

Supporting Information

Bonding Situation in Be[N(SiMe₃)₂]₂ - An Experimental and Computational Study

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Experimental Section

General Procedures. All manipulations were performed in an atmosphere of purified argon using standard Schlenk and glove-box techniques. Toluene, Diethylether and hexane were dried using mBraun Solvent Purification System. Deuterated solvents were dried over activated molecular sieves (4 Å) and degassed prior to use. Anhydrous nature of the solvents were verified by Karl Fischer titration.

Chemicals. KN(Tms)₂ (Sigma Aldrich), BeCl₂ was prepared by burning Be-metal in Chlorine at temperatures > 500 °C.

Instrumentation. ¹H (300 MHz), ⁹Be (42.2 MHz), ¹³C{¹H} (75.5 MHz), ¹⁴N (21.7 MHz) and ²⁹Si (59.6 MHz) NMR (δ in ppm) spectra were recorded using a Bruker Avance DPX-300 spectrometer and the spectra were referenced to the trace of respective protonated solvent impurities present in the deuterated solvents. In case of ⁹Be the spectra were referenced externally to a 0.43 M solution of BeSO₄ in D₂O. For ¹⁴N the spectra were referenced externally to a 90 % solution of H₃C-NO₂ in CDCl₃. The ²⁹Si spectra were referenced to an external standard of neat Si(CH₃)₄ (TMS). IR spectra were measured in an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. The spectrometer was placed in a glovebox to allow measurement in inert gas atmosphere.

Synthesis of Be[N(SiMe₃)₂]₂ (**1**)^[1]

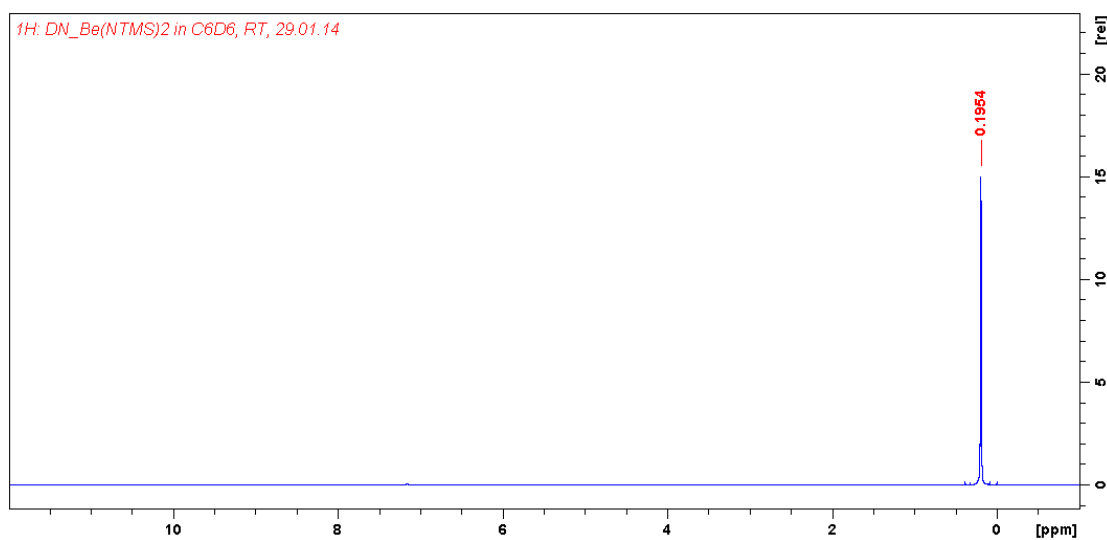
A mixture of BeCl₂ (3.996 g, 50 mmol) and KN(Tms)₂ (19.948 g, 100 mmol) was suspended in 100 mL of toluene at ambient temperature and 100 mL of Et₂O were added. The solution was heated to reflux for 12h and then filtered through a P4 glass frit, yielding in a clear yellow solution. All volatiles were removed in vacuo and the resulting viscous residue was distilled at 0.1 mbar. The product was collected as colourless viscous liquid **1** with a boiling point of 75 °C. Yield: 14.15 g (43 mmol, 86 %). mp: 8 °C. IR (neat): ν 2951 (m), 1312 (m), 1249 (m), 947 (s), 816 (s), 755 (s), 679 (m), 616 (m), 402 (m) cm⁻¹. ¹H NMR (C₆D₆, 300 MHz): δ 0.20 (s, 72 H, Be(N(SiCH₃)₂)₂). ⁹Be (C₆D₆, 42.2 MHz): δ 12.29 (s, Be(N(SiCH₃)₂)₂). ¹³C NMR (C₆D₆, 75.5 MHz): δ 4.40 (Be(N(SiCH₃)₂)₂). ¹⁴N (C₆D₆, 21.7 MHz): -326.40 (s, Be(N(SiCH₃)₂)₂). ²⁹Si (C₆D₆, 59.6 MHz): -1.85 (s, Be(N(SiCH₃)₂)₂). ¹H NMR (Tol-*d*₈, 300 MHz): δ 0.16 (s, 72 H, Be(N(SiCH₃)₂)₂). ⁹Be (Tol-*d*₈, 42.2 MHz): δ 12.41 (s, Be(N(SiCH₃)₂)₂). ¹³C NMR (Tol-*d*₈, 75.5 MHz): δ 4.41 (Be(N(SiCH₃)₂)₂). ¹⁴N (Tol-*d*₈, 21.7 MHz): -326.48 (s, Be(N(SiCH₃)₂)₂). ²⁹Si (Tol-*d*₈, 59.6 MHz): -1.87 (s, Be(N(SiCH₃)₂)₂). ¹H NMR (THF-*d*₈, 300 MHz): δ 0.05 (s, 72 H, Be(N(SiCH₃)₂)₂). ⁹Be (THF-*d*₈, 42.2 MHz): δ 9.55 (s, Be(N(SiCH₃)₂)₂). ¹³C NMR (THF-*d*₈, 75.5

