Structure and Conformational Properties of 1,3,3-Trimethyl-1,3-Azasilinane – Gas Electron Diffraction, Dynamic NMR and Theoretical Study

Bagrat A. Shainyan,*[a] Svetlana V. Kirpichenko,[a] Sergei A. Shlykov*[b] and Erich Kleinpeter,*[c]

[a]A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Division of the Russian Academy of Science, 1 Favorsky Street, 664033, Irkutsk, Russian Federation. E-mail: bagrat@irioch.irk.ru

[b]Ivanovo State University of Chemistry and Technology, Dep. of Physics, Engels ave, 7, 153000, Ivanovo, Russian Federation. E-mail: shlykov@isuct.ru

[c]Chemisches Institut der Universität Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam (Golm), Germany. E-mail: ekleinp@uni-potsdam.de

Supporting Information

	Page
Experimental procedure	2
2D{^{1}H–^{13}C} NMR spectrum of 1,3,3-trimethyl-1,3-azasilinane	3
Results of G2, DFT and MP2 calculations of 1,3,3-trimethyl-1,3-azasilinane	4 – 9

Experimental procedure

General

Solvents were freshly distilled from the appropriate drying agents immediately before use (diethyl ether, sodium benzophenone ketyl; benzene, CaH_2). ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Brucker DPX 400 spectrometer (^1H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz). Chemical shifts (ppm) were determined relative to residual $CHCl_3$ (^1H, δ 7.27, $CDCl_3$), internal $CDCl_3$ (^{13}C, δ 77.0, $CDCl_3$), and external TMS (^{29}Si, δ 0.00, $CDCl_3$). The assignment of the ^1H and ^{13}C signals was made from the *j*-mod and 2D{^1H–^{13}C} NMR spectra.

