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Why are trimethylsilyl groups asymmetrically coordinated? Gas-phase molecular structures of 1-trimethylsilyl-1,2,3-benzotriazole and 2-trimethylsilyl-1,3-thiazole†

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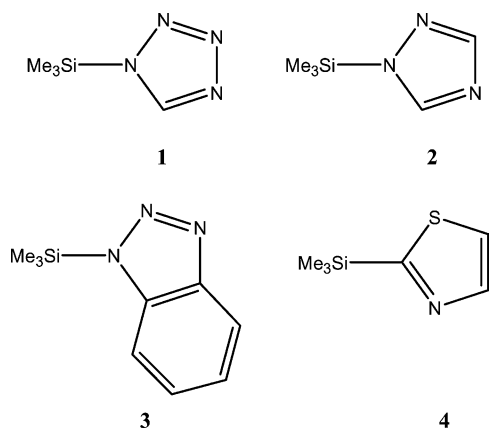
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The structures of 1-trimethylsilyl-1,2,3-benzotriazole and 2-trimethylsilyl-1,3-thiazole have been determined by gas electron diffraction and computational methods. While 1-trimethylsilyl-1,2,3-benzotriazole shows a significant asymmetry in the way the SiMe₃ groups bonds to the ring system, the same is not true for 2-trimethylsilyl-1,3-thiazole. However, it has been shown that when the positions of formal single and double bonds in the rings systems are considered, the silyl groups in both compounds are displaced towards the neighbouring ring nitrogen atom. Calculated structures of a series of analogous compounds with different substituents on silicon show only minor variations in the extent of the distortion, although with hydrogen instead of a silyl group the displacement is significantly smaller.

Introduction

One might expect that when a silyl group is bonded to a nitrogen atom of an aromatic ring, the angles between the N–Si bond and the two adjacent ring bonds would be more or less equal. They are not. In 1-trimethylsilyltetrazole (**1**) they differ by more than 15°, as shown by experimental (gas electron diffraction) and computational work, with the NNSi angle being larger than CNSi.¹ Similarly highly asymmetric coordination of an SiMe₃ group to nitrogen in an unsaturated ring was observed in 1-trimethylsilyl-1,2,4-triazole (**2**).¹ Calculations have shown that this effect is mostly an inherent property of the tetrazole or triazole ring. Simple VSEPR theory also predicts asymmetric coordination, although it cannot predict the size of the difference.



These phenomena have been studied further by determining the structures of 1-trimethylsilyl-1,2,3-benzotriazole (**3**) and 2-trimethylsilyl-1,3-thiazole (**4**) using gas-phase electron diffraction (GED) and computational chemistry techniques. By doing this we have widened the study of asymmetric coordination to include an example with a similar motif to those in 1-trimethylsilyltetrazole and 1-trimethylsilyl-1,2,4-triazole, but with an extra fused ring present, and to one that is rather different.

In **3** the silyl group is bound to a ring nitrogen atom, and the group is bent towards the second ring nitrogen. In **4** the silyl group is coordinated to carbon and the adjacent ring atoms are sulfur and nitrogen. In this case, because there is a double bond adjacent to the substituent atom, one might expect the N=C–Si and N=C–S angles to be rather similar, and much wider than the Si–C–S angle, but in fact the SiMe₃ group is coordinated almost symmetrically to the ring. So in both molecules, although they are of rather different types, the Si–X–N angles are narrower than might be expected at first sight. Does this indicate that there is an attractive force between silicon and nitrogen, even though the nitrogen does not have a lone pair of electrons in an orbital that would allow donation to silicon? To answer this question computational studies have been performed on both molecules, and also on a range of related molecules with different substituents on silicon.

Experimental

Computational

Ab initio calculations were performed for both **3** and **4** and a number of other 1-silyl-1,2,3-benzotriazole and 2-silyl-1,3-thiazole derivatives using the Gaussian 03 suite of programs.² Most calculations were performed using the computational resources of the NSCCS.³ Potential-energy scans were used to identify conformational isomerism with respect to rotation about the Si–N or Si–C bonds. Geometry optimisations were then carried out using several methods, namely restricted Hartree–Fock

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† Electronic supplementary information (ESI) available: GED experimental parameters, calculated and refined amplitudes of vibration and curvilinear distance corrections, least-squares correlation matrices, GED coordinates, calculated coordinates and energies, molecular-scattering intensity curves. See DOI: 10.1039/b822154e

(RHF), MP2, and hybrid-DFT (B3PW91 and B3LYP). Pople-style basis sets 3-21G, 6-31G, and 6-311G including both diffuse (+) and polarisation (*) functions for both heavy and light atoms were used. In addition, frequency calculations were performed using the RHF and hybrid-DFT methods to evaluate whether an optimised structure represented a minimum (all real frequency values) or otherwise on the potential-energy surface (PES).

Gas-phase electron diffraction

1-Trimethylsilyl-1,2,3-benzotriazole (**3**) and 2-trimethylsilyl-1,3-thiazole (**4**), both with stated purity in excess of 97%, were purchased from Sigma-Aldrich and used without further purification.

Electron diffraction data for both **3** and **4** were collected on Kodak Electron Image films using the Edinburgh gas-phase electron diffraction apparatus.⁴ The sample and nozzle temperatures for the experiments are listed in Table S1.† The accelerating voltage of 40 kV resulted in an electron wavelength of *ca.* 6 pm. Nozzle-to-film distances were determined by analysis of the scattering patterns of benzene, recorded immediately before or after the sample patterns. Details of weighting functions, *s* ranges, scale factors and correlation parameters are also given in Table S1.†

Scattering intensities were digitised using an Epson Expression 1680 Pro flatbed scanner and corrected to mean optical densities as a function of the scattering variable, *s*, using an established program.⁵ The data were reduced and analysed with the ed@ed v2.1 program⁶ using the scattering factors of Ross *et al.*⁷

