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Molecular Structure and Conformations of 2,2-Di-*tert*-butyl-1,3-diaza-2-silacyclopentane: Gas Electron Diffraction and Quantum Chemical Calculations

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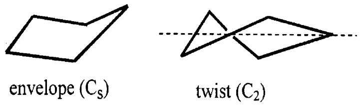
The geometric structure and conformational properties of the saturated five-membered-ring compound 2,2-di-*tert*-butyl-1,3-diaza-2-silacyclopentane, $(t\text{-Bu})_2\text{Si(NH)}_2(\text{CH}_2)_2$, was investigated by gas electron diffraction and quantum chemical methods (B3LYP and MP2 with 6-31G* basis sets). The compound exists as a mixture of two conformers, both possessing a twist conformation and C_2 symmetry. In the prevailing form (76(6) % at 305 K) the N–H bonds stagger the adjacent CH_2 groups, and in the minor form the N–H bonds eclipse the CH_2 groups. This conformational mixture corresponds to a free energy difference of $\Delta G° = 0.69(19)$ kcal/mol. The B3LYP method predicts a preference for the eclipsed conformer. The largest torsion occurs around the C–C bond with $\tau(\text{NCCN}) = 29.2(24)°$. The degree of puckering in the title compound is considerably smaller than that in silacyclopentane with $\tau(\text{CCCC}) = 49.7(14)°$. This has been rationalized by larger angle strain in the title compound.

Introduction

The conformation of saturated five-membered rings depends on a delicate balance between angle strain and torsional strain around the individual bonds.[1] Whereas angle strain favors a planar structure with mean endocyclic angles of 108°, torsional strain leads to a preference for puckered structures. If the ring contains atoms with lone pairs such as nitrogen or oxygen, orbital interactions (anomeric effects) also influence the ring structure.[2] In principle, such five-membered rings can adopt 10 envelope conformations depending on which ring atom is above or below the plane of the four remaining atoms, and 10 twist configurations in which rotation occurs clockwise or counterclockwise around one of the five ring bonds.[3,4] The preference for an envelope or twist conformation depends on the relative magnitude of torsional strain around the individual bonds. In cyclopentane this strain is equal for all five bonds, and envelope and twist conformers possess equal energies. This ring exhibits nearly free pseudorotation. In substituted cyclopentanes and in five-membered rings with heteroatoms torsional strain around the individual bonds differs and leads to a preference for either an envelope or a twist conformation.[4] Pyrrolidine, with one CH_2 group in the ring replaced by NH, and substituted pyrrolidines adopt envelope structures with the nitrogen atom above the plane of the carbon atoms (C_s symmetry).[5,6] In

Chart 1



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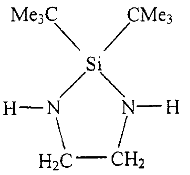
10.1021/ic0497836 CCC: $27.50

Chart 2



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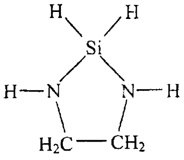


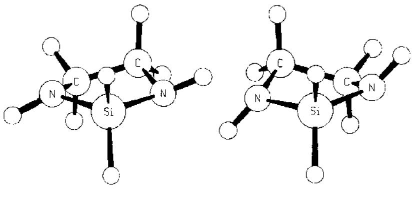
2

this conformation the largest torsional angle exists around the N−C bonds, and the torsional angle around the C−C bond opposite to the nitrogen atom is zero. On the other hand, silacyclopentane with one CH_2 group replaced by SiH_2 adopts a twist conformation possessing C_2 symmetry with the C_2 axis through the silicon atom and the center of the opposite C−C bond.[7] In this structure the largest rotation occurs around the C−C bond opposite to silicon and the smallest rotation around the Si−C bonds.

