedures and by a Coupled Cluster approach. Relative to the analogous potential curve for the uncharged adduct, $H_3N\cdots SiH_4$, a considerable increase of the long-range Si⋯N interaction accompanied by bond shortening is predicted. For chemical comparison, the structure of the "double R_2N-twister" dication salt, $[C_6H_4(CH_2NR_2)_2-Si-(R_2NCH_2)_2C_6H_4]^{++}Cl_2^-$, reported in the literature as a non-crystalline solid, was optimized by DFT calculations and a minimum for the hexacoordinated organosilicon center with each two Si⋯N bonds of different lengths was located. To test the reliability of the quantum chemical procedure, in addition the analogous and structurally characterized dication salt, $[(3\text{-picoline})_4SiH_2]^{++}[Cl^-\cdots(HCCl_3)_2]_2$, which contains a hexacoordinated Si center with 4 equivalent Si⋯N interactions, has been selected to reproduce its structure by DFT optimization. Both hexacoordinated, tetra-*N*-surrounded Si dications, substantiate the increase of long-range Si⋯N interactions as predicted by the potential curves for the model adduct $H_3N\cdots SiH_3^+$ based on highly correlated calculations.
Keywords: Amines; Silanes; Donor/acceptor complexes; *Ab initio* calculations; DFT; Coupled cluster method; MP2; MP4.

The preceding report[1] on hypercoordinate organosilicon molecules emphasized, that Si centers in organosilicon compounds exhibit[2] coordination

---

numbers between 1 and 10 and that especially Si···N distances vary over a wide range. For illustration, 1-amino-8-silylnaphthalene derivatives were selected, in which they stretch from covalent bonds of about 175 pm length *via* donor/acceptor adducts with distances between 210 and 250 pm to long Si···N contacts from 260 to 350 pm and even longer[1]. A search in the Cambridge Structural Database reveals a total of 574 entries for distances d_{Si-N} above 200 pm (Fig. 1), the borderline of the so-called "Si–N single bonds". Compounds with Si–N distances between 210 and 250 pm have been repeatedly defined as intramolecular donor/acceptor complexes[1].

What type of interaction is, however, represented by the numerous distances Si···N exceeding 260 pm? Density functional theory (DFT) calculations at the B3LYP level with large basis sets and accounting for intramolecular van der Waals attraction as well as repulsion have been carried out for each one hepta- and one octacoordinate organosilicon molecule containing three or four dimethylamino substituted hydrocarbon ligands, yielding enthalpies for long-range Si···N bond formation between 2 and 14 kJ mol^{-1}. In addition, a highly correlated potential curve for the
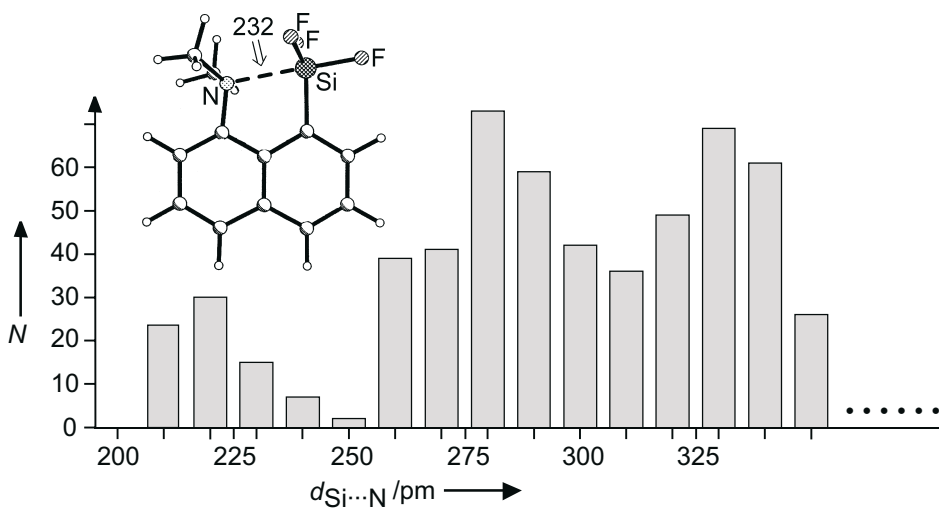

FIG. 1

Histogram for various Si–N bond lengths in the range between 200 and 350 pm, as revealed by a search in the Cambridge Structural Database (*N*, number of hits within 10 pm intervals) and the structure of a representative 1-amino-8-silylnaphthalene derivative

simplest model compound $H_3N\cdots SiH_4$ has been calculated at the MP4/aug-cc-pVDZ quality[1] (Fig. 2).

