The nature of the intramolecular transannular Si···N interaction in crystalline 1-methylsilatrane, as found from X-ray diffraction data

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The primarily electrostatic nature of the intramolecular transannular Si···N interaction was found from the electron-density distribution in crystalline 1-methylsilatrane at 100 K.

Silatranes are of great interest in theoretical chemistry because of the dominance of the *endo*-form in their structure, which is related to the intramolecular transannular Si···N interaction (see, for example, ref. 1). Numerous structural studies have shown that the Si···N distance in silatranes varies in a wide range (2.0–2.3 Å) and depends on the nature of the substitutent at the silicon atom.[2] The character of the Si···N interaction, as well as the electron influence of a substituent at the silicon atom on the Si···N distance, is usually described in terms of a hypervalent model as a three-centre–four electron bond (3*c*–4*e* bond).[2–3] To test this model, we carried out a topological analysis of the electron-density distribution function $\rho(r)$ in crystalline 1-methylsilatrane **1** on the basis of high-resolution X-ray diffraction data at 100 K (Figure 1).† Experimental studies of the $\rho(r)$ in silatranes are limited only by a qualitative analysis of the deformation electron density (DED) distribution in 1-fluorosilatrane[4(*a*)] and 1-chloromethylsilatrane.[4(*b*)]

The molecular geometry parameters of **1** at 100 K (Figure 1) are close to those at 298 K.[5] Molecules of **1** in a crystal are characterised by the approximate C_3 symmetry. The Si and N atoms that participate in the Si···N interaction have distorted bipyramidal and trigonal configurations with the deviations in opposite directions from the planes of their neighbouring atoms by 0.202 and 0.371 Å, respectively. The Si···N distance [2.1604(3) Å] is typical of silatranes with electron-donor substitutients.[2] The Si(1)–C(7) bond is significantly elongated [1.8801(4) Å] in comparison with the corresponding values for alkylsiloxanes (1.858 Å).[6] Because of the weak C–H···O contacts in crystalline **1** [C(3)–H(3B)···O(3) (2 – *x*, –*y*, 1 – *z*), H(3B)···O(3) 2.48 Å, C(3)–H(3B)–O(3') 156°, C(3)···O(3) 3.4864(5) Å], the molecules are arranged in centrosymmetrical dimers.

An analysis of the electron-density distribution‡ was performed by the DED maping and topological analysis of the $\rho(r)$ function in terms of the Bader theory 'Atoms in molecules' (AIM).[7,§] According to the DED map in the plane of Si(1), N(1), O(1) and C(7) atoms, a concentration of the electron density is observed in the covalent Si–C, Si–O and C–H bonds and along the line of the hypervalent Si(1)···N(1) interaction. The corresponding DED maximum (0.7 *e* Å^{-3}) at the Si(1)···N(1) line is significally shifted towards the nitrogen atom and is located at an approximate distance of 0.45 Å. This fact allowed us to suggest that the nitrogen lone pair which participates in the formation of the 3*c*–4*e* bond (according to the hypervalent model) has a predominantly atomic character.

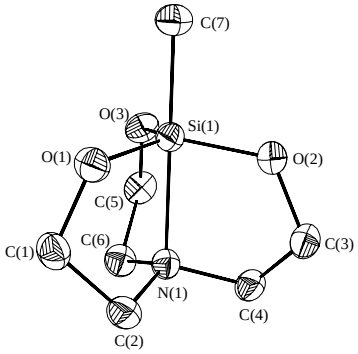

Figure 1 The molecular structure of **1** (85% probability level). The hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si(1)–O(2) 1.6776(3), Si(1)–O(3) 1.6795(3), Si(1)–O(1) 1.6803(3), Si(1)–C(7) 1.8801(4), Si(1)–N(1) 2.1604(3), O(1)–C(1) 1.4199(5), O(2)–C(3) 1.4235(4), O(3)–C(5) 1.4196(5), N(1)–C(2) 1.4722(5), N(1)–C(6) 1.4735(5), N(1)–C(4) 1.4765(4); selected bond angles (°): O(2)–Si(1)–O(3) 119.246(16), O(2)–Si(1)–O(1) 118.925(16), O(3)–Si(1)–O(1) 117.554(16), O(2)–Si(1)–C(7) 96.80(2), O(3)–Si(1)–C(7) 97.00(2), O(1)–Si(1)–C(7) 96.92(2), O(2)–Si(1)–N(1) 83.19(1), O(3)–Si(1)–N(1) 83.01(1), O(1)–Si(1)–N(1) 83.08(1), C(7)–Si(1)–N(1) 179.99(2), C(2)–N(1)–C(6) 113.77(3), C(2)–N(1)–C(4) 114.25(3), C(6)–N(1)–C(4) 113.67(3), C(2)–N(1)–Si(1) 104.56(2), C(6)–N(1)–Si(1) 104.67(2), C(4)–N(1)–Si(1) 104.48(2).