Interesting ring systems are 1,3-diaza-2-silacyclopentanes which contain two nitrogen atoms and one silicon atom in the saturated five-membered ring.[8] Although N,N′-bis(silylated) 1,3-diaza-2-silacyclopentanes were synthesized as early as in 1959,[8−10] the first crystal structure determinations were carried out in 2000.[10,11] The measured compounds possess five-membered rings with a twist conformation, and the largest torsional angle occurs around the C−C bond. In contrast to all other tested dihalosilanes, $(Me_3C)_2SiF_2$ reacts smoothly with the dilithium salt of ethylenediamine to form the NH-functionalized five-membered ring.[12] In the present study we report the gas phase structure of this new 2,2-di-*tert*-butyl-1,3-diaza-2-silacyclopentane (**1**) using gas electron diffraction (GED) and quantum chemical calculations. Attempts to obtain single crystals for X-ray crystallography failed.

Quantum Chemical Calculations

In the first step geometry optimizations were performed for the parent ring 1,3-diaza-2-silacyclopentane (**2**) to obtain information about the conformational properties of this ring system. The MP2 approximation with 6-31G* basis sets was applied. In principle, five different envelope and six different twist conformations are feasible for this ring. Independent of the chosen starting geometry, only two minima were obtained on the energy surface, both corresponding to a twist conformation with C_2 symmetry (Figure 1). The two structures differ by the orientation of the two N−H bonds. In **2a** the N−H bonds stagger the adjacent CH_2 groups, and in **2b** they eclipse the CH_2 groups. Conformation **2b** is predicted to be higher in energy by 1.7 kcal/mol. Transition between **2a** and **2b** can occur either by inversion of the ring, i.e., torsion around the C−C bond, or by inversion at the nitrogen atoms. The barrier for transition via nitrogen inversion (2.2 kcal/mol) is predicted to be lower than the barrier for ring inversion (3.9 kcal/mol). The optimization of an envelope conformation with the silicon atom out of plane and C_s symmetry resulted in a transition state, characterized by two imaginary frequencies and 4.2 kcal/mol higher in energy than **2a**. Very similar results are derived also by the hybrid method B3LYP/6-31G*, whereas the HF approximation with the same basis sets predicts only a single stable conformer **2a**.



2a (staggered) **2b** (eclipsed)

Figure 1. Stable conformers for 1,3-diaza-2-silacyclopentane (**2**).

The geometries of the two twist conformations of the *tert*-butyl-substituted ring **1a** (staggered) and **1b** (eclipsed) were optimized with MP2 and B3LYP methods and 6-31G* basis sets. Both methods predict the eclipsed form **1b** to be higher in energy by 1.0 kcal/mol. Frequency calculations were performed for both conformers with the B3LYP method. In the staggered conformer **1a** low frequency vibrations at 52 and 75 cm^{-1} correspond to torsions of the two *tert*-butyl groups, and ring deformations occur at 106 cm^{-1} and higher. In **1b** the two low frequency vibrations at 55 and 69 cm^{-1} correspond to complicated motions involving ring deformation and *tert*-butyl torsion, and the next frequency at 81 cm^{-1} relates to a pure torsion of the *tert*-butyl groups. In general, some vibrations in the eclipsed form **1b** are predicted at slightly lower frequencies, resulting in a higher entropy than that of the staggered conformer **1a** by about 4 cal/K·mol. Thus, the B3LYP method predicts conformer **1b** to possess a lower Gibbs free energy than **1a** by $\Delta G° = -0.5$ kcal/mol. All quantum chemical calculations were performed with the Gaussian 98 program package.[13]

Experimental Section

The synthesis and purification of compound **1** are described in ref 12. Electron diffraction patterns were recorded with the techniques described in refs 14 and 15. Preliminary mass spectrometric experiments demonstrated that slow decomposition of **1** or interactions with the inlet system occurred in inlet systems made of stainless steel, glass, and Teflon. Therefore, an effusion cell of stainless steel filled with small pieces of Schottki filter as absorber of the liquid sample was used in the GED experiment. The effusion cell with a cylindrical nozzle of 0.6 × 1.0 mm size (diameter × length) was filled with the sample directly before the GED/MS experiment. The mass spectra of the vapor under investigation were recorded simultaneously with the diffraction patterns for long and short camera distances. The mass spectra proved that no decomposition of the sample occurred at the temperature of the GED