The geometry-optimized potential energy curve for the simplest model adduct $H_3N\rightarrow SiH_4$ (Fig. 2), calculated with augmented correlation-consistent double-zeta basis sets at MP2 and MP4 levels, shows a minimum of –11 kJ mol^{-1} estimated for the N→Si interaction contribution at that distance. Remarkably, both the higher ($\Delta E_{Si-N} \approx 5$ kJ mol^{-1} for $d_{Si-N} = 289$ pm) and the lower value ($\Delta E_{Si-N} \approx 2$ kJ mol^{-1} for $d_{Si-N} = 312$ pm) follow the prediction of the potential curve: the higher one is shifted 11 pm from the minimum towards the steeper repulsive slope and the lower one 11 pm towards its flatter dissociative part. The rather small DFT calculated energy differences[1] (estimated deviation limit ±2 kJ mol^{-1}) are, therefore, convincingly confirmed by the nonlinear correlation (Fig. 2).

For a tentative proposal concerning a possible origin of bonding in long-range N···Si interactions, the pure electrostatic attraction between the calculated DFT/NBO (Natural Bond Orbital) charges $q_{Si} \approx +1.6$ and $q_N \approx -0.5$ at 300 pm distance has been estimated to be about 60 kJ mol^{-1}. Accord-
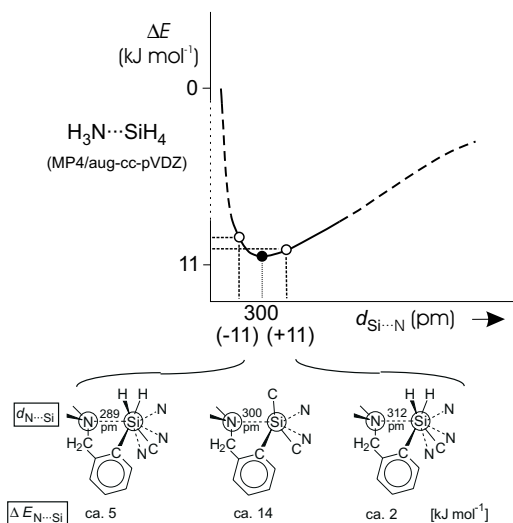

FIG. 2

Potential energy curve for the model adduct $H_3N\rightarrow SiH_4$, calculated with aug-cc-pVDZ basis sets using the MP2 optimized geometry and MP4 single point correlated calculations. For experimental verification of the N→Si interaction contributions, DFT estimates based on the crystal structures of the amino organosilyl compounds investigated with seven- and eight-coordinate Si centers are given[1] (*cf.* the text)

ingly, a Coulomb-dominated donor/acceptor bonding is proposed for the hypercoordinate N···Si compounds investigated[1]. In the theoretical study[3] of pentacoordinated neutral silicon compounds, containing the Si←N dative bond was shown, that the Si···N bond distance is very sensitive to inductive effect, which largely affects charges on Si and N moieties. The assumption of a Coulomb-dominated donor/acceptor bonding can be further substantiated by the evaluation of increased Si···N interactions in positively charged organosilicon cations.