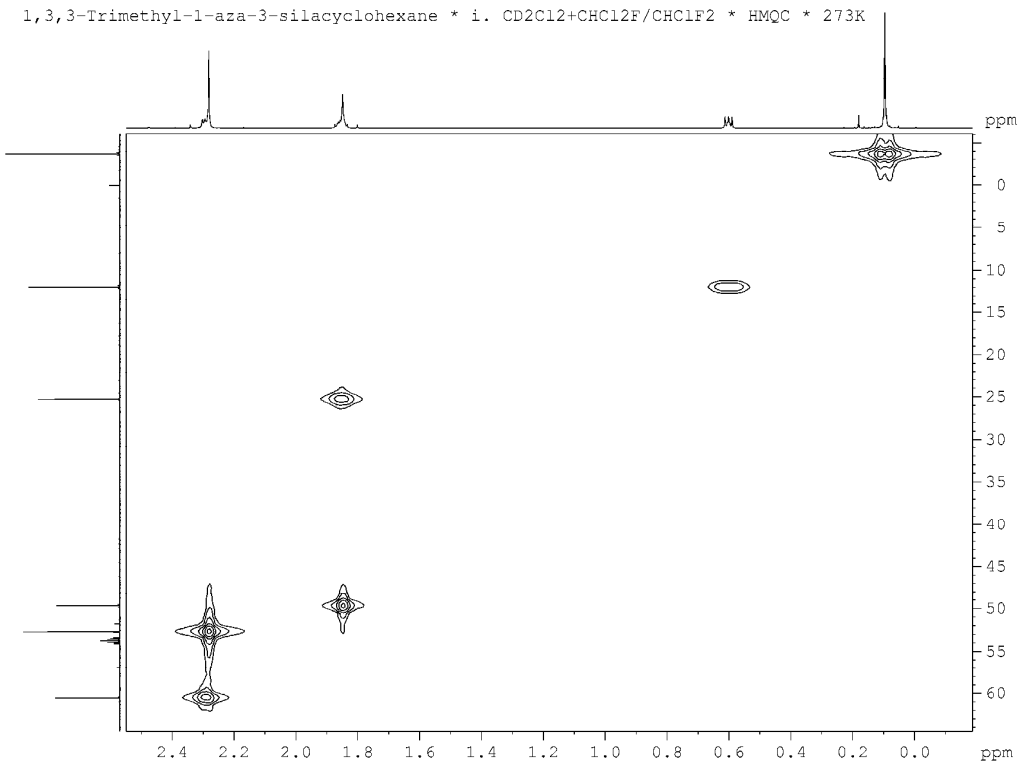
Synthesis

1,3,3-Trimethyl-1,3-azasilinane ***1*** was synthesized following a modified procedure (to avoid water workup) described earlier.[1] A solution of (chloromethyl)(3-chloropropyl)dimethylsilane **2** (3.407 g, 18.4 mmol) and $MeNH_2$ (2.775 g, 92.5 mmol) in C_6H_6 (20 ml) was heated in a sealed ampule for 6 h at 150 °C. The precipitate formed was filtered off, washed with ether and the solvents were distilled off. Vacuum distillation gave compound **1** (1.348 g, 51%), bp 55 °C/30 mm Hg. $\delta_{Si}(CDCl_3)$:

(Chloromethyl)(3-chloropropyl)dimethylsilane ***2*** was prepared from $(ClCH_2)Me_2SiH$ and allyl chloride in 38% yield by a described procedure.[2] Bp 78 °C/8 mm Hg, 89–90 °C/15 mm Hg.[1] $\delta_H(CDCl_3)$: 0.14 (6H, s, MeSi), 0.77 (2H, m, $SiCH_2CC$), 1.81 (2H, t.t, J 7.0, 7.8 Hz, $SiCCH_2C$), 2.79 (2H, s, $SiCH_2Cl$), 3.53 (2H, t, J 6.8 Hz, CCH_2Cl). $\delta_C(CDCl_3)$: –4.64 (CH_3Si), 11.48 ($SiCH_2CC$), 27.28 (CCH_2C), 29.97 (CH_2Cl), 47.69 (CCH_2Cl). $\delta_{Si}(CDCl_3)$: 3.30. ^1H NMR data for **1** (Table 2) and **2** coincide with the earlier reported.[1]

1 R. Dedeyne and M. J. O. Anteunis, *Bull. Soc. Chim. Belg*., 1976, **85**, 319–331.

2 Z. V. Belyakova, M. G. Pomerantseva and S. A. Golubtsov, *Zh. Obshch. Khim*., 1965, **35**, 1048−1052.



2D{^{1}H–^{13}C} NMR spectrum of 1,3,3-trimethyl-1,3-azasilinane **1**

1,3,3-Trimethyl-1,3-azasilinane **1**, NMe_{ax} B3LYP/aug-cc-pVTZ
E_{total} = −621.403774 au, μ = 0.73 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.243021	−0.817091	−1.118294
2	14	0	1.121882	−0.062576	−0.005741
3	6	0	0.399058	1.640311	0.413169
4	6	0	−1.115647	1.555811	0.686398
5	6	0	−1.899321	0.876127	−0.453570
6	7	0	−1.628978	−0.538132	−0.697048
7	6	0	2.740073	0.085252	−0.969106
8	6	0	1.433156	−1.063795	1.568619
9	6	0	−2.136909	−1.430027	0.327976
10	1	0	−0.110749	−0.390127	−2.120533
11	1	0	−0.132304	−1.896711	−1.243599
12	1	0	0.919230	2.096873	1.259289
13	1	0	0.570980	2.303709	−0.441443
14	1	0	−1.299537	1.019611	1.621706
15	1	0	−1.529549	2.558391	0.831360
16	1	0	−2.970228	0.974801	−0.260912
17	1	0	−1.698654	1.415381	−1.386012
18	1	0	3.505553	0.590196	−0.376095
19	1	0	2.605214	0.654384	−1.890520
20	1	0	3.131168	−0.897628	−1.239790
21	1	0	2.256032	−0.631103	2.142220
22	1	0	1.701884	−2.095887	1.334887
23	1	0	0.556285	−1.090203	2.216289
24	1	0	−3.199236	−1.232812	0.482380
25	1	0	−1.639482	−1.352447	1.307730
26	1	0	−2.034449	−2.462978	−0.008392