MHz): δ 5.64 (Be(N(SiCH₃)₂)₂). ¹⁴N (THF-*d*₈, 21.7 MHz): -337.31 (s, Be(N(SiCH₃)₂)₂). ²⁹Si (THF-*d*₈, 59.6 MHz): -5.80 (s, Be(N(SiCH₃)₂)₂).

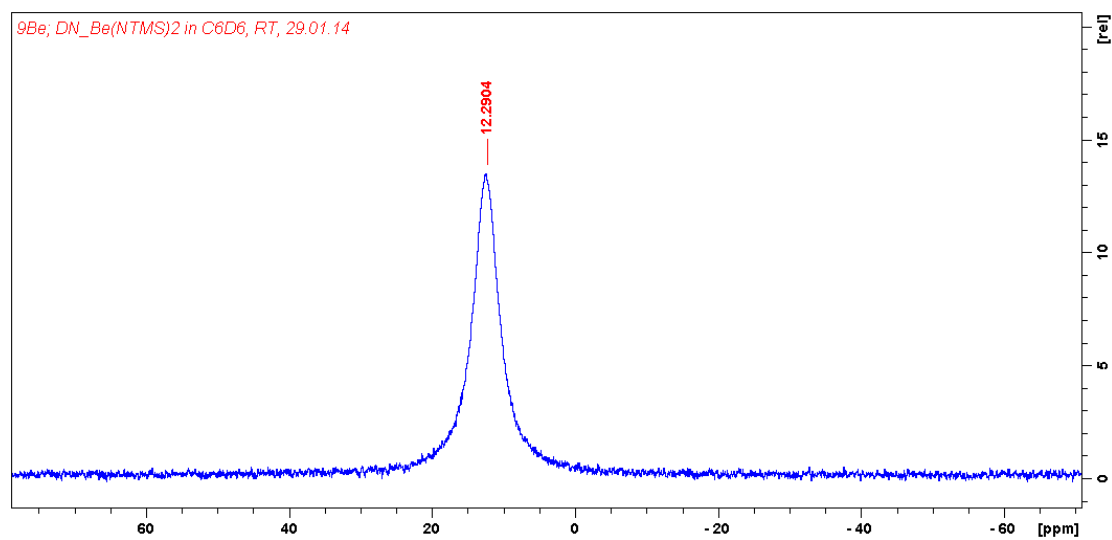
Overview of the chemical shifts of ¹H, ⁹Be, ¹³C, ¹⁴N and ²⁹Si (ppm) in Be(N(SiMe₃)₂)₂ in dependence on different solvents