RESULTS AND DISCUSSION

Correlated Potential Curves for a $H_3N\cdots SiH_3^+$ Model Cation

The interaction on adduct formation between H_3N and the SiH_3^+ cation has been investigated quantum chemically at several levels of sophistication: Electron correlation was introduced by using the perturbation approaches MP2 (refs[4,5]) as well as MP4 (refs[4,6]) and even coupled cluster CCSD(T) theory, which includes all the single and double substitutions and, in addition, non-iteratively the triple substitutions[7,8]. To further test the accuracy of the density functional theory procedure, a calculation at the B3LYP level[9] with a basis set of aug-cc-pVTZ quality[10] was performed. For the respective po-
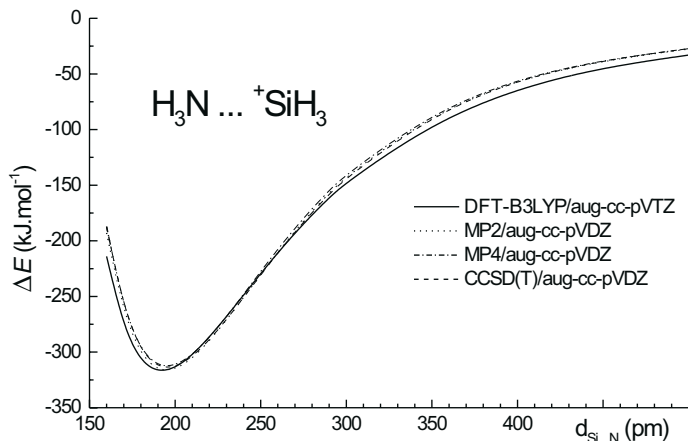

FIG. 3

Distance-dependent potential energy curves for the adduct of ammonia to the silicon cation $H_3N\cdots SiH_3^+$ at different levels of correlated wavefunctions: Density functional theory (DFT-B3LYP) with a basis set of triple-zeta quality (aug-cc-pVTZ), MP2 as well as MP4 and coupled cluster CCSD(T) calculations with double-zeta basis set (aug-cc-pVDZ)

tential curves (Fig. 3), the distance N···Si has been changed between 200 and 500 pm in steps of 10 pm and all the remaining degrees of freedom were optimized.

All four calculation modes yield nearly comparable results as suggested by the set of potential energy curves obtained (Fig. 3): The coupled cluster CCSD(T) approach (every single point needed about 3 h of CPU time at the NEC SX4 supercomputers used) produces the minimum at a N–Si distance of 194 pm and an interaction energy of 313 kJ mol^{-1} (Fig. 3). Remarkably, also the density functional theory calculation with a basis set of triple-zeta quality deviates only slightly with a minimum at about 192 pm and a N–Si interaction energy of about 316 kJ mol^{-1} (Fig. 3). Moreover, the force constants, predicted at both CC and DFT levels, are practically identical.

Most striking on structural comparison of the neutral and charged adducts, H_3N···SiH_4 *versus* H_3N–SiH_3^+ containing five- and four-coordinate Si centers, is the shortening of the 310 pm long N···Si distance to the cationic N–Si$^+$ bond of only 194 pm length, considerably polarized N$^{\delta-}$–Si$^{\delta+}$ due to the large difference in the effective nuclear charges. The cationic charge is predominantly localized in the SiH_3 group ($\Sigma q_{SiH_3} \approx +2/3$), although the H_3N fragment ($\Sigma q_{NH_3} \approx +1/3$) indicates some ammonium character. In contrast, the neutral and very weakly bonded complex $H_3N{\rightarrow}SiH_4$ (Fig. 4) exhibits a
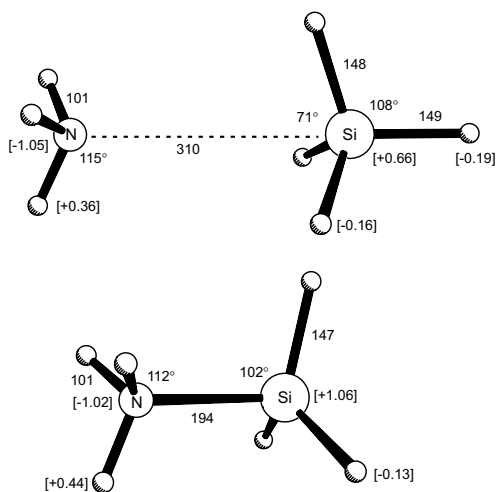

Fig. 4
CCSD(T) optimized structures of the ammonia adducts to silane H_3N···SiH_4 (a) and to silicon cation H_3N···SiH_3^+ (b) together with DFT/NBO charges[12] at the individual centers (*cf.* the text)

rather small σ electron transfer N→Si as indicated also by the slightly elongated axial Si–H bond. Altogether as demonstrated by the differing charges of the N and SiH centers, the interaction causes a considerable charge transfer $N^{\delta-} \leftarrow Si^{\delta+}$.

The partly surprising information from the highly correlated calculations of neutral or positively charged ammonia adducts to silane or to related cation, stimulated a literature search concerning "experimental" structural evidence for *N*-substituted organosilicon cations and dications.