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Table 1. Conditions of GED Experiment

nozzle-to-plate distance, mm	338	598
beam current, μA	0.99	0.67
accelerating voltage, kV	80.6	80.6
temp of effusion cell, °C	34(2)	31(2)
ionization voltage, V	50	50
exposure time, s	130	85
residual gas pressure, Torr	2.6×10^{-6}	3.2×10^{-6}

Table 2. Mass Spectral Data of the Saturated Vapor of $C_{10}H_{24}N_2Si$ ($U_{\mathrm{ioniz}} = 50$ V)

ion	*m/e*	abundance, %
$[C_{10}H_{24}N_2Si]^+$	200	5
$[C_{10}H_{24}N_2Si - (C_2H_2)]^+$	174	3
$[C_{10}H_{24}N_2Si - (C(CH_3)_3)]^+$	143	100
$[C_{10}H_{24}N_2Si - (C(CH_3)_3) - (C_2H_2) + (CH_3)]^+$	135	6
$[C_{10}H_{24}N_2Si - 2(C(CH_3)_3) + (CH_3)]^+$	101	93
$[C_{10}H_{24}N_2Si - 2(C(CH_3)_3)]^+$	86	26
$[SiNHC_2H_4]^+$	74	14
$[SiNH_2(CH_3)_2]^+$	71	8
$[(CH_3)_3]^+$	57	26

experiment (305 K). The conditions of the GED/MS experiment and the relative abundance of the characteristic ions of **1** in the mass spectrum are shown in Tables 1 and 2, respectively. The temperature of the effusion cell was measured by a W/Re-5/20 thermocouple that was calibrated by the melting points of Sn and Al. The electron wavelength was measured by polycrystalline ZnO. Electron image Kodak films were used for the registration of the diffraction patterns. The optical densities were measured by a computer-controlled MD-100 (Carl Zeiss, Jena) microdensitometer.[16] For each film (5 films for the long camera distance and 4 films for the short one) a rectangular area of about $130 \times 9-15$ mm^2 was scanned along both film diagonals. The data array for the diagonal consisted of 33−49 lines, 1299 points each. The step along a scan line was 0.1 mm, and the distance between the lines was about 0.28 mm. Scanning of the films with ZnO diffraction patterns for calibration of electron wavelength was done with a finer step width of 0.0125 mm.

The background functions $G(s)$ for the intensities $I(s)$ of the long and short camera distances were approximated by smooth lines, using polynomial fitting in the program. Analysis of the first and second-order derivatives of the $G(s)$ functions was used to eliminate oscillations of the initial $G(s)$, which were close to the oscillations of the $sM(s)$ function. No elimination of the high frequency oscillations was done. The molecular intensities $sM(s)$ were obtained in the ranges 4.5−28.5 Å^{-1} and 1.2−16.1 Å^{-1} for the short and long camera distances, respectively, and are presented in Figure 2.

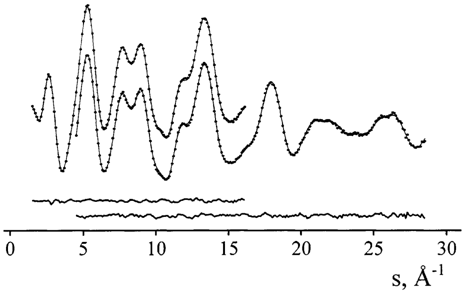

Figure 2. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) camera distances and residuals for mixture of **1a** and **1b**.