	¹ H	⁹ Be	¹³ C	¹⁴ N	²⁹ Si
C ₆ D ₆	0.20	12.29	4.40	-326.40	-1.85
Tol- <i>d</i> ₈	0.16	12.41	4.41	-326.48	-1.87
THF- <i>d</i> ₈	0.05	9.55	5.64	-337.31	-5.80

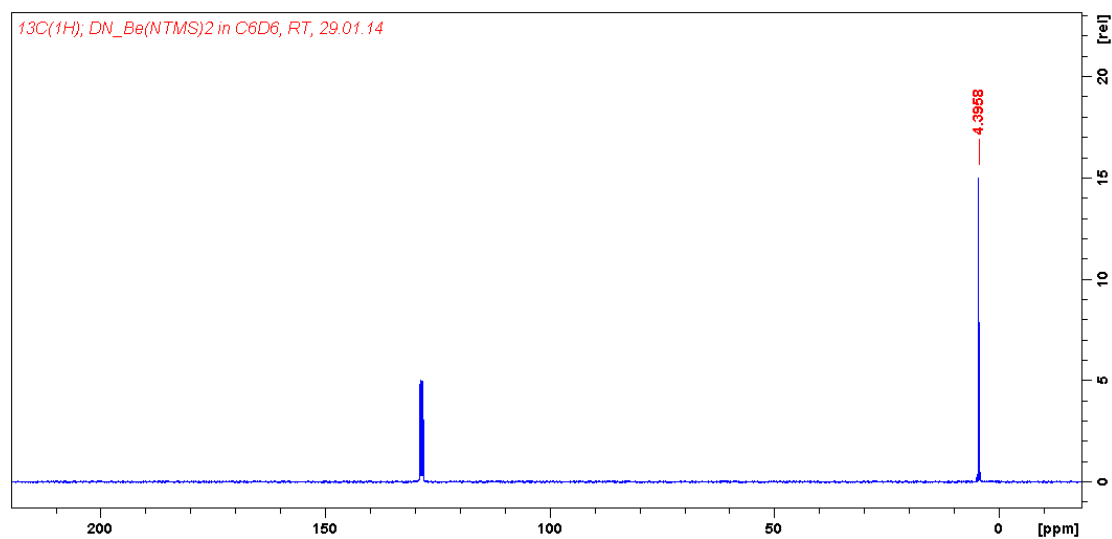
¹H-NMR: Be(N(Tms)₂)₂ in C₆D₆