DFT Structure Evaluation of the "Double Twister" Dication $[C_6H_3(CH_2N(CH_3)_2)_2–Si–((CH_3)_2NCH_2)_2C_6H_3]^{++}$ with a Hexacoordinated Si Center

In 1994 the synthesis and structure characterization of a tetrakis(dimethyl-amino) twister-substituted Si octacoordinate diphenylsilane have been reported[11] (Scheme 1, **M**).
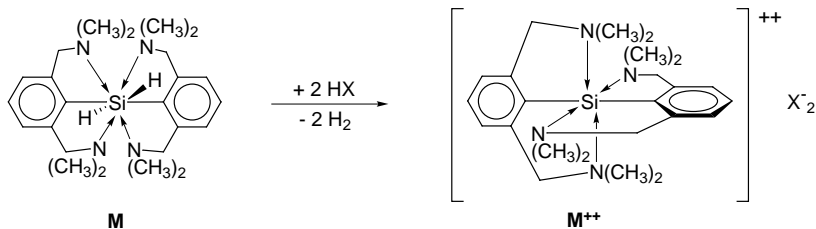
SCHEME 1

The oily solid isolated after the twofold deprotonation (Scheme 1) did not allow to determine the structure for the interesting dication[11]. Therefore, its geometry was fully optimized by DFT approximation at the B3LYP/6-31G* level. As a starting point, the proposed structure[11] (Scheme 1, **M++**) with almost equivalent distances N→Si, but slightly perturbed overall symmetry, was selected. The optimization procedure changed the initial coordinates rather rapidly by generating two pairs of N→Si contacts with different distances and by bending the central C–Si–C linkage. Most of the computer time (altogether about two weeks on a double-processor SGI Octane computer) required, however, has been spent for the relaxation of the mutual methyl group orientation. The predicted structure based on full convergency of the calculation, including all of its

$(3 \times 67 - 6) = 195$ degrees of freedom (Fig. 5), seems to represent a reasonable local minimum, although the complexity of the problem prevented any attempt to prove, by calculating and analyzing the corresponding Hessian matrix, that it corresponds to a minimum.

For the tetrakis(dimethylamino) twister-substituted diphenylsilane dication, the DFT optimization of all its 195 degrees of freedom predicts a local minimum (Fig. 5), in which the cationic species (Scheme 1) exhibits C_2 symmetry and shows two short N–Si^{++} bonds of 198 pm length (*cf.* Fig. 4) as well as two long-range N⋯Si^{++} contacts at the 353 pm distance. Due to the dication charge perturbation, the C–Si–C linkage is bent by 144° from the linear one in the neutral compound with an octacoordinate Si center (Scheme 1, **M**). One of the structural consequences is that the angles N–Si–N and N⋯Si⋯N differ by 15°. For the intuitively reasonable structure, the charge distribution resulting from a DFT/NBO analysis is given in Fig. 5: Expectedly, the hexacoordinate central Si center with its rather low effective nuclear charge is the most positively charged one (Fig. 5: [+2.15]), compensated to some extent by the surrounding six negatively charged C and N centers. The negative N center charges (Fig. 5: [–0.52] and [–0.65]) are reduced to about [–0.10] by their two-electron donating methyl substituents. Analogously, the C center charge (Fig. 5: [–0.65]) is considerably delocalized within the benzene rings. Nevertheless, the ligand bonds to the hexa-
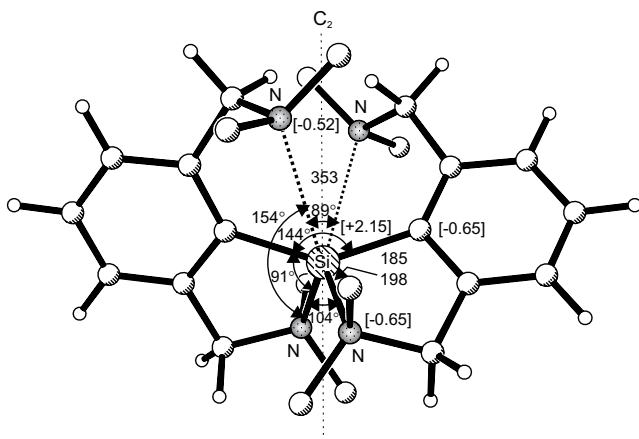

FIG. 5
Fully DFT-optimized structure of bis{2,6-bis[(dimethylamino)methyl]phenyl}silane dication with selected bond lengths as well as N⋯Si contact distances (in pm) and angles around the hexacoordinate Si center and with selected DFT/NBO (ref.[10]) charges in brackets. Methyl hydrogen atoms are omitted for clarity

coordinated Si center are strongly polarized: $Si^{\delta+}-C^{\delta-}$ and $Si^{\delta+}-N^{\delta-}$ as well as $Si^{\delta+}\cdots N^{\delta-}$.