GED Analysis

The heaviest ion in the mass spectrum was the parent ion $C_{10}H_{24}N_2Si^+$ (Table 2). The other ions can be assigned to dissociation fragments of **1** due to electron impact in the ionization chamber of the mass spectrometer. No ions were observed which could be assigned to a decomposition product of the sample. Thus, the mass spectra demonstrate that the vapor consists only of the species with the stoichiometry $C_{10}H_{24}N_2Si$. No conclusions could be drawn about the conformational composition of the sample.

A conventional least-squares analysis of $sM(s)$ was carried out using a modified version of Program11 (least-squares refinement of intensity data).[17] Scattering amplitudes and phases of ref 18 were used. According to quantum chemical calculations, two stable conformers of **1** exist, namely, staggered (**1a**) and eclipsed (**1b**), each of which possesses C_2 symmetry. C_s symmetry was assumed for the *tert*-butyl groups, and the methyl groups were constrained to C_{3v} symmetry with a possible tilt angle between the C_3 axis and the C−C bond direction. The molecular model for both conformers was described by the same set of 25 geometric parameters. Atom numbering for the staggered conformer is shown in Figure 3. The geometry of the five-membered ring was described by the C−C and C−N bond lengths, the Si···X distance (X is a dummy atom at the center of the C−C bond), the NCC bond angle, and the torsional angle τ(N1C1C2N2). Furthermore, five bond lengths (C1−H, N−H, C5−H, Si−C, and C3−C5), twelve bond angles ($\angle$C3SiN1, $\angle$C3SiN2, $\angle$C5C3Si, $\angle$C7C3Si, $\angle$C5C3C6, $\angle$HN1Si, $\angle$HN1C1, $\angle H_{ax}$C1N1, $\angle H_{ax}$C1C2, $\angle H_{eq}C1H_{ax}$, $\angle H_{eq}$C1N1, and $\angle(HCH)_{\mathrm{methyl}}$), the tilt(CH$_3$) angle, and two torsional angles (τ(C5C3SiC4), $\tau(H_{\mathrm{trans}}$C5C3Si)) were used.

A preliminary least-squares analysis of $sM(s)$ demonstrated that the six ring hydrogen atoms give a small contribution to the $sM(s)$ function, in comparison with the 18 hydrogen atoms of the *tert*-butyl groups. Therefore, C1−H and N−H bond lengths, as well as the corresponding bond angles (see below), could not be refined as independent parameters. In the following steps of the least-squares analysis additional

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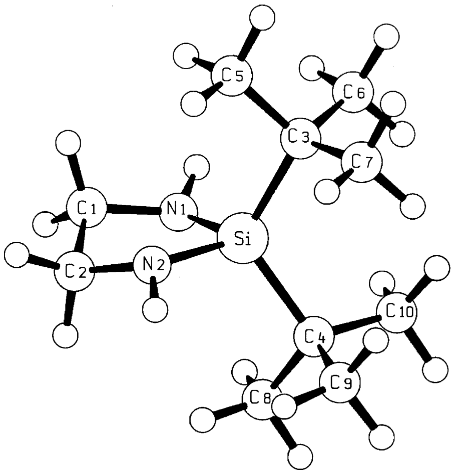

Figure 3. Structural model of 2,2-di-*tert*-butyl-1,3-diaza-2-silacyclopentane (**1a**) with atom numbering.

restrictions on the set of 25 structural parameters were made: ∠HN1Si, ∠HN1C1, ∠H_{ax}C1N1, ∠H_{ax}C1C2, ∠H_{eq}C1H_{ax}, ∠H_{eq}C1N1, and tilt(CH_3) were set to the calculated (B3LYP) values. Furthermore, the differences between the bond lengths (C1−C2) − (C3−C5), (C1−H) − (N1−H), and (C1−H) − (C5−H) and between the angles (∠C3SiN1) − (∠C3SiN2) and (∠C5C3Si) − (∠C7C3Si) were set to the calculated values. In the final analyses, 13 structural parameters (p_1 to p_{13} in Table 3) of the 25 above mentioned were refined simultaneously. The starting values for bond distances and angles were taken from the B3LYP calculations. For both conformers the starting values for vibrational amplitudes, as well as the vibrational corrections Δr, were derived from calculated (B3LYP/6-31G*) force fields using the approach of Sipachev incorporated in the program SHRINK.[19] This method takes the nonlinear relation between Cartesian and internal coordinates into account and corrects r_a distances to r_{h1} values.