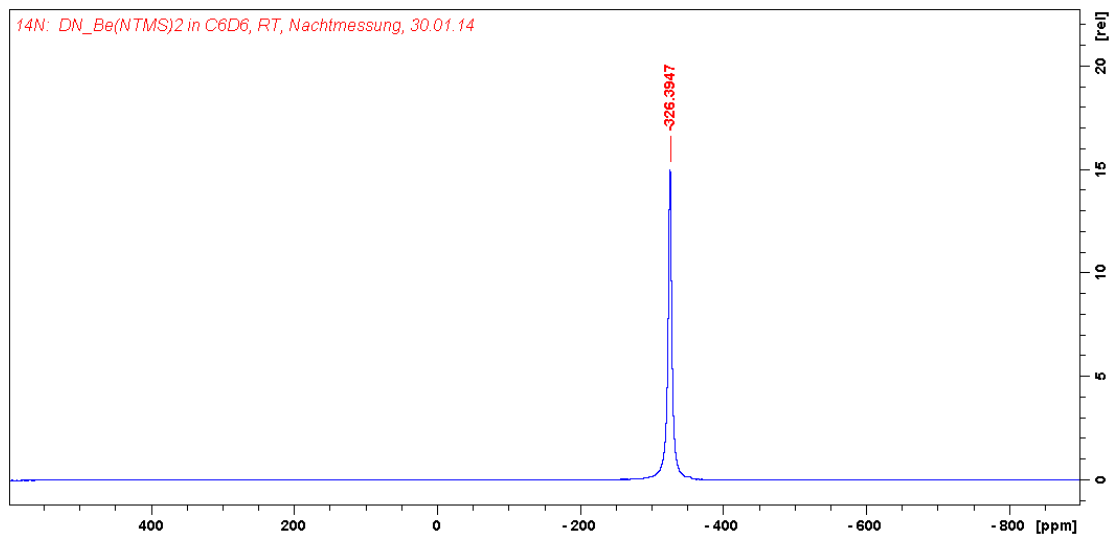
^9Be -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in C_6D_6



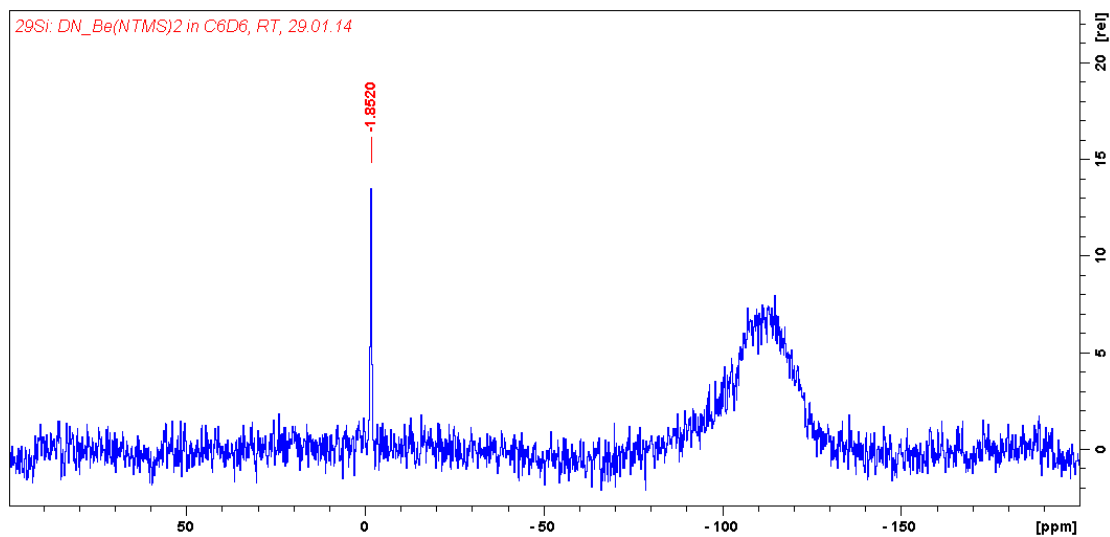
^{13}C -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in C_6D_6