Results

Computational study

Derivatives of 1,2,3-benzotriazole. For eight 1- $X_{3-n}X'_n$ Si derivatives of 1,2,3-benzotriazole ($X, X' = H, F, Cl, Me; n = 1-3$) potential-energy scans about the XSiNN dihedral were performed at the RHF/6-31G* level to identify any conformational isomers. For each of 1- H_3 Si-1,2,3-benzotriazole and 1- F_3 Si-1,2,3-benzotriazole the scans showed that only one conformer exists, namely a C_s -symmetric structure with one silyl substituent *anti* to the nitrogen atom (Fig. 1). In addition to the *anti* conformer, the curve for 1- Me_3 Si-1,2,3-benzotriazole (**3**) shows the presence of a second conformer, with a methyl carbon *syn* to the nitrogen

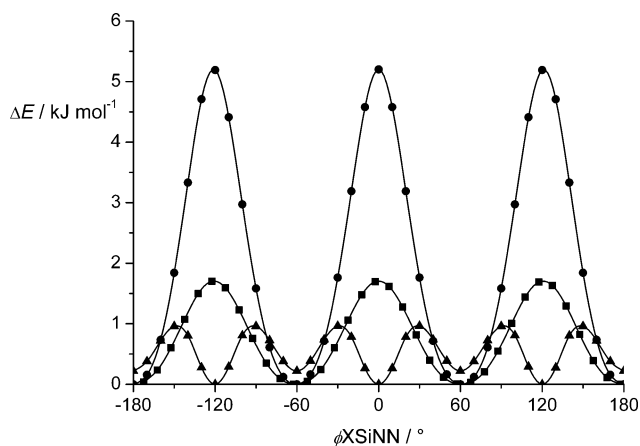


Fig. 1 Potential-energy scans (RHF/6-31G*) of ϕ_{XSiNN} for 1- X_3 Si-1,2,3-benzotriazole [$X = H$ (■), F (●), Me (▲)].

atom. The potential-energy scan indicates that the *syn* conformer is approximately 0.3 kJ mol⁻¹ (RHF/6-31G*) more stable than the *anti* conformer. Fig. 2 shows the structures of generic *anti* and *syn* conformers for SiX_3 compounds. The presence or otherwise of these conformers can be explained by reference to the nature of the substituents. In the $SiMe_3$ case *syn* and *anti* conformers are more or less equally likely and there is no reason to believe that for steric reasons this would be any different for the other SiX_3 compounds. However, when X is a halogen atom, the $X \cdots H(C)$ distance is approximately 260 pm and this attractive interaction could stabilise the *anti* conformation.

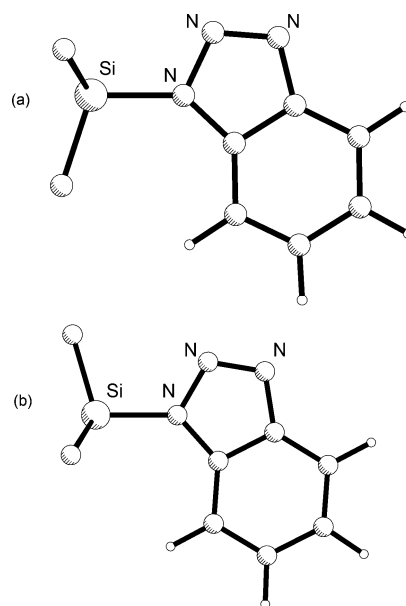


Fig. 2 Diagrams showing generic (a) *anti* and (b) *syn* conformers of 1- X_3 Si-1,2,3-benzotriazole.

The scans for the remaining molecules [1- FH_2 Si-1,2,3-benzotriazole, 1- ClH_2 Si-1,2,3-benzotriazole and 1- $ClMe_2$ Si-1,2,3-benzotriazole (Fig. 3) and 1- Cl_2 HSi-1,2,3-benzotriazole (Fig. 4)] are more complicated. 1- $ClMe_2$ Si-1,2,3-benzotriazole has an extremely shallow minimum representing a *syn* conformer (*i.e.* the

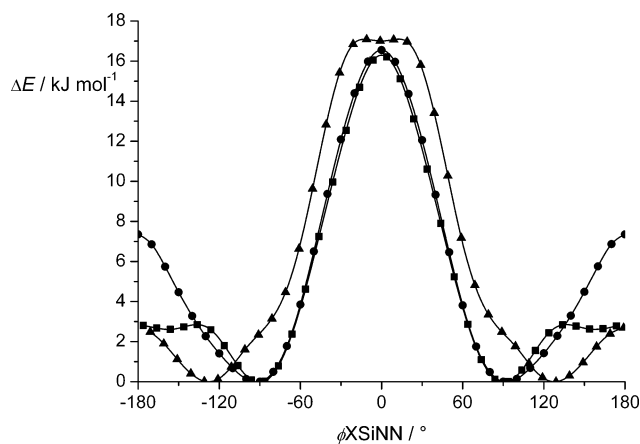


Fig. 3 Potential-energy scans (RHF/6-31G*) of ϕ_{XSiNN} for 1- FH_2 Si-1,2,3-benzotriazole ($X = F$; ■), 1- ClH_2 Si-1,2,3-benzotriazole ($X = Cl$; ●) and 1- $ClMe_2$ Si-1,2,3-benzotriazole ($X = Cl$; ▲).

halogen is *syn* with respect to nitrogen), although this is about 17 kJ mol⁻¹ higher in energy than its *gauche* conformer. While 1-ClH₂Si-1,2,3-benzotriazole has only one conformer (with a dihedral angle of approximately 90°) 1-FH₂Si-1,2,3-benzotriazole also has a shallow potential minimum about 3 kJ mol⁻¹ higher in energy, with a dihedral angle of approximately 150°.

The potential-energy scan for 1-Cl₂HSi-1,2,3-benzotriazole (Fig. 4) is completely different, as it has two minima differing by 180° in the HSiNN dihedral angle. The hydrogen atom can therefore eclipse the nitrogen atom in the ring or, 6 kJ mol⁻¹ higher in energy, eclipse the carbon atom. In each case both chlorine atoms lie out of the ring plane by 60°. So overall, of the four compounds studied, one has one minimum, and the other three each have two, but separated by 60, 120 and 180°.

