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Molecular structure of tris(cyclopropylsilyl)amine as determined by gas electron diffraction and quantum-chemical calculations

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Abstract

The molecular structure and conformation of tris(cyclopropylsilyl)amine (TCPSA) has been studied by means of gas-phase electron diffraction at 338 K and quantum-chemical calculations. A total of 12 relatively stable conformations of TCPSA molecule were considered. According to the experimental results and the DFT calculations the most stable conformer corresponds to a configuration (according to the Prelog–Klyne notation) of the type (−ac)(−ac)(+ac)-(−ac)(−ac)(+ac), where the first three parentheses describe the three different Si–N–Si–C torsional angles and the latter ones depict the rotation of the three cyclopropyl groups about the C_{ring}–Si axes, respectively. The quantum-mechanical calculations were performed using various density functional (B3LYP, X3LYP and O3LYP) and perturbation MP2 methods in combination with double- and triple-ζ basis sets plus polarization and diffuse functions. The most important experimental geometrical parameters of TCPSA (r_a Å, $\angle_{h1}$ degrees) are: $(\text{Si–N})_{av} = 1.741(3)$, $(\text{Si–C})_{av} = 1.866(4)$, $(\text{C–C})_{av} = 1.510(3)$, $(\text{C–C(Si)})_{av} = 1.535(3)$, $(\text{N–Si–C})_{av} = 115.1(18)°$. For the purpose of comparison and searching for reasons leading to the planarity of the Si_3N moiety in trisilylated amines we carried out NBO analysis and optimized the geometries of numerous silylamines. Among these compounds was tris(allylsilyl)amine (TASA), which is isovalent and isoelectronic to TCPSA. Utilizing the structural results we obtained we could show that $Si^+\cdots Si^+$ electrostatic repulsive interaction is predominantly responsible for the planarity of the Si_3N skeleton in TCPSA and in all other trisilylamines we considered. We also found that regardless the size and partial charges of the substituents the Si–N–Si bond angle in various disilylamines amounts to $130 \pm 2°$.

Keywords: Tris(cyclopropylsilyl)amine; Electron diffraction; Conformational analysis; Quantum mechanical calculations; $Si^+\cdots Si^+$ electrostatic repulsion; Tris(allylsilyl)amine; Isovalency

1. Introduction

The Si–N bond has attracted the attention of numerous research groups for many decades. Perhaps the versatile nature of this bond due to its occurrence as a dative, covalent, or ionic bond is the main reason for this great deal of interest. Also the ability of the silicon atom to undergo penta- [1–4] and hypercoordination [5–12] is an additional intriguing aspect for this substantial interest.

Possibly, the most intensively investigated compounds, which incorporate a pentacoordinated silicon with a transannular dative Si ← N bond [13–15] are the silatranes [16–19] and azasilatranes [20–25]. These atranes in addition to the corresponding carbasilatranes [13] and many other compounds with C–Si–N bonding configuration have proven to possess a distinctive biological activity and chemical reactivity [7,17–20,26–34].

On the background of the peculiarities of the C–Si–N bonding arrangement we synthesized the novel cyclopropylsilylamine series $(c\text{-Pr–SiH}_2)_n\,NH_{3-n}$, where $n = 1–3$ [35].

In the present investigation we report the gas phase structures and conformational properties of tris(cyclopro-

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pylsilyl)amine (TCPSA) as explored by gas-phase electron diffraction (GED) and quantum chemical calculations.

The main objectives for undertaking the present work are: (i) To continue our systematic exploration of the particular sensitivity of the Si–C bond to the effects of substituents and whether the variation of this bond as a result of substitution represents a systematic behaviour which can be utilized to predict some chemical and physical properties of molecules containing silicon. We have been also interested in scrutinizing the intriguing electronic interaction between silicon and electron rich moieties and the contribution of silicon to the electronic delocalization and thus its role as a charge mediator between these fragments. In a number of papers [36–46] we investigated the role of the silicon atom by transferring electronic effects between cyclopropane ring and electronegative atoms attached to the silicon. In the present case we are interested in elucidating the consequences of the electronic interactions between the nitrogen lone pair and the pseudo π-system, cyclopropane, under the mediation of the electropositive silicon atom. (ii) To contribute to a better understanding of the controversy has arisen about the planar arrangement at the nitrogen in silylated nitrogen compounds. It is generally known that the successive increase of the number of the silyl substituents on a central nitrogen atom contributes to a corresponding lowering of the barrier for inversion of the nitrogen atom. Should such a correlation be also valid for TCPSA we expect a considerable lowering of the inversion barrier of the central nitrogen leading to a distinctly shallow potential function and thus to a planar coordination at the nitrogen atom. (iii) To investigate the conformational distribution in this multi-rotor molecule and to try to understand the reasons leading to the preference of one conformer or the other.