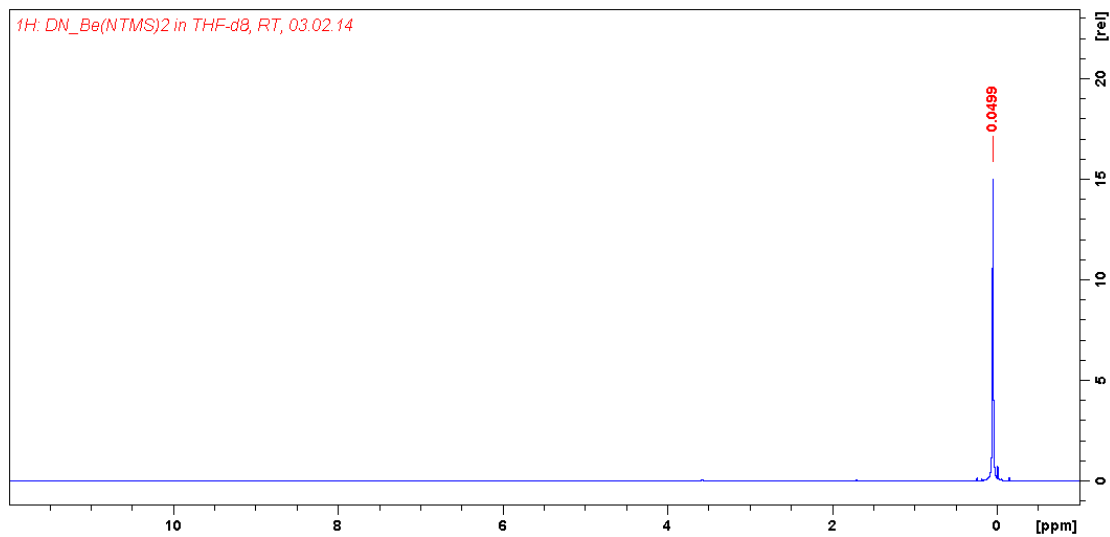
^{14}N -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in C_6D_6



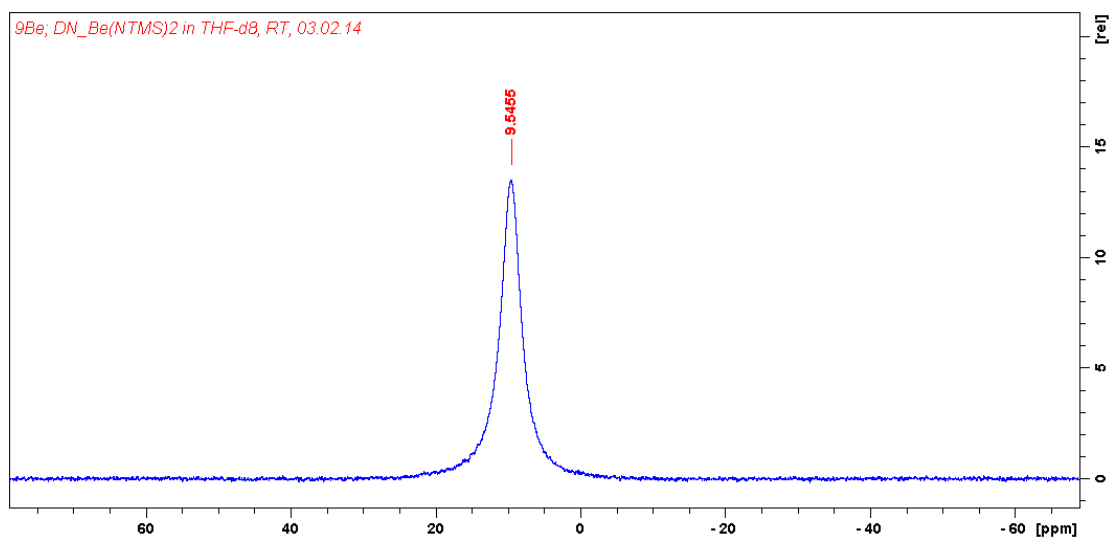
^{29}Si -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in C_6D_6