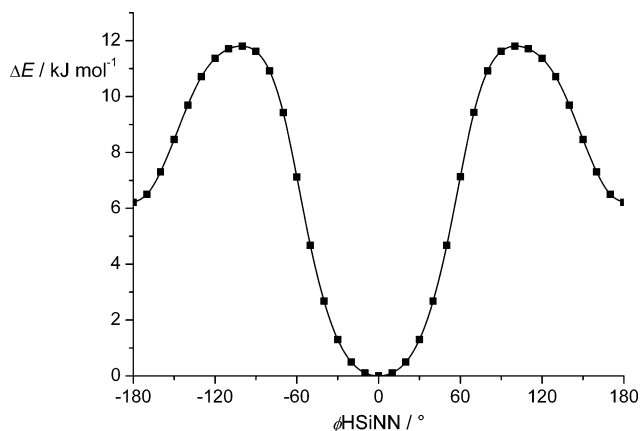


Fig. 4 Potential-energy scan (RHF/6-31G*) of ϕ HSiNN for 1-Cl₂HSi-1,2,3-benzotriazole.

Geometry optimisations and frequency calculations were performed at RHF and hybrid-DFT levels of theory, confirming that the minima found in the potential-energy scans were real. MP2 calculations were then performed to obtain more accurate geometrical parameters for each molecule. Table 1 gives a selection of bond lengths and angles for the *syn* conformer of **3** calculated at different levels of theory and compares them with results from the GED experiment. Parameters for the *anti* conformer were close to those listed, except for the angles specifically identified in the table.

Derivatives of 2-silyl-1,3-thiazole. Potential-energy scans were performed at the RHF/6-31G* level for three 2-X₃Si and four 2-X₂X'Si derivatives of 1,3-thiazole (X, X' = H, F, Cl, Me), to identify the presence of different conformers. For each of the X₃Si derivatives the potential-energy curves showed minima only for the *anti* conformations. The energy barriers for rotation to the next *anti* conformation were around 1.5 kJ mol⁻¹ for the H₃Si and Me₃Si compounds, but for the F₃Si derivative were comparatively high, at 3.7 kJ mol⁻¹ (Fig. 5). This reflects what was observed for the equivalent H₃Si and F₃Si derivatives of 1,2,3-benzotriazole, although this time there were no intermediate potential minima for the Me₃Si derivative.

The potential-energy curves for the monohalogenated derivatives of thiazole identify *anti* conformers as having the lowest energies (Fig. 6). The curves for the FH₂Si and ClH₂Si derivatives are very similar, with the exception of the energy differences

Table 1 Comparison of *ab initio* and hybrid-DFT (6-311++G**) and GED data for 1-trimethylsilyl-1,2,3-benzotriazole, **3** (bond lengths in pm and angles in °)

Parameters	GED	RHF	MP2	B3PW91
<i>r</i> SiN	180.6(8)	179.8	181.0	181.3
<i>r</i> SiC	186.1(3)	187.3	186.6	187.2
<i>r</i> CH	109.5(4)	108.3	109.2	109.1
<i>r</i> N(2)C(6)	136.3(4)	136.7	137.1	137.3
<i>r</i> N(2)N(3)	138.7(5)	134.7	137.4	137.6
<i>r</i> N(3)N(4)	131.3(5)	124.7	131.7	128.3
<i>r</i> N(4)C(5)	136.3(4)	137.3	137.2	137.6
<i>r</i> C(5)C(6)	142.0(4)	138.2	141.5	140.7
<i>r</i> C(5)C(13)	140.9(1)	139.8	140.9	140.1
<i>r</i> C(6)C(7)	140.9(1)	140.2	140.9	140.2
<i>r</i> C(7)C(9)	138.7(4)	137.1	139.1	138.5
<i>r</i> C(9)C(11)	142.5(4)	141.2	142.1	141.2
<i>r</i> C(11)C(13)	138.3(4)	136.9	138.9	138.2
∠NSiC	106.8(3)	107.6	106.2	107.0
∠SiCH	111.9(5)	111.0	110.9	111.0
∠Si(1)N(2)N(3) <i>syn</i>	117.4(6)	119.9	119.9	119.8
∠Si(1)N(2)N(3) <i>anti</i>	112.6(6)	115.2	114.3	114.9
∠Si(1)N(2)C(6) <i>syn</i>	134.2(10)	132.3	131.1	132.1
∠Si(1)N(2)C(6) <i>anti</i>	138.2(10)	137.0	136.7	136.8
∠N(2)N(3)N(4)	109.8(4)	111.7	109.8	110.5
∠N(3)N(2)C(6)	109.2(3)	107.7	109.0	108.2
∠N(3)N(4)C(5)	107.3(3)	108.3	107.9	108.4
∠N(4)C(5)C(6)	110.0(2)	107.8	108.8	108.3
∠N(2)C(6)C(5)	103.7(2)	104.6	104.5	104.6
∠C(5)C(6)C(7)	121.6(5)	121.1	121.8	121.2
∠C(6)C(7)C(9)	117.9(5)	116.7	116.5	116.9
∠C(7)C(9)C(11)	121.0(6)	122.2	121.9	122.1
∠C(9)C(11)C(13)	121.1(8)	120.9	121.6	121.1
∠C(5)C(13)C(11)	118.9(9)	117.2	117.1	117.4
∠C(6)C(5)C(13)	119.6(8)	121.9	121.0	121.4
∠C(6)C(7)H(8)	123.6(11)	122.5	122.5	122.3
∠C(7)C(9)H(10)	120.1(13)	119.1	119.0	119.0
∠C(9)C(11)H(12)	119.1(7)	119.0	118.8	119.0
∠C(11)C(13)H(14)	121.0(11)	122.0	122.2	122.1