Summarizing, both the fully DFT-optimized structure of the diphenyl-silane dication with two "double twister ligands" as well as the calculated DFT/NBO charge distribution (Fig. 5) confirm that the quantum chemically located minimum is a rationalizable possibility. The severe distortion around the hexacoordinated Si center predicted inbetween a twofold N···Si perturbed tetrahedron and a twisted octahedron with a bent C–Si–C axis fixed in the crystal should be a dynamic system in solution[11].

DFT Structure Reproduction of Dihydridotetrakis(3-picoline)silicon Dication with a Hexacoordinated Si Center

For a test of the DFT optimization quality, fortunately, the intense litera-ture search afforded another and structurally characterized dication with a fourfold nitrogen substituted silicon center of total coordination number six: the dihydridotetrakis(3-picoline)silicon dichloride, in which the chlo-ride anions are each solvated by two chloroform molecules[13]. Based on de-tailed information from elaborate NMR investigation of chloroform solutions of 3-picoline and bis(dichlorosilyl)amine, an elegant synthesis by a simple nucleophilic substitution of the dichlorosilane-bis(3-picoline) adduct with excess of 3-picoline has been designed[13] (Scheme 2).
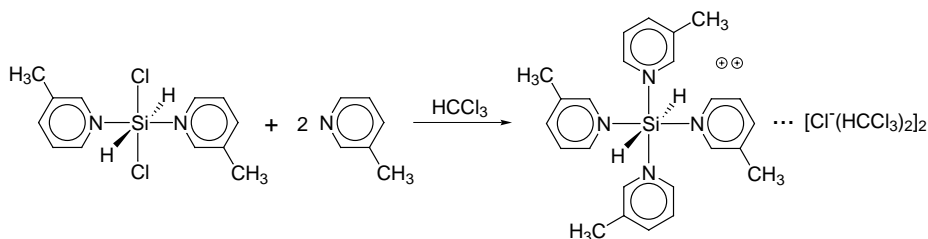
SCHEME 2

The single crystals of the $Cl^-\cdots HCCl_3$ hydrogen-bonded aggregate isolated contain the *N*-tetrasubstituted, hexacoordinate Si dication of slightly dis-torted C_{2h} symmetry[13]. The DFT fully optimized structure of a model com-pound, with the picolines substituted by pyridines, reproduced the crystal structure of the Si dication very well (*cf.* Fig. 6).

The proved quality of the DFT calculation enhances trust in the predicted structure of the "double twister" dication. The remarkable difference in

both structures, equivalent Si–N bonds in the dihydrotetrakis(3-picoline)silicon dication and two different Si···N interactions in the "double twister" dication, can be explained from the Si$^+$···N potential curves (Fig. 3): due to steric requirements, the "double twister" molecules can form only two highly stabilized bonds of 200 pm length with an interaction energy of approximately $2 \times 320 = 640$ kJ mol^{-1} and two week bonds of 353 pm with the interaction of $2 \times 100 = 200$ kJ mol^{-1}. The total interaction Si–N energy therefore amounts to 840 kJ mol^{-1}. If four intermediate Si···N bonds of average distance of 275 pm are formed, the total interaction energy is $4 \times 180 = 720$ kJ mol^{-1} and, therefore, the bent structure is much more stable. In the picoline aggregate the steric strain is missing and the molecule can form four equivalent Si–N strong bonds.