† *Crystallographic data for* **1**: crystals of $C_7H_{15}NO_3Si$ are monoclinic at 100 K, space group $P2_1/n$, a = 7.5663(1) Å, b = 12.0408(2) Å, c = 9.6210(1) Å, β = 91.740(1)°, V = 876.11(2) Å^3, Z = 4, M = 189.29, d_{calc} = 1.435 g cm^{-3}, μ(MoKα) = 0.236 mm^{-1}, F(000) = 408. Intensities of 20349 reflections were measured with a Smart 1000 CCD diffractometer at 100 K [λ(MoKα) = 0.71072 Å, ω-scans with a 0.3° step in ω and 10 s per frame exposure, $2\theta < 90°$], and 7397 independent reflections (R_{int} = = 0.0135) were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to wR_2 = 0.0911 and GOF = = 1.031 for all independent reflections [R_1 = 0.0307 was calculated against F for 6305 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0 on IBM PC AT. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, 2000, Issue 1. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/64.

‡ The analytical form of the electron density was obtained by a multipole refinement based on the Hansen–Coppens[8] formalism using the XD program package.[9] The level of the multipole expansion was hexadecapole for Si(1) and N(1), octadecapole for all oxygen and carbons atoms and dipole for hydrogens. The scattering factor of the hydrogen atoms was calculated from the contracted radial density functions (k = 1.2). The refinement was carried out against F without any symmetry restraints with the exception of hydrogens for which a cylindrical symmetry was assumed. The refinement converged to R = 0.0211, wR = 0.0238, GOF = = 1.69. The ratio of the number of reflections to the number of refined parameters was more than 20.

§ According to the AIM theory, a chemical bond is described by means of analysis of the electron density $\rho(r)$ and its Laplacian $\nabla^2\rho(r)$ values in the so-called critical points (CPs), where gradient of the electron density vanishes, $\nabla\rho(r) = 0$. The type of the CP is determined by the number of non-zero eigenvalues of the Hessian matrix, as well as by the sum of their signs. A set of the nondegenerated CP constitutes a molecular graph in which CP of the (3, –3) type correspond to a nuclear position, (3, +3), to a cage, (3, +1) to a cycle, and (3, –1), to a chemical bond. Thus, the existence of the CP (3, –1) is equivalent to the existence of a bond path (line of the maximum electron-density gradient) and is a necessary condition for the formation of a chemical bond.

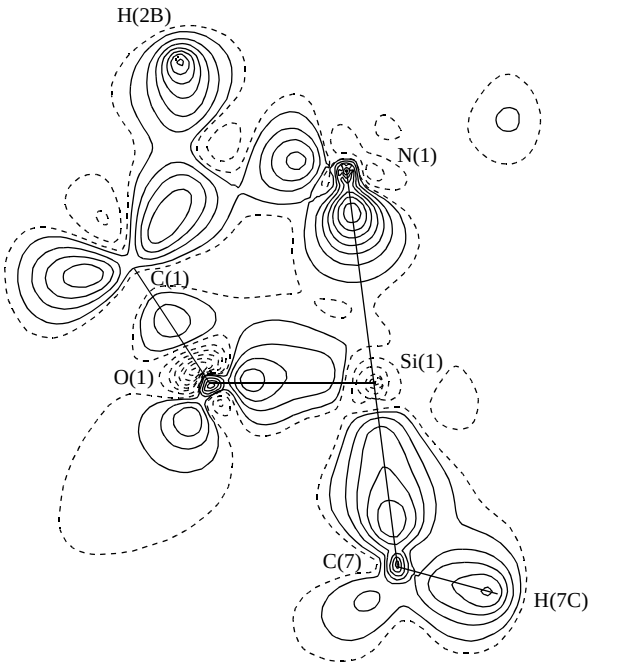

Figure 2 Static deformation electron density in the plane of Si(1), O(1), N(1) and C(7) atoms [atoms C(1) and C(2) are deviated from this plane by 0.15 and –0.44 Å, respectively]. Interval between isolines is 0.05 *e* Å^{-3}, negative contours are dashed.