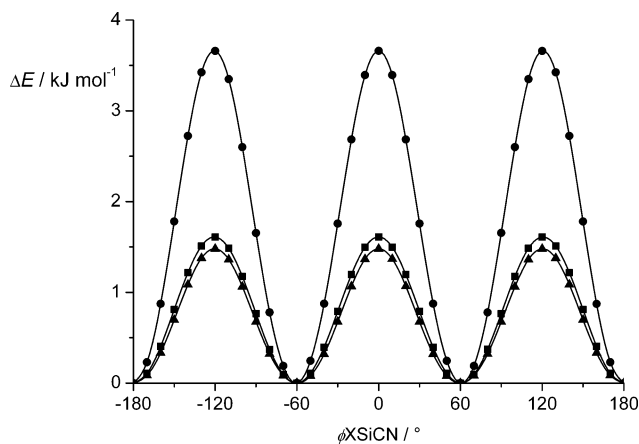


Fig. 5 Potential-energy scans (RHF/6-31G*) of ϕ XSICN for 2-X₃Si-1,3-thiazole [X = H (■), F (●), Me (▲)].

between their respective *anti* and *gauche* conformations. The minimum for the *gauche* conformer of 2-ClH₂Si-1,3-thiazole is predicted to be very shallow. There is no minimum apparent at the corresponding *gauche* position in the potential-energy curve for the ClMe₂Si derivative, but subsequent geometry optimisations and frequency calculations did give a structure with only real frequencies. It may be that the step size used for the potential-energy scan for this compound was too large. However,

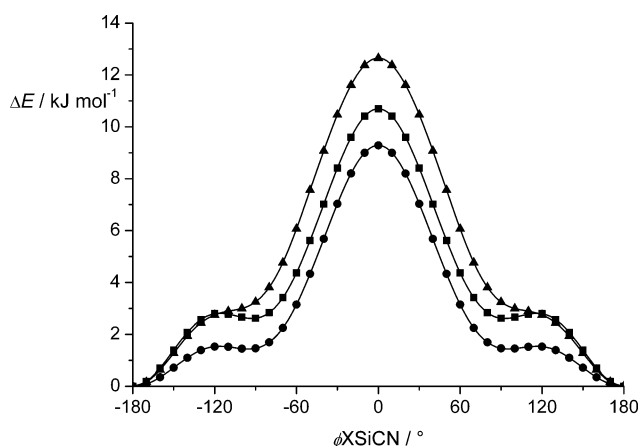


Fig. 6 Potential-energy scans (RHF/6-31G*) of ϕ XSICN for 2-FH₂Si-1,3-thiazole (X = F; ■), 2-ClH₂Si-1,3-thiazole (X = Cl; ●) and 2-ClMe₂Si-1,3-thiazole (X = Cl; ▲).

MP2/6-311++G** calculations showed that the *gauche* conformation fell back into an *anti* minimum and therefore confirmed the potential-energy scan for 2-ClMe₂Si-1,3-thiazole.

The potential-energy scan for 2-FH₂Si-1,3-thiazole predicted the presence of both *gauche* and *anti* conformers, but the geometry optimisations and frequency calculations that followed showed that at the RHF/6-311G* level the *gauche* form transformed into the *anti* conformer. The size of the basis set used in the calculations therefore has a critical influence on the number of conformers predicted. MP2 calculations were then performed to obtain more accurate geometric data for all identified conformers.

The potential-energy curve for 2-Cl₂HSi-1,3-thiazole (Fig. 7) is quite different. The chlorine atoms would be *anti* with respect to the ring nitrogen atom when the HSICN dihedral angle was $\pm 60^\circ$. In fact there are two minima, at about $\pm 30^\circ$, with a very shallow barrier between them. A third minimum, about 5 kJ mol⁻¹ higher in energy, exists for a dihedral angle of 180° .

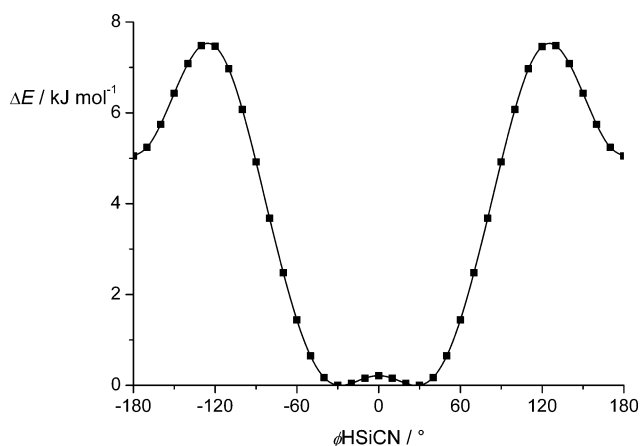


Fig. 7 Potential-energy scan (RHF/6-31G*) of ϕ HSICN for 2-Cl₂HSi-1,3-thiazole.

Selected bond lengths and angles for **4** calculated at various levels of theory and their experimental equivalents are given in Table 2.

Table 2 Comparison of *ab initio* and hybrid DFT (6-311++G**), and GED data of 2-trimethylsilyl-1,3-thiazole, **4** (bond lengths in pm and all angles in °)