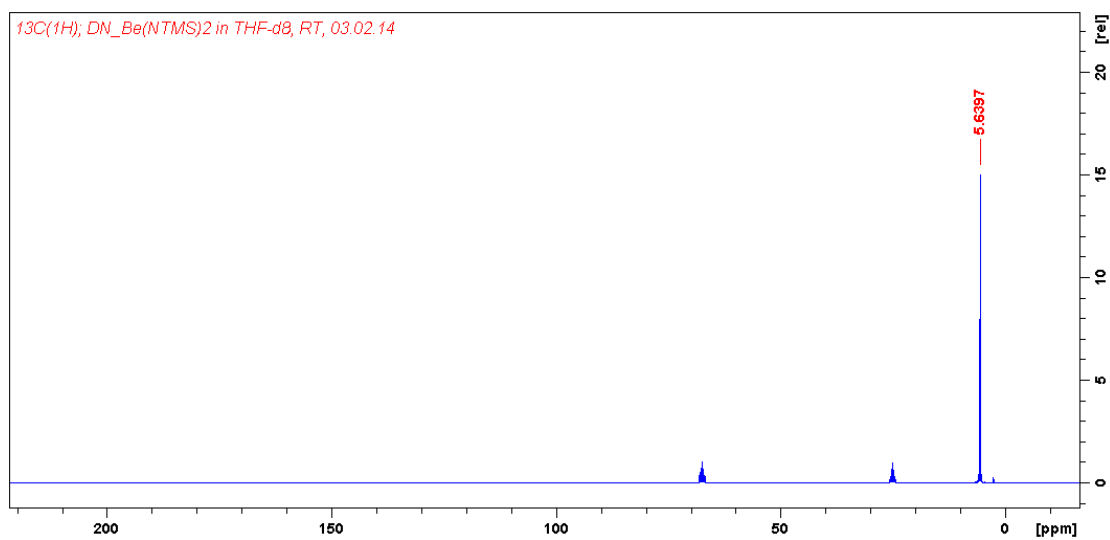
$^1\text{H-NMR}$: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{THF-}d_8$



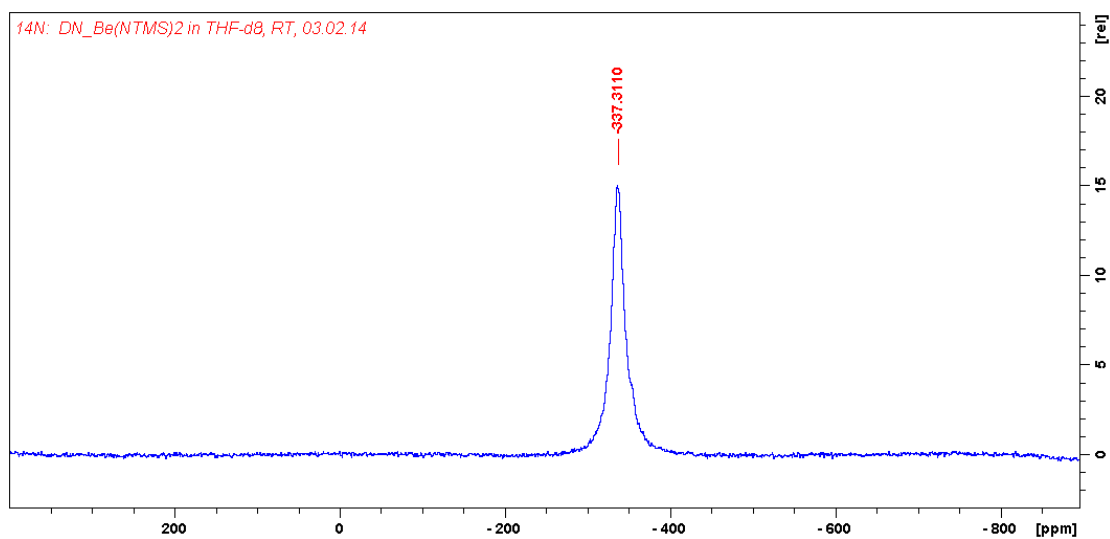
$^9\text{Be-NMR}$: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{THF-}d_8$