Similar conclusions can be made from the results of a topological analysis of the electron density distribution, in particular, from the values of $\rho(r)$ and $\nabla^2\rho(r)$ at the critical points (CPs) of the type (3, –1) bonds.§ A topological analysis of the $\rho(r)$ demonstrated the coincidence between the molecular graph obtained by the CP analysis and the structural formula. Note that CP (3, –1) were found not only at the Si–O, C–C, C–H and N–C bonds, but also in the regions of the transannular Si···N interaction and the intermolecular C–H···O contact. The Si···N bond resulted in the appearance of three CPs of the type (3, +1), which correspond to the cycle formation. Thus, the characteristic set of CPs in 1-methylsilatrane satisfies the Poincare–Hopf equation.[10] The difference between the bond path length[7,§] and the interatomic distances in **1** does not exceed 0.002 Å. This fact is indicative of the absence of steric strains in the five-membered rings formed by the Si···N transannular interaction.

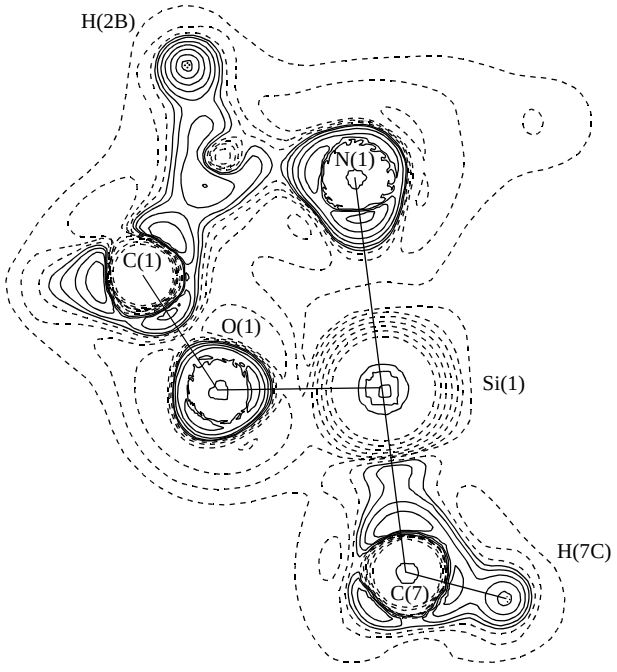

Figure 3 Laplacian of the electron density [$-\nabla^2\rho(r)$] in the plane shown in Figure 2. Negative lines are dashed, contours are drawn using logarithmic scale.

An analysis of the atomic charges calculated from the monopole occupancies showed that the positive charge (0.44 *e*) is mainly localised at the Si atom, while the negative charge (–0.34 and –0.42 *e*), at the N and O atoms. The dipole moment was calculated to be 6.9 D, which is close to the experimental value of 5.3 D.[11] A similar increase in the molecular dipole moment in a crystal is usually related to the molecular polarization in a crystal field.[12]