Parameters	GED	RHF	MP2	B3PW91
r SiC _{Me}	185.5(2)	188.1	187.5	189.7
r Si(1)C(2)	188.3(5)	190.9	188.5	187.9
r CH	110.8(3)	108.4	109.2	109.2
r C(2)N(3)	134.5(6)	128.6	133.4	130.9
r C(2)S(6)	171.8(5)	174.3	173.9	175.5
r N(3)C(4)	137.0(5)	137.4	136.6	136.6
r C(4)C(5)	138.7(6)	134.4	138.3	136.5
r C(5)S(6)	170.0(5)	172.1	170.6	171.7
\angle Si(1)C(2)N(3)	120.4(4)	121.4	121.9	122.7
\angle Si(1)C(2)S(6)	125.4(4)	125.6	125.1	124.6
\angle C(2)N(3)C(4)	110.0(4)	112.3	111.2	112.2
\angle N(3)C(2)S(6)	114.3(4)	113.0	113.0	112.7
\angle N(3)C(4)C(5)	115.4(4)	115.6	115.5	115.7
\angle C(4)C(5)S(6)	110.0(2)	109.4	109.7	109.6
\angle C(5)S(6)C(2)	90.3(2)	89.7	90.5	89.9
\angle C(5)C(4)H(7)	124.8(2)	125.3	124.7	124.8
\angle S(6)C(5)H(8)	121.9(1)	122.3	122.1	121.8
\angle C(2)Si(1)C(9)	111.8(7)	108.6	108.0	108.4
\angle C(2)Si(1)C(13/17)	107.1(7)	107.7	107.6	107.7
\angle SiCH	112.1(4)	111.0	110.9	111.0
ϕ N(3)C(2)Si(1)C(9)	180.0(2)	180.0	180.0	180.0
ϕ N(3)C(2)Si(1)C(13/17) ^a	59.2(3)	59.9	59.9	59.7
ϕ C(2)Si(1)CH(14/18) ^a	57.2(7)	57.6	57.0	57.2
ϕ C(2)Si(1)CH(15/20) ^a	62.8(7)	62.4	62.4	62.6
ϕ C(2)Si(1)CH(16/19) ^a	177.2(7)	177.5	177.2	177.0
ϕ C(2)Si(1)CH(10/11) ^a	60.0(3)	60.6	60.5	60.6
ϕ C(2)Si(1)CH(12)	180.0(3)	180.0	180.0	180.0

^a Only the absolute value is considered.

GED

1-Trimethylsilyl-1,2,3-benzotriazole. The *ab initio* potential-energy surface scans had revealed two minima (representing *anti* and *syn* conformers; Fig. 1) for 1-trimethylsilyl-1,2,3-benzotriazole, and zero-point corrected free energies (RHF/3-21G*) give the energy difference as 0.16 kJ mol⁻¹, with the *syn* conformer lower in energy. Because the calculated difference in energy between the two conformers was much smaller than kT a dynamic model of the torsional motion was used. A potential-energy function (eqn (1)) was used to model six pseudo-conformers with C(15)Si(1)N(2)N(3) torsion angles (ϕ) of 5, 15, 25, 35, 45 and 55°, numbered 1 to 6, respectively. See Fig. 8 for the structure of conformer **1** and the atom numbering scheme.

$$E_n(\phi_n) = A(1 - \cos 3\phi_n) + B(1 - \cos 6\phi_n) \quad (1)$$

where n is the number of the conformer (1 to 6), E_n is the energy of conformer n in kJ mol⁻¹ and ϕ_n is the C(15)Si(1)N(2)N(3) dihedral angle of conformer n .

The Boltzmann distribution was then used to give the relative abundances of these six conformers, which together represent the complete distribution of torsion angles.

The potential-energy scan of ϕ C(15)Si(1)N(2)N(3) also revealed that the SiNC and SiNN angles depended on ϕ C(15)Si(1)N(2)N(3). An additional equation (eqn (2)) was therefore implemented in the model to define the SiNC angle for each conformer

$$a_n(\phi_n) = a_{syn} + \Delta a(1 - \cos 3\phi_n) \quad (2)$$

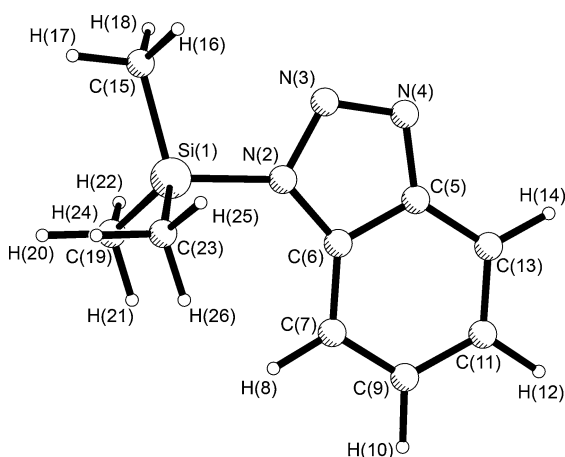


Fig. 8 Molecular structure and numbering scheme used for conformer 1 of 1-trimethylsilyl-1,2,3-benzotriazole (**3**). Numbering for conformers 2 to 6 is obtained by adding $(n - 1) \times 26$ to the numbering scheme below.

where n is the number of the conformer (1 to 6), a_n is the SiNN angle of conformer n , ϕ_n is the C(15)Si(1)N(2)N(3) dihedral in conformer n , a_{syn} is the SiNC angle of the *syn* (lowest energy) conformer and Δa is the difference between \angle SiNC for the *syn* and *anti* conformers.

As the molecule was planar at nitrogen throughout the series of geometry optimisations, the SiNN angle was calculated using eqn (3)

$$a_n(\text{SiNN}) = 360^\circ - a_n(\text{SiNC}) - a_n(\text{CNN}) \quad (3)$$

where $a_n(\text{SiNN})$ represents \angle Si(1)N(2)N(3) for conformer n , $a_n(\text{SiNC})$ represents \angle Si(1)N(2)C(6) for conformer n and $a_n(\text{CNN})$ represents \angle C(6)N(2)N(3) for conformer n .

Because the amount of experimental data available was limited and many parameters were required to model six different conformations, some assumptions were incorporated into the model describing the geometry of 1-trimethylsilyl-1,2,3-benzotriazole. From the geometry optimisations (MP2/6-311++G**) of the *syn* and *anti* conformers it was noted that equivalent bond lengths within the aromatic ring system differed by no more than 0.1 pm and that the bond angles in the benzotriazole moiety differed by no more than 0.5°. It was therefore decided to use a single value for each separate bond length and angle in the benzotriazole moiety to reduce the number of parameters. Very similar observations were made for the remainder of the molecule. The only exceptions were the Si(1)N(2)N(3)/C(6) angles and the torsion angles. As both the methyl and trimethylsilyl groups were calculated (MP2/6-311++G**) to be close to C_{3v} local symmetry, all SiC, SiN and CH bond lengths were replaced by an average value in each case, as were the HCH and CSiC angles. All six conformers were therefore modelled with local C_{3v} symmetry for the methyl and silyl groups and an identical benzotriazole moiety. These assumptions and the implementation of eqn (1) and (3) (*i.e.* modelling the conformation and the SiNN/C angle) enabled a reduction in the number of independent parameters to 29 instead of the 150 or so that would have been required if each conformer had an individual set of parameters.