1,3,3-Trimethyl-1,3-azasilinane **1**, NMe_{eq} B3LYP/aug-cc-pVTZ
E_{total} = −621.411155 au, μ = 0.38 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.414188	−1.112639	−0.382665
2	14	0	1.181404	−0.147302	−0.009329
3	6	0	0.671897	1.641431	−0.352923
4	6	0	−0.745295	1.911476	0.185238
5	6	0	−1.795595	0.903160	−0.286909
6	7	0	−1.585635	−0.456494	0.210680
7	6	0	2.575727	−0.721867	−1.144571
8	6	0	1.681292	−0.386698	1.794336
9	6	0	−2.783307	−1.267615	0.054749
10	1	0	−0.535874	−1.235729	−1.476803
11	1	0	−0.340067	−2.122764	0.028742
12	1	0	1.383203	2.354948	0.069996
13	1	0	0.685117	1.801760	−1.436170
14	1	0	−0.738382	1.907320	1.277978
15	1	0	−1.077619	2.908184	−0.119121
16	1	0	−2.772668	1.232168	0.070571
17	1	0	−1.845706	0.915100	−1.392841
18	1	0	3.488342	−0.149683	−0.966127
19	1	0	2.308811	−0.601772	−2.195858
20	1	0	2.812112	−1.774901	−0.978796
21	1	0	2.550061	0.223913	2.048156
22	1	0	1.939683	−1.428603	1.993878
23	1	0	0.867632	−0.112211	2.466458
24	1	0	−3.063944	−1.414538	−1.002867
25	1	0	−3.623512	−0.798437	0.568109
26	1	0	−2.620592	−2.250564	0.497017

1,3,3-Trimethyl-1,3-azasilinane **1**, NMe_{ax} MP2/aug-cc-pVTZ
E_{total} = −619.793394 au, μ = 0.95 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.231936	−0.798024	−1.139679
2	14	0	1.107576	−0.050175	−0.008214
3	6	0	0.374940	1.635600	0.415640
4	6	0	−1.134914	1.511904	0.701827
5	6	0	−1.903910	0.854588	−0.460003
6	7	0	−1.630795	−0.555779	−0.730577
7	6	0	2.726881	0.101331	−0.953719
8	6	0	1.413189	−1.044302	1.562924
9	6	0	−2.053932	−1.429325	0.351601
10	1	0	−0.102701	−0.345272	−2.135334
11	1	0	−0.106654	−1.878622	−1.286467
12	1	0	0.894347	2.099739	1.263575
13	1	0	0.515475	2.307627	−0.443003
14	1	0	−1.301522	0.935321	1.620704
15	1	0	−1.570735	2.503865	0.879212
16	1	0	−2.982020	0.945411	−0.277777
17	1	0	−1.684366	1.411853	−1.382004
18	1	0	3.484229	0.615208	−0.352086
19	1	0	2.593324	0.667960	−1.880781
20	1	0	3.124531	−0.884783	−1.216388
21	1	0	2.284800	−0.647071	2.095457
22	1	0	1.614131	−2.096785	1.336507
23	1	0	0.560399	−1.006343	2.246759
24	1	0	−3.106309	−1.228420	0.577653
25	1	0	−1.481089	−1.327356	1.288871
26	1	0	−1.968244	−2.470067	0.022581