Figure 4 shows radial distribution functions $f(r)$ for the two possible conformers **1a** (staggered) and **1b** (eclipsed), derived with calculated geometric parameters and vibrational amplitudes. These two functions differ appreciably in the range $r > 3$ Å. The differences are predominantly due to different orientations of the *tert*-butyl groups in the two conformers. Thus, electron diffraction intensities are sensitive to the conformational properties of this compound. Comparison of calculated functions with the experimental radial distribution function demonstrates that the staggered form **1a** is prevailing.

Table 3. Experimental and Calculated Geometric Parameters of Staggered Conformer **1a** (Å, deg)[a]

	GED r_{h1}	B3LYP/6-31G* r_e	MP2/6-31G* r_e
	Parameters of the Ring Fragment		
C1−H	1.119(2) p_1[d]	1.101	1.099
N−H	1.031(2) (p_1)	1.013	1.016
Si•••X[b]	2.544(5) p_2	2.546	2.534
Si−N1	1.724(5)	1.757	1.757
N1−C1	1.466(9) p_3	1.470	1.470
C1−C2	1.545(3) p_4	1.539	1.528
∠N1C1C2	107.0(3) p_5	106.4	105.7
τ(N1C1C2N2)	−29.2(24) p_6	−38.4	−42.5
∠N1SiN2	93.0(9)	92.6	92.5
∠SiN1C1	112.6(8)	110.7	109.9
∠HN1Si	121.9 p^*	121.9	121.2
∠HN1C1	113.6 p^*	113.6	113.6
∠H_{eq}C1H_{ax}	107.5 p^*	107.5	107.9
τ(SiN1C1C2)	23.7(14)	30.6	33.8
τ(N1SiN2C2)	−9.3(10)	−11.8	−12.9
Σα(ring)	532.2(15)	526.8	523.7
Σα(N)	348.1(8)	346.2	344.7
	Parameters of *tert*-Butyl Groups		
C5−H	1.115(3) (p_1)	1.097	1.096
C3−C5	1.551(3) (p_4)	1.545	1.534
Si−C	1.896(5) p_7	1.936	1.917
∠C3SiN1	111.0(3) p_8	111.7	111.5
∠C3SiN2	110.8(3) (p_8)	111.4	111.3
∠C5C3Si	107.9(2) p_9	108.0	107.7
∠C7C3Si	111.6 (2) (p_9)	111.7	111.8
∠C5C3C6	107.6(6) p_{10}	108.3	108.3
∠$(HCH)_{methyl}$	108.0(7) p_{11}	107.4	107.8
tilt(CH_3)[c]	1.3 p^*	1.3	1.4
τ(C5C3SiC4)	166.0(12) p_{12}	165.6	166.1
τ(H_{trans}C5C3Si)	169.8(40) p_{13}	178.6	178.0

[a] Error limits are $3\sigma_{LS}$ values. For atom numbering see Figure 3. [b] X is the central point of C1−C2 bond. [c] tilt(CH_3) = ²/₃(∠H_{trans}C5C3 − ∠H_{gauche}C5C3). [d] p_i: refined parameter. (p_i): the difference to parameter p_i was set to calculated value. p^*: not refined. Parameters without label are dependent parameters.