The set of 29 parameters, which included four bond lengths and nine difference parameters, eight bond angles and one difference parameter, four tilt parameters for hydrogen atoms, one torsion

angle and two potential-energy terms, A and B , used for eqn (1), is listed in Table S2;† Fig. 8 shows the numbering scheme. Once all conformers were built and their energy differences obtained with respect to the lowest energy form, the relative amounts of each conformer were calculated using the Boltzmann distribution and the temperature of the experiment. After a full refinement had been performed, a scan of the terms A and B in the potential-energy equation was made to evaluate esd values for those parameters. For each step of the scans the R_G values were obtained and used to produce a plot (Fig. 9) of $R_G/R_{G(\text{min})}$ against the terms A and B . Hamilton's tables of R -factor ratios⁸ established the esds.

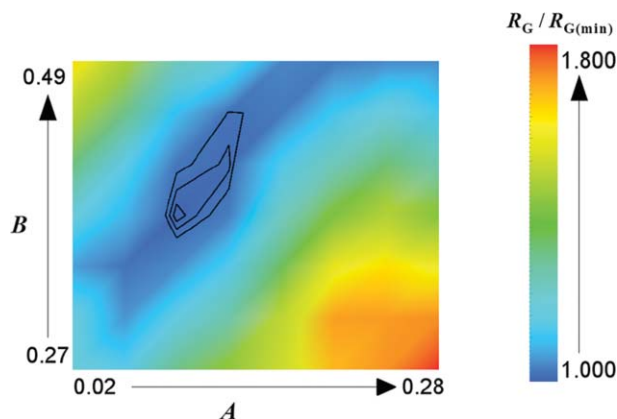


Fig. 9 Plot of $R_G/R_{G(\text{min})}$ against potential-energy terms A (p_{28}) and B (p_{29}) for 1-trimethylsilyl-1,2,3-benzotriazole. A and B are in kJ mol^{-1} ; $R_G/R_{G(\text{min})}$ is dimensionless. The innermost region indicates the 50% confidence limit, the next region just around it represents the 75% limit and the outermost enclosed region represents the 90% confidence limit.

Of the 29 parameters used for the refinement of the GED structure of 1-Me₃Si-1,2,3-benzotriazole, 21 were refined, subject to 10 restraints applied using the SARACEN method.⁹ One dependent angle was also restrained. In addition, nine sets of amplitudes of vibration were refined. The overall R_G value for the refinement was 0.080 ($R_D = 0.051$). The final observed and difference (experimental minus theoretical) radial-distribution curves are shown in Fig. 10 and the molecular-scattering intensity curves in Fig. S1.†

Interatomic distances and amplitudes of vibration for the refinement are given in Table S3, and the final least-squares correlation matrix in Table S4.† Final GED coordinates and calculated coordinates (MP2/6-311++G**) for conformer **1** are given in Tables S5 and S6, respectively.†

2-Trimethylsilyl-1,3-thiazole. A model of 2-trimethylsilyl-1,3-thiazole was built in C_s symmetry, consistent with the results of the *ab initio* calculations. Applying local C_{3v} symmetry to methyl and silyl groups, a total of 19 parameters was required. The molecule, including atom numbering, is shown in Fig. 11. A full description of the model is given in Electronic Supplementary Information (Table S7).†

All but two of the 19 parameters used in the GED model were refined. Restraints were applied to nine parameters. In addition seven sets of amplitudes were refined, of which five required restraints. The structure refined to give a final R_G value of 0.082 ($R_D = 0.058$). Fig. 12 shows the final observed and difference radial-distribution curves. The molecular-scattering

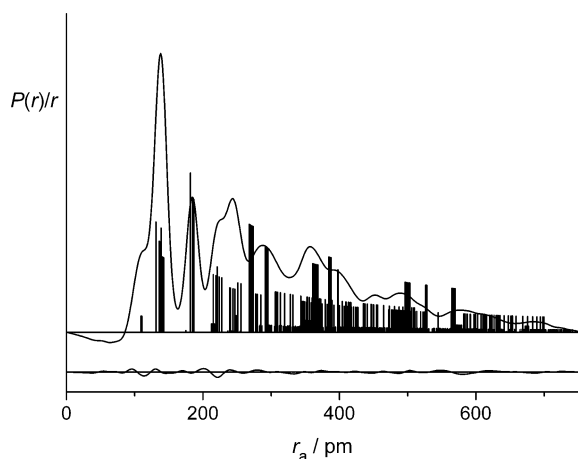


Fig. 10 Radial distribution curve for the refined structure of 1-trimethylsilyl-1,2,3-benzotriazole (**3**). Before Fourier inversion the scattering data were multiplied by $s \times \exp(-0.00002s^2)/(Z_{\text{Si}} - f_{\text{Si}})(Z_{\text{N}} - f_{\text{N}})$.

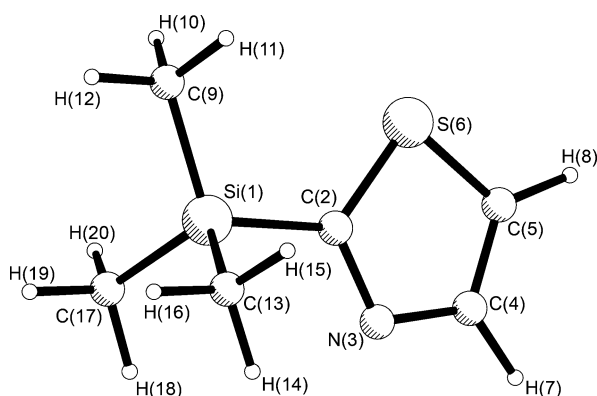


Fig. 11 Refined gas-phase structure of 2-trimethylsilyl-1,3-thiazole (**4**).