CONCLUSIONS

The Si···N long-range interactions in cationic species exhibit a considerable increase of the interaction energy and corresponding shortening of the Si–N distance, comparing to the uncharged complexes. The optimum Si–N distance, if no other affects are present, is between 190 to 200 pm, with in-
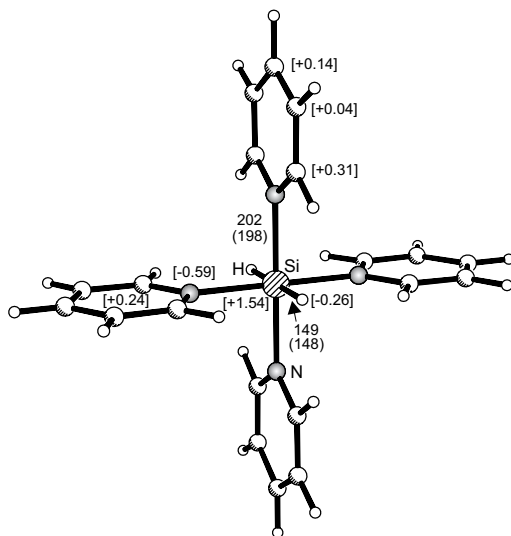

F<small>IG</small>. 6
Fully DFT-optimized structure of the dihydridotetrakis(pyridine)silicon dication with selected calculated *versus* experimental (in parentheses) bond lengths and charges (in brackets) from a DFT/NBO analysis (*cf.* the text)

teraction energy of about 310 kJ mol^{-1}. The coulombic origin of the Si–N interaction suggests sensitivity to the polarization and induction effects. The DFT method at B3LYP level can predict this type of interactions very well, even in details, provided at least the polarized double-zeta quality basis set is used.

The structure of the "double R$_2$N-twister" dication salt, [C$_6$H$_4$(CH$_2$NR$_2$)$_2$–Si–(R$_2$NCH$_2$)$_2$C$_6$H$_4$]$^{++}$Cl$_2^-$, was predicted with two different Si–N bond types. The bent structure of the molecule results in the equilibrium between Si–N bonds strength and steric requirements.

REFERENCES

1. Bock H., Havlas Z., Krenzel V.: *Angew. Chem.* **1998**, *110*, 3305; *Angew. Chem., Int. Ed. Engl.* **1998**, 37, 3163; and references therein.
2. Bock H.: *Angew. Chem.* **1989**, *101*, 1659; *Angew. Chem., Int. Ed. Engl.* **1989**, *2*, 1627; and references therein.
3. Angalada J. M., Bo C., Bofill J. M., Crehuet R., Poblet J. M.: *Organometallics* **1999**, *18*, 5584.
4. Møller C., Plesset M. S.: *Phys. Rev.* **1934**, *46*, 618.
5. a) Head-Gordon M., Pople J. A., Frisch M. J.: *Chem. Phys. Lett.* **1988**, *153*, 503; b) Frisch M. J., Head-Gordon M., Pople J. A.: *Chem. Phys. Lett.* **1990**, *166*, 275 and 281.
6. Krischnan R., Pople J. A.: *Int. J. Quantum Chem.* **1978**, *14*, 91.
7. a) Čížek J.: *Adv. Chem. Phys.* **1969**, *14*, 35; b) Purvis G. D., Bartlett R. J.: *J. Chem. Phys.* **1982**, *76*, 1910; c) Scuseria G. E., Jansen C. L., Schaefer III, H. F.: *J. Chem. Phys.* **1998**, *89*, 7382; d) Scuseria G. E., Schaefer III, H. F.: *J. Chem. Phys.* **1989**, *90*, 3700.
8. Pople J. A., Head-Gordon M., Raghavachari K.: *J. Chem. Phys.* **1987**, *87*, 5968.
9. a) Becke D.: *J. Chem. Phys.* **1993**, *98*, 5648; b) Lee C., Yang W., Parr R. G.: *Phys. Ber. B* **1988**, *37*, 785; c) Miehlich B., Sariu A., Stoll H., Preuss H.: *Chem. Phys. Lett.* **1989**, *157*, 200.
10. Dunning T. H., Jr.: *J. Chem. Phys.* **1989**, *90*, 1007.
11. Carré F., Chuit C., Corriu R. J. P., Mehdi A., Reyé C.: *Angew. Chem.* **1994**, *106*, 1152; *Angew. Chem., Int. Ed. Engl.* **1994**, *93*, 1097; and references therein.
12. Reed A. E., Curtiss L. A., Weinhold F.: *Chem. Rev. (Washington, D. C.)* **1988**, *88*, 899.
13. Fleischer H., Hensen K., Stumpf T.: *Chem. Ber.* **1996**, *129*, 765.