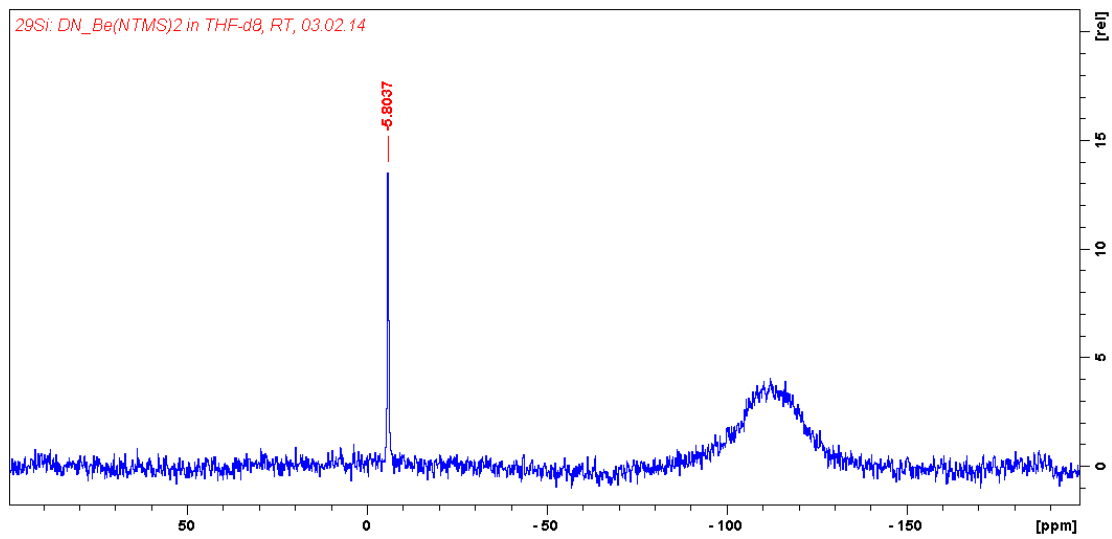
^{13}C -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{THF-}d_8$



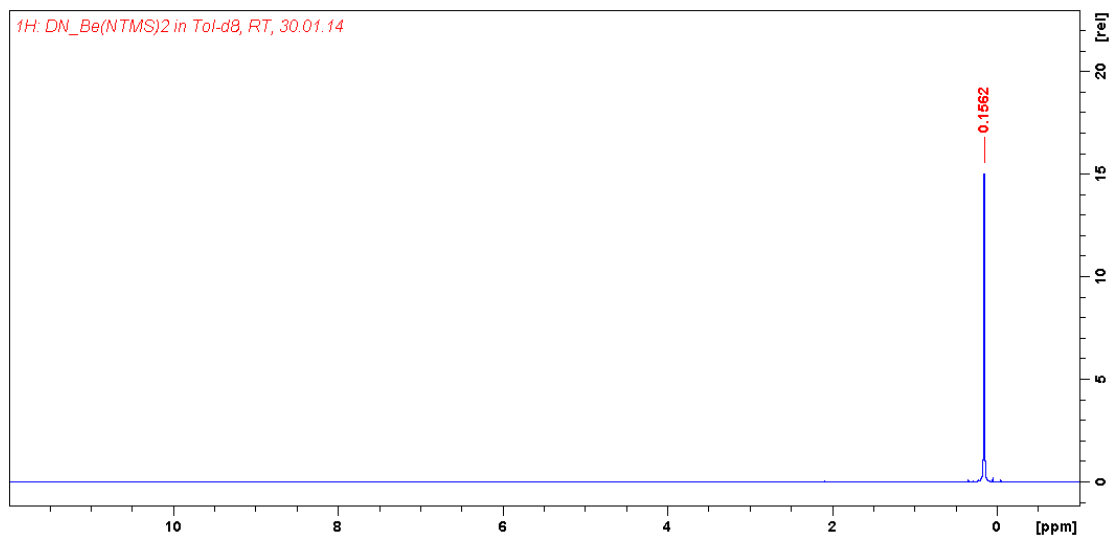
^{14}N -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{THF-}d_8$