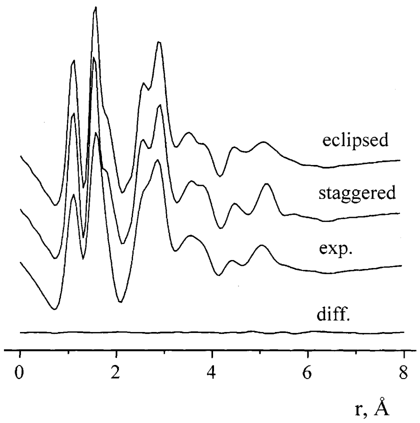

Figure 4. Radial distribution functions for calculated (B3LYP/6-31G*) geometries of staggered conformer **1a** and eclipsed conformer **1b**, experimental function, and difference curve for mixture.

Least-squares analyses were carried out for staggered and eclipsed models separately. In each case the 13 structural parameters and 12 groups of vibrational amplitudes (see Table 4) were refined simultaneously. Within each group the differences between the amplitudes were fixed to the calculated values. Good agreement between experimental and calculated molecular intensities with $R_f = 4.5\%$ was obtained for the staggered model **1a**, and significantly worse agreement for the eclipsed form **1b** with $R_f = 9.0\%$. It should be pointed out that the refined geometric parameters for the staggered conformer are very close to calculated values, except the for Si−N and Si−C bond lengths. These bond distances are predicted to be too long by both quantum chemical methods. On the other hand, some refined structural parameters for the eclipsed form differ appreciably from calculated values.

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Table 4. Interatomic Distances, Experimental and Calculated Vibrational Amplitudes, and Vibrational Corrections (without Nonbonded Distances Involving Hydrogen Atoms) for Staggered Conformer **1a**[a]

	r_a	l_{exp}	l_{calc}[b]	$\Delta r = r_\alpha - r_a$	group[c]
N1−H	1.026	0.075(2)	0.071	0.0050	1
C5−H	1.110	0.081(2)	0.077	0.0054	1
C1−H	1.113	0.082(2)	0.078	0.0055	1
N1−C1	1.465	0.048(5)	0.050	0.0015	2
C1−C2	1.543	0.050(5)	0.052	0.0025	2
C4−C8	1.549	0.050(5)	0.052	0.0018	2
Si−N1	1.723	0.057(4)	0.049	0.0012	3
Si−C3	1.894	0.064(4)	0.056	0.0016	3
N1···C2	2.417	0.063(4)	0.064	0.0034	4
C5···C6	2.498	0.072(4)	0.073	0.0049	4
C6···C7	2.540	0.073(4)	0.074	0.0051	4
N1···N2	2.500	0.066(4)	0.067	0.0021	4
Si···C1	2.650	0.059(4)	0.060	0.0085	4
Si···C5	2.789	0.085(3)	0.079	0.0054	5
Si···C6	2.852	0.093(3)	0.087	0.0063	5
N1···C3	2.974	0.097(3)	0.092	0.0080	5
N1···C4	2.980	0.094(3)	0.089	0.0032	5
N1···C8	3.140	0.139(3)	0.138	0.0000	5
C3···C4	3.237	0.084(9)	0.083	0.0050	6
N1···C5	3.358	0.187(9)	0.186	0.0156	6
N1···C5	3.404	0.160(9)	0.159	0.0134	6
C3···C10	3.578	0.134(6)	0.133	0.0053	7
C7···C9	3.595	0.175(6)	0.174	−0.0017	7
N1···C10	3.654	0.188(6)	0.187	0.0153	7
C1···C5	3.760	0.207(6)	0.206	0.0113	7
C7···C10	3.854	0.204(6)	0.202	0.0111	7
C3···C9	3.855	0.125(6)	0.124	0.0071	7
C1···C3	3.853	0.125(6)	0.123	0.0139	7
C1···C8	3.936	0.168(6)	0.167	0.0119	7
C1···C4	4.031	0.093(6)	0.097	0.0154	7
N1···C9	4.273	0.094(6)	0.098	0.0155	8
N1···C7	4.318	0.086(6)	0.090	0.0193	8
C1···C6	4.486	0.199(9)	0.203	0.0250	9
C3···C8	4.500	0.086(9)	0.090	0.0137	9
C6···C9	4.753	0.171(25)	0.149	0.0139	10
C1···C10	4.978	0.193(25)	0.171	0.0290	10
C6···C8	5.048	0.173(45)	0.150	0.0166	11
C7···C8	5.048	0.151(45)	0.129	0.0157	11
C1···C9	5.089	0.162(45)	0.140	0.0275	11
C1···C7	5.151	0.164(45)	0.142	0.0289	11
C5···C8	5.566	0.096(189)	0.104	0.0223	12