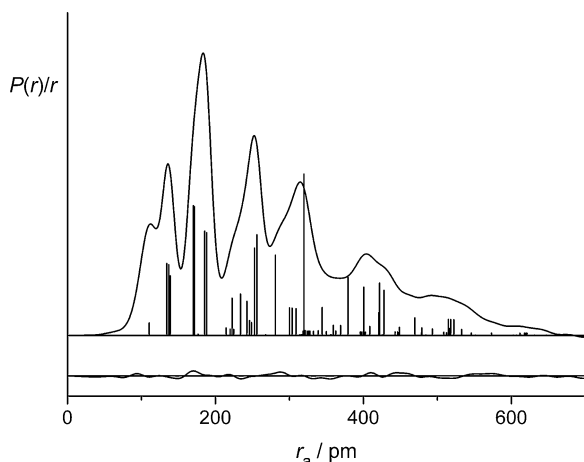


Fig. 12 Radial-distribution curve of the refined structure of 2-trimethylsilyl-1,3-thiazole (**4**). Before Fourier inversion the scattering data were multiplied by $s \times \exp(-0.00002s^2)/(Z_{\text{S}} - f_{\text{S}})(Z_{\text{N}} - f_{\text{N}})$.

intensity curves are shown in Fig. S2.† Interatomic distances and amplitudes of refinement are given in Table S8, and the final least-squares correlation matrix in Table S9. Final GED coordinates

and calculated coordinates (MP2/6-311++G**) are given in Tables S10 and S11, respectively.†

Discussion

1,2,3-Benzotriazole and its derivatives

The refined geometric parameters for 1-Me₃Si-1,2,3-benzotriazole are in reasonable agreement with *ab initio* and hybrid-DFT parameters (Table 1). From *ab initio* and hybrid-DFT calculations it was apparent that 1-Me₃Si-1,2,3-benzotriazole does not show strong interaction between silicon and the second ring nitrogen atom—the so-called α effect (here referring to the interaction between nitrogen acceptor and geminal silicon donor atom),¹¹ but there are aspects of the molecular structure that require explanation. The experimental SiNN angle for the *anti* conformer is, at 112.6°, the smallest in this series of molecules with anchored SiNN units, whereas the experimental SiNC angle is the largest, at 138.2°. The difference between these two parameters is 25.6°, so the coordination of the trimethylsilyl group to the ring is markedly asymmetric. However, in order to gauge the relevance of the sizes of these angles, *ab initio* and hybrid DFT calculations were performed on the parent 1,2,3-benzotriazole and on some of its 1-X_{3-n}X_n'Si-1,2,3-benzotriazole derivatives (X, X' = H, Me, F, Cl).

The parent molecule, 1,2,3-benzotriazole, can serve as a benchmark. Its calculated angles at N1 [N(2) in our numbering scheme] are given in Table 3, and the significant parameter in terms of asymmetric coordination of the substituent on this nitrogen atom is the difference between the calculated HNC and HNN angles, 11.4°. This difference parameter, which is a measure of the asymmetry of the coordinate to the substituent on nitrogen, varies from 6.3 to 22.4° in the compounds listed in Table 3. The largest value is for the *anti*-Me₃Si compound, and the smallest for *syn*-ClMe₂Si-1,2,3-benzotriazole.

There are three types of interactions that have significant impact on these angles. In simple terms, they are (a) repulsion between a methyl group on silicon and the hydrogen atom on C(7) [see Fig. 8 for the atom numbering scheme], (b) attraction between a halogen atom, in an equivalent position on silicon, and the hydrogen atom on C(7), and (c) attraction between silicon and the ring nitrogen atom, N(3). None of these can apply to the parent 1,2,3-benzotriazole, so the modest asymmetry of the coordination of the hydrogen atom to nitrogen in this case has to be an inherent property of the ring system. The N(2)N(3) and

Table 3 Comparison of bond angles (°) around N(2) of derivatives of 1,2,3-benzotriazole from *ab initio* calculations (MP2/6-311++G**)

Derivative	$\angle X(1)-N(2)N(3)$	$\angle X(1)-N(2)C(6)$	XNC–XNN	$\angle N(3)-N(2)C(6)$
H-	118.5	129.9	11.4	111.6
<i>anti</i> -H ₃ Si-	117.1	133.7	16.6	109.2
<i>syn</i> -Me ₃ Si-	119.9	131.1	11.2	109.0
<i>anti</i> -Me ₃ Si-	114.3	136.7	22.4	109.0
<i>anti</i> -F ₃ Si-	116.6	134.0	17.4	109.4
<i>gauche</i> -FH ₂ Si-	117.9	132.6	14.7	108.9
<i>gauche</i> -ClH ₂ Si-	119.1	132.8	13.7	107.9
<i>gauche</i> -ClMe ₂ Si-	118.6	131.0	12.4	109.1
<i>syn</i> -ClMe ₂ Si-	122.3	128.6	6.3	109.1
<i>syn</i> -Cl ₂ HSi-	118.1	132.6	14.5	109.3

N(3)N(4) distances in the NH compound are 135.6 and 131.6 pm, respectively. The N(2)N(3) distance is longer than N(3)N(4), as was the case for **3**, although the difference is larger in **3**. For both these molecules the lengths of the bonds N(2)N(3) relative to N(3)N(4) suggests that the former is more like single bond. For **3** N(2)C(6) and N(4)C(5) are almost equal in length and in the hydrogen-substituted analogue they differ by only 1.2 pm, and are therefore close to what one would expect for a fully aromatic system. More double-bond character in the ring on one side of the nitrogen atom than the other would lead to one angle to the substituent being larger than the other. The picture is therefore at least self-consistent.