1,3,3-Trimethyl-1,3-azasilinane **1**, NMe_{eq} MP2/aug-cc-pVTZ
E_{total} = -619.801607 au, μ = 0.61 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.408400	-1.096318	-0.442151
2	14	0	1.172242	-0.150354	-0.011858
3	6	0	0.679833	1.632839	-0.358767
4	6	0	-0.730761	1.907976	0.194558
5	6	0	-1.776056	0.897161	-0.283133
6	7	0	-1.552596	-0.457279	0.225899
7	6	0	2.612094	-0.707184	-1.084051
8	6	0	1.570436	-0.405231	1.805619
9	6	0	-2.753773	-1.259726	0.027172
10	1	0	-0.566297	-1.150254	-1.540563
11	1	0	-0.337267	-2.131427	-0.083131
12	1	0	1.400539	2.349309	0.054095
13	1	0	0.671538	1.785772	-1.447264
14	1	0	-0.720058	1.884158	1.290768
15	1	0	-1.066759	2.909909	-0.102168
16	1	0	-2.760468	1.219438	0.074456
17	1	0	-1.815047	0.898715	-1.393182
18	1	0	3.514923	-0.133036	-0.850728
19	1	0	2.391154	-0.568774	-2.147116
20	1	0	2.840196	-1.765772	-0.921257
21	1	0	2.391907	0.241629	2.130880
22	1	0	1.863751	-1.442572	1.999228
23	1	0	0.692229	-0.185194	2.419497
24	1	0	-3.594361	-0.810429	0.564716
25	1	0	-2.586102	-2.264989	0.423550
26	1	0	-3.023327	-1.347677	-1.042542

1,3,3-Trimethyl-1,3-azasilinane **1**, NMe_{ax} G2
E_{total} = −620.096713 au, μ = 0.96 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.232564	−0.792385	−1.145091
2	14	0	1.104830	−0.051821	−0.008127
3	6	0	0.378971	1.640196	0.404409
4	6	0	−1.124374	1.517004	0.698070
5	6	0	−1.901182	0.857947	−0.451280
6	7	0	−1.626510	−0.550376	−0.724640
7	6	0	2.733110	0.087432	−0.947964
8	6	0	1.398943	−1.042805	1.571112
9	6	0	−2.056505	−1.434369	0.344351
10	1	0	−0.110857	−0.330342	−2.137085
11	1	0	−0.112019	−1.871460	−1.304329
12	1	0	0.901196	2.112225	1.246056
13	1	0	0.518484	2.307281	−0.457792
14	1	0	−1.283837	0.944525	1.620472
15	1	0	−1.559527	2.508802	0.880346
16	1	0	−2.977945	0.943001	−0.258655
17	1	0	−1.699653	1.414721	−1.377419
18	1	0	3.492569	0.597863	−0.347400
19	1	0	2.609932	0.651152	−1.877522
20	1	0	3.127182	−0.900274	−1.207138
21	1	0	2.275106	−0.656799	2.102707
22	1	0	1.583558	−2.099509	1.354601
23	1	0	0.548214	−0.988116	2.255581
24	1	0	−3.114194	−1.245925	0.553300
25	1	0	−1.502115	−1.336546	1.291857
26	1	0	−1.956539	−2.470595	0.007034

1,3,3-Trimethyl-1,3-azasilinane **1**, NMe_{eq} G2
E_{total} = −620.103662 au, μ = 0.58 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.407527	−1.098680	−0.441120
2	14	0	1.169852	−0.148556	−0.011379
3	6	0	0.676928	1.632028	−0.367924
4	6	0	−0.726217	1.901416	0.192053
5	6	0	−1.774982	0.900309	−0.283933
6	7	0	−1.552838	−0.455630	0.219706
7	6	0	2.612791	−0.713470	−1.082757
8	6	0	1.570810	−0.396363	1.809925
9	6	0	−2.753514	−1.259778	0.030429
10	1	0	−0.560187	−1.167502	−1.538791
11	1	0	−0.338443	−2.130027	−0.071856
12	1	0	1.397024	2.352795	0.038305
13	1	0	0.665466	1.784365	−1.456124
14	1	0	−0.709499	1.871080	1.287565
15	1	0	−1.061871	2.908043	−0.090337
16	1	0	−2.755041	1.225775	0.082739
17	1	0	−1.829085	0.910617	−1.392402
18	1	0	3.516984	−0.139055	−0.858749
19	1	0	2.392870	−0.586330	−2.146854
20	1	0	2.843708	−1.769803	−0.913461
21	1	0	2.387359	0.254782	2.136631
22	1	0	1.868871	−1.430299	2.010211
23	1	0	0.692749	−0.179140	2.423847
24	1	0	−3.592463	−0.804952	0.564969
25	1	0	−2.585356	−2.259281	0.439939
26	1	0	−3.030886	−1.364647	−1.034301