[a] Values in Å. Uncertainties are $3\sigma_{LS}$ values. For atom numbering see Figure 3. [b] B3LYP/6-31G*. [c] Group number of amplitude.

In the last step of the structural analysis the possibility of a mixture of both conformers was considered. The structural model of each conformer was described by the above-mentioned set of 25 parameters, 13 of which were refined independently together with the 12 groups of vibrational amplitudes. The differences between geometric parameters of staggered and eclipsed conformers were fixed to calculated (B3LYP) values. Preliminary refinements were performed with fixed vapor compositions. A plot of the *R* factors vs percentage of staggered conformer is shown in Figure 5. The best agreement between experimental and calculated *sM*(*s*) functions was achieved at a ratio of staggered and eclipsed conformers of 77%:23%. The uncertainty in the vapor composition was estimated from the relative increase of the *R* factor by Hamilton's method,[20] and it was 9% at a significance level of 0.05 (see Figure 5). Simultaneous refinement of geometric parameters, vibrational amplitudes, and vapor composition gave the ratio of 76(6)%:24(6)% (uncertainty is $3\sigma_{LS}$ value). Four correlation coefficients had values larger than 0.7: $p_3/p_4 = 0.86$, $p_3/p_6 = 0.72$, $p_5/p_6 = 0.80$, $p_9/p_{13} = 0.72$.

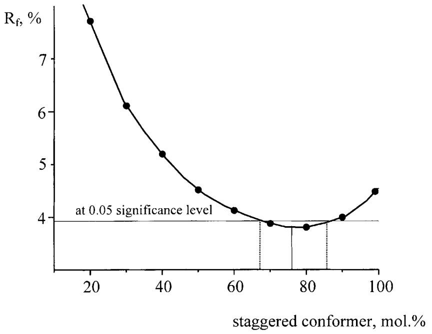

Figure 5. Agreement factor R_f for different contributions of staggered conformer **1a**.

The agreement factor for the mixture decreased to $R_f = 3.6\%$. The results for the staggered conformer, together with calculated values, are listed in Table 3. In addition to the refined independent parameters, some important dependent parameters were included in Table 3. Interatomic distances, experimental and calculated vibrational amplitudes, and vibrational corrections (without nonbonded distances involving hydrogen atoms) are shown in Table 4. The difference curves between experimental and calculated *sM*(*s*) and *f*(*r*) functions are shown in Figures 2 and 4.

Discussion

According to the GED data, the dominant species (76(6)%) of the vapor of **1** at 305 K is the staggered conformer **1a**, which is shown in Figure 3. The concentration of the eclipsed conformer **1b** does not exceed 24(6)%. This corresponds to a difference in free enthalpies of $\Delta G° = 0.69(19)$ kcal/mol. Both quantum chemical methods, MP2 and B3LYP, predict **1a** to be lower in energy than **1b** by 1.0 kcal/mol. According to the B3LYP method, however, the Gibbs free energy of the eclipsed form **1b** is lower than that of the staggered conformer **1a** by $\Delta G° = -0.5$ kcal/mol, corresponding to a contribution of 65% of the eclipsed form under the conditions of the GED experiment. Such a high contribution is not compatible with the GED intensities. The five-membered ring in **1** possesses a twist conformation with the largest torsional angle around the C−C bond (τ(NCCN) = −29.2(24)°) and the smallest torsional angle around the Si−N bonds (τ(NSiNC) = −9.3(10)°). The torsional angle around the N−C bonds is intermediate (τ(SiNCN) = 23.7(14)°).