Replacing the hydrogen substituent on N(2) with a silyl (SiH₃) group has remarkably little effect, and for the *syn* conformer of the Me₃Si derivative the situation is similar. But twist the trimethylsilyl group to give the *anti* conformer and the SiNN and SiCN angles each change by more than 6°. *Ab initio* calculations (MP2/6-311++G**) showed that the distance between H(8) and the hydrogen atoms H(16) and H(18) was just 240.1 pm, which is almost exactly the sum of van der Waals radii between two hydrogen atoms. As the hydrogen atoms are all bonded to carbon atoms, they carry a partial positive charge. Therefore, if the hydrogen atoms come too close to one another the repulsion terms increase and consequently raise the energy of the molecule. However, the overall energy is barely raised. This suggests that there is more to the angle change than just a steric effect. The methyl groups withdraw electron density from silicon, leaving it with a partial positive charge, and thus facilitating electrostatic attraction between N(3) and Si(1)—but this should not depend on the conformation adopted by the trimethylsilyl group.

In the case of 1-F₃Si-1,2,3-benzotriazole only the *anti* conformer exists. There could be attraction between a fluorine atom and the hydrogen on C(7), and relative to the trimethylsilyl analogue there is a 2° shift of the substituent away from N(3) and towards C(6). The distance between the *anti* fluorine and H(8) is 258.3 pm. The combined van der Waals radii of hydrogen and fluorine amount to 267 pm, so the short interaction suggests that there is a weak intramolecular hydrogen bond. Its presence appears to be the reason why the trifluorosilyl derivative has the largest barrier to internal rotation of any of the 1-X₃Si-1,2,3-benzotriazole derivatives investigated in this study (Fig. 1). Considering that intramolecular hydrogen bonds can be stabilising factors for certain conformations of a molecule, it is at first sight surprising that the SiNN angle is not larger, thus strengthening the hydrogen bond between H(8) and the *anti*-positioned fluorine. The *anti* fluorine atom is more than 310 pm away from the nearest carbon atom of the benzene moiety, so there is no conflict there. The more likely explanation for this phenomenon is that of electrostatic attractions between silicon and its geminal nitrogen. The three fluorine atoms draw the electron density away from silicon leaving it with a high partial positive charge. Nitrogen, on the other hand, carries a partial negative charge. The charge difference between these two atoms appears to cause the SiNN angle to contract relative to the HNN angle found in 1,2,3-benzotriazole.

1,3-Thiazole and its derivatives

The experimental and theoretical SiCN angles in 2-Me₃Si-1,3-thiazole (**4**), 120.4(4) and 121.9°, respectively, do not of themselves

Table 4 Comparison of bond angles (°) from *ab initio* calculations (MP2/6-311++G**) around C(2) of halogenated and non-halogenated derivatives of 1,3-thiazole

Derivative	∠X(1)C(2)N(3)	∠X(1)C(2)S(6)	∠N(3)C(2)S(6)
H-	123.8	120.7	115.4
<i>anti</i> -H ₃ Si-	122.1	124.5	113.4
<i>anti</i> -Me ₃ Si-	121.9	125.1	113.0
<i>anti</i> -F ₃ Si-	120.6	125.2	114.1
<i>anti</i> -FH ₂ Si-	119.8	126.3	113.8
<i>gauche</i> -ClH ₂ Si-	121.7	124.6	113.6
<i>anti</i> -ClH ₂ Si-	119.4	126.7	113.8
<i>anti</i> -ClMe ₂ Si-	119.1	127.3	113.6
<i>anti</i> -Cl ₂ HSi ^a	122.3	123.9	113.9
<i>gauche</i> -Cl ₂ HSi ^a	119.5	126.3	114.0

^a The single H atom is *anti* or *gauche* to the nitrogen atom.

suggest that they are narrowed by any intramolecular effects such as the α effect, although they are a little smaller than the SiCS angles, 125.4(4) and 125.1°. However, the structure needs to be analysed more carefully. In the thiazole ring, C(2)N(3) and C(4)C(5) are formally double bonds. Angles at the sp²-hybridised atoms involved in double bonds are not all close to 120°, but those adjacent to the double bond are usually substantially larger, particularly with a silicon substituent. For example, the Si–C=C angle in *trans*-1,2-dichloro-1,2-disilylene is 128.1(1)°.¹⁰ The observed angles in **4**, with SiCN about 4° smaller than SiCS, suggests that there is a displacement of the trimethylsilyl group towards the ring nitrogen atom by an amount broadly comparable to that in the benzotriazole.

We have therefore investigated 1,3-thiazole and a series of its 2-silyl derivatives by theoretical means (Table 4). There is a consistent pattern in the silyl compounds, with the SiCN angle smaller than SiCS in every case, by 1.6 to 8.2°. However, in the parent compound, with hydrogen instead of silicon bonded to C(2), the HCS angle is smaller than HCN. This difference seems strange, but again we need to remember that C(2)N(3) is formally a double bond, whereas C(2)S(6) is single. Allowing for this, the C(2)H bond is displaced towards, not away from, the ring nitrogen atom, but the amount of the displacement is several degrees smaller than those of the silyl groups. The pattern is therefore exactly the same as we have observed in the benzotriazole derivatives.

The largest differences between the SiCN and SiCS angles were found for the *anti* conformer of 2-ClH₂Si-1,3-thiazole, at 7.3°, and for *anti* 2-ClMe₂Si-1,3-thiazole, at 8.2°. The N(3)C(2)S(6) angles of the silyl derivatives of thiazole were mostly around 113.6°, but 115.4° in the parent compound.

Conclusions

Experimental and computed structures of a series of 1-silyl-1,2,3-benzotriazole and 2-silyl-1,3-thiazole derivatives, with different substituents on silicon, show significant distortion of the silyl groups towards the neighbouring ring nitrogen atom. The extent of the distortion varies a little with the nature and conformation of the substituents, but when there is a hydrogen atom instead of a silyl group the displacement is significantly smaller.

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