An analysis of the topological characteristics of $\rho(r)$ in the CP (3, –1) for the Si···N and Si–O bonds and C–H···O contacts revealed that $\nabla^2\rho(r)$ values are positive for these bonds (0.83, 7.17 and 0.78 e A^{-5}, respectively). Thus, the formation of chemical bonds results in an electron density depletion rather than accumulation in the interatomic region. This is typical of the 'closed shell' type interaction.[7,¶] The character of the interatomic interaction in the area of the C–H···O contact is clear, while positive $\nabla^2\rho(r)$ values at the covalent Si–O and transannular Si···N bonds makes it impossible to describe their nature unambiguously. It was found previously by quantum-chemical calculations for Si–O bonds that despite of an electron-density depletion in the Si–O bond, $\rho(r)$ values in the corresponding CP (3, –1) are relatively high, and the local energy density $E(r)$ is negative, which is a typical characteristic of the intermediate type interaction.[13,16,17] Probably, such a character of the Si–O bond is caused by its high polarity, as well as by a repulsion of the electron density of the Si–O bond and nonbonded oxygen lone pairs (lone pair weakening effect[18]). An analysis of the electron density and its topology demonstrated that the value of $\rho(r)$ at the Si–O bond (0.99 *e* A^{-3}) is significantly higher than that at the Si···N and C–H···O bonds (0.45 and 0.04*e* Å^{-3}, respectively), and the $\nabla^2\rho(r)$ for the last two bonds are almost equal [for comparison, $\rho(r)$ and $\nabla^2\rho(r)$ in the LiF molecule are 0.51 *e* Å^{-3} and 9.23 *e* Å^{-5}, respectively, and $E(r)$ is positive (0.0198 a.u.)[15]].

Thus, we can conclude that the Si···N bond has most probably an electrostatic nature. Such a character of the Si···N bond is consistent with its high polarizability and explains an essential decrease of the Si···N distance in the transition from a gas phase (2.45 Å)[19] to a crystal [2.1604(3) Å].

On the contrary, the $\nabla^2\rho(r)$ values for C–C, C–O, N–C and C–H covalent bonds are negative and equal to –9.78, 10.83, –11.29 and –14.77 *e* Å^{-5}, respectively. The $\rho(r)$ values for these bonds (1.66, 1.79, 1.73 and 1.75 *e* Å^{-3}, respectively) are much higher in comparison with the corresponding values for the Si···N and C–H···O bonds. The electron-density topology characteristics at the CP (3, –1) for C–C, C–H, C–N and C–O bonds in **1** are in good agreement with experimental and theoretical data on the $\rho(r)$ in organic compounds (see, for example, refs. 20 and 21).

Thus, the X-ray diffraction study of the electron density in 1-methylsilatrane demonstrated that the distribution in the transannular Si···N interaction belongs to the so-called closed-shell interaction with a very small covalent contribution. A further investigation into silatrane derivatives with acceptor substituents will make it possible to evaluate the influence of substituents at the Si atom on the character of the transannular interaction and to check the correctness of the theoretical procedures used for the description of hypervalent bonds.

¶ 'Shared interactions' and 'closed shell' interactions differ mainly by the sign of the $\nabla^2\rho(r)$ in the CP (3, –1).[7] Shared interactions are characterised by negative $\nabla^2\rho(r)$ values and high $\rho(r)$ values, while in the closed shell interactions the value of $\nabla^2\rho(r)$ is positive, and the total $\rho(r)$ is small.[13–15] However, the positive $\nabla^2\rho(r)$ value is not a unique criterion of the closed shell interaction, the necessary condition is the positive value of the local energy density, which is related to $\nabla^2\rho(r)$ by the equation: $E(r) = V(r) + G(r) = G(r) - (\hbar^2/4m)\nabla^2\rho(r)$, where $V(r)$ and $G(r)$ are the local potential and kinetic energy densities, respectively. It can be seen that if the $\nabla^2\rho(r)$ is positive, the value of $E(r)$ may remain negative if the potential energy density (*a priori* negative) exceeds the kinetic energy in the absolute value. The bonds characterised by a positive value of $\nabla^2\rho(r)$ and a negative value of $E(r)$ correspond to an intermediate type of the interatomic interaction.

Note that the recent theoretical calculation [MP2/6-31G(d), B3LYP/6-31G(d)][22] of 1-methylsilatrane supported the idea that Si···N is the closed-shell interaction and hence is characterised by the electrostatic nature. For comparison, the $\rho(r)$ and $\nabla^2\rho(r)$ values in the CP (3, –1) for the Si···N bond, according to the MP2/6-31G(d) calculations, are 0.26 *e* Å^{-3} and 0.82 *e* Å^{-5}, respectively. These values are close to the experimental data (0.45 *e* Å^{-3} and 0.83 *e* Å^{-5}) taking into account the elongation of this bond by 0.28 Å in the theoretical calculation.

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