Table 5 compares important geometric ring parameters of **1** with those of silacyclopentane (**3**) and 1,1-difluorosilacyclopentane (**4**). The degree of puckering of the ring in **1** is considerably smaller than that of **3** and **4**. This is evident from the torsional angles around the C−C bond opposite to the silicon atom (49.7(14)° and 56.0(32)° in **3** and **4**, respectively, vs 29.2(24)° in **1**) and from the sum of the endocyclic bond angles, Σα(ring), which increases from 520.3(12)° in **3** and 513.1(31)° in **4** to 532.2(15)° in **1** (see Table 5). For a planar ring Σα(ring) would be 540°. This low degree of puckering in **1** can be rationalized by increased

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Table 5. Comparison of Important Ring Parameters in Saturated Five-Membered Rings of the Type $SiR_2X_2(CH_2)_2$

	$Si(t\text{-}Bu)_2(NH)_2$-$(CH_2)_2$ (**1**)[a] X = NH	$SiH_2Si(CH_2)_2$-$(CH_2)_2$ (**3**)[b] X = CH_2	$SiF_2(CH_2)_2$-$(CH_2)_2$ (**4**)[c] X = CH_2
Si−X	1.724(5)	1.892(2)	1.853(3)
∠XSiX	93.0(9)	96.3(3)	98.5(20)
∠SiXC	112.6(8)	103.6(3)	101.3(13)
$\Sigma\alpha_{ring}$[d]	532.2(15)	520.3(12)	513.1(31)
τ(XCCX)	−29.2(24)	−49.7(14)	−56.0(32)
τ(SiXCC)	23.7(14)	36.1(10)	38.3(22)
τ(XSiXC)	−9.3(10)	−13.3(4)	−13.7(8)

[a] This work. [b] Reference 7. [c] Reference 21. [d] Sum of endocyclic angles

angle strain in the ring system of **1**. The SiNC angle in unstrained silyldimethylamine (120.9(3)°)[22] is considerably larger than the SiCC angle in unstrained 1-silabutane (113.0(6)°).[23] In the cyclic compound **1** the SiNC angle (112.6(8)° is also about 9° larger than the SiCC angle (103.6(3)°) in **3.** Therefore, increased angle strain leads to a less puckered, i.e., more nearly planar ring in **1** than in **3** or **4**.

Both computational methods (B3LYP and MP2 with 6-31G* basis sets) result in similar geometric parameters. The MP2 approximation predicts the C−C bond lengths to be about 0.01 Å shorter and the sum of the endocyclic bond angles, Σα(ring), about 3° smaller than does the B3LYP method. The two theoretical methods reproduce the experimental structure satisfactorily, except for the Si−N and Si−C bond lengths and the degree of puckering. Both methods predict the Si−N and Si−C bonds to be too long (see Table 3). Because of ring strain the experimental Si−N bond (1.724(5) Å) in **1** is slightly longer than those in unstrained silyldimethylamine (1.713(5) Å)[22] or in bis(dimethylamino)-silane (1.708(3) Å).[24] The Si−N bond length in **1** is, however, well within the range of Si−N bond lengths observed in gaseous silylamines (1.70−1.74 Å).[25] The experimental Si−C bond length in **1** (1.897(5) Å) is longer than those in tetramethylsilane (1.875(2) Å)[26] and in di-*tert*-butyldifluorosilane (1.869(3) Å).[27] Si−C bond lengths depend strongly on the substituents at silicon and carbon and vary in a wide range from 1.82 to 1.94 Å.[25] Both quantum chemical methods predict a slightly larger degree of puckering of the five-membered ring than the GED method. This is evident from the torsional angles around the individual ring bonds in Table 3 and from the sum of the endocyclic bond angles, Σα(ring). The predicted values are about 5° (B3LYP) and 9° (MP2) smaller than the experimental sum.

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