2. Quantum-chemical and vibrational calculations

The geometry optimization and vibrational frequencies were computed by using the popular three parameter hybrid functional B3LYP [47] paired with the basis sets 6-31G(d) and 6-311+G(d,p). These calculations were performed with Gaussian03 program suite [48]. For the purpose of comparison and in order to more accurately calculate the total energies for the various conformers of TCPSA we also applied two of the recently developed density functionals X3LYP (extended hybrid functional combined with Lee–Yang–Parr correlation functional) [49] and O3LYP (Handy and Cohen's three parameter hybrid functional combined with LYP correlation functional) [50]. X3LYP and O3LYP calculations were performed with PC GAMESS 7.0 program [51].

For denoting of the TCPSA (Fig. 1) conformations the following six torsion angles were introduced: $\alpha_1 = \phi(Si_4–N_1–Si_2–C_5)$, $\alpha_2 = \phi(Si_2–N_1–Si_3–C_8)$, $\alpha_3 = \phi(Si_3–N_1–Si_4–C_{11})$, $\beta_1 = \phi(N_1–Si_2–C_5–X_1)$, $\beta_2 = \phi(N_1–Si_3–C_8–X_2)$ and $\beta_3 = \phi(N_1–Si_4–C_{11}–X_3)$, where X_1, X_2 and X_3 are the middles of the bonds ($C_6–C_7$), ($C_9–C_{10}$) and ($C_{12}–C_{13}$), respectively. Twelve different conformations, which were found by the B3LYP/6-31G(d) computations, are described in Table 1 following the Prelog–Klyne convention [52]. The calculations at B3LYP/6-311+G(d,p) level of theory predict only 11 stable conformations. Table 2 shows the values of the torsional angles for various conformers of TCPSA as obtained from different levels of computations. From this table it can be seen that the sign of the β_2 torsional angle in the XII conformer varies depending on the density functional method is used. However, the absolute values of this angle are very close to zero.

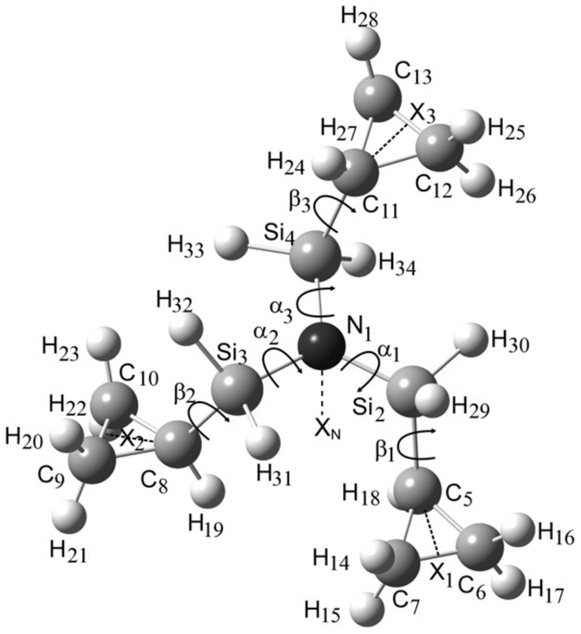

Fig. 1. Atomic numbering of TCPSA (conformation VI is shown).

The harmonic force field and frequencies of TCPSA were calculated at the B3LYP/6-31G(d) level of theory. The lowest frequency for each conformation was less than 30 cm^{-1}, which indicates the non-rigidity of the TCPSA molecule. Applying an ideal gas model with uncoupled translation, rotation, and vibration motions [53] the theoretical frequencies were used to calculate the ΔG values at

Table 1
Description of the TCPSA conformations

Conformer	Symmetry	α_1	α_2	α_3	β_1	β_2	β_3
I	C_3	−sc	−sc	−sc	−ac	−ac	−ac
II	C_3	+sp	+sp	+sp	−ac	−ac	−ac
III	C_1	−sc	−sc	+sc	−sp	+ac	−ac
IV	C_1	−sc	−sc	+sc	+ac	−ac	−ac
V	C_1	−sc	−sc	+sc	+ac	+ac	+ac
VI[a]	C_1	−ac	−ac	+ac	−ac	−ac	+ac
VII	C_1	−ac	−ac	+ac	−ac	+ac	−sp
VIII	C_1	−ac	−ac	+ac	−ac	−ac	−sp
IX	C_1	−ac	−ac	+sp	−ac	−ac	−ac
X	C_1	−ac	−ac	+ac	−ac	+sp	−sp
XI	C_1	−sc	−sc	+sc	+sc	−sp	+sp
XII	C_1	−ac	−ac	+ac	+ac	−sp	−sp

[a] The lowest energy conformer.