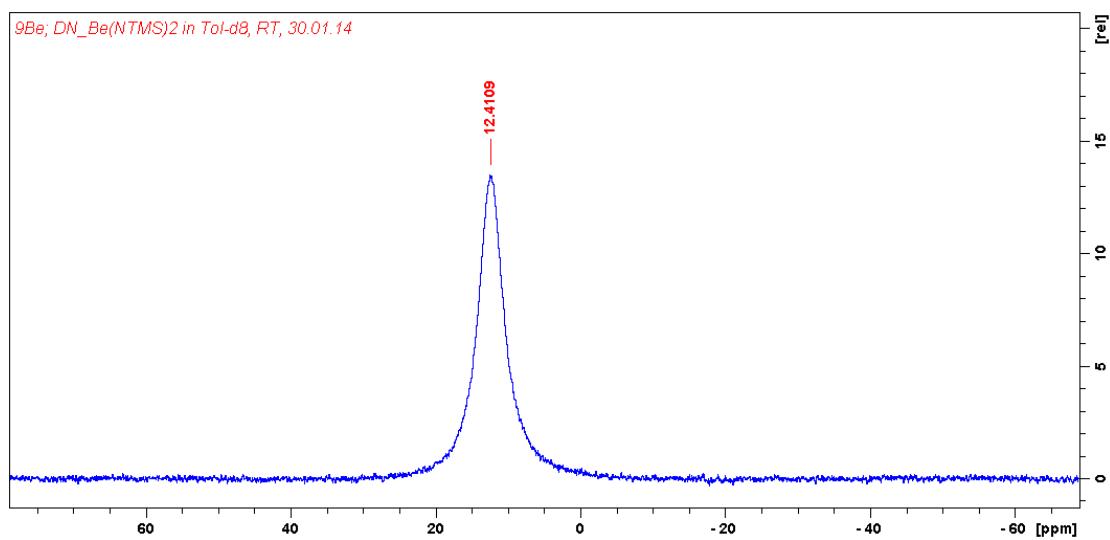
^{29}Si -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{THF-}d_8$



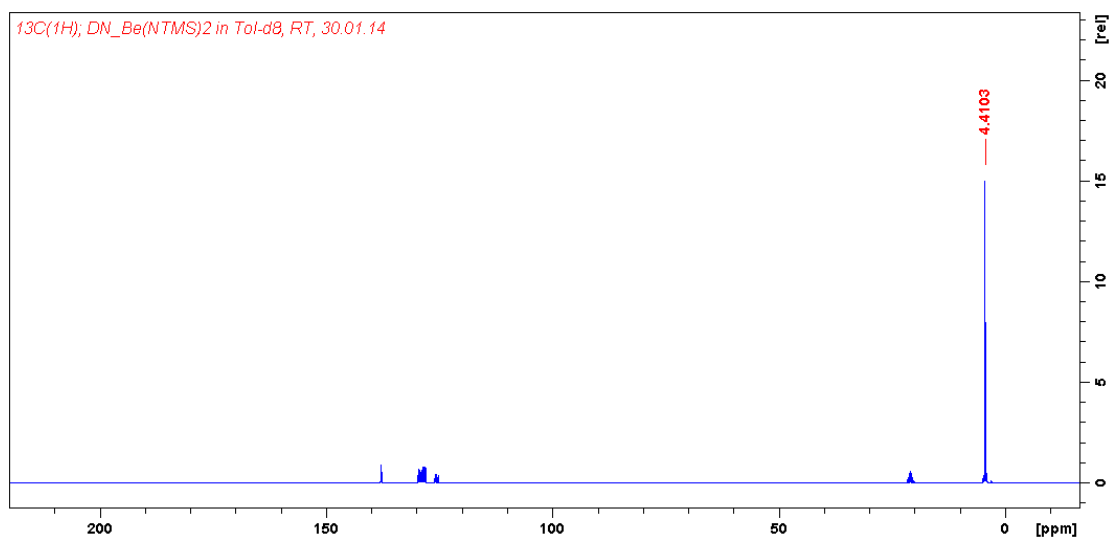
^1H -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{Tol-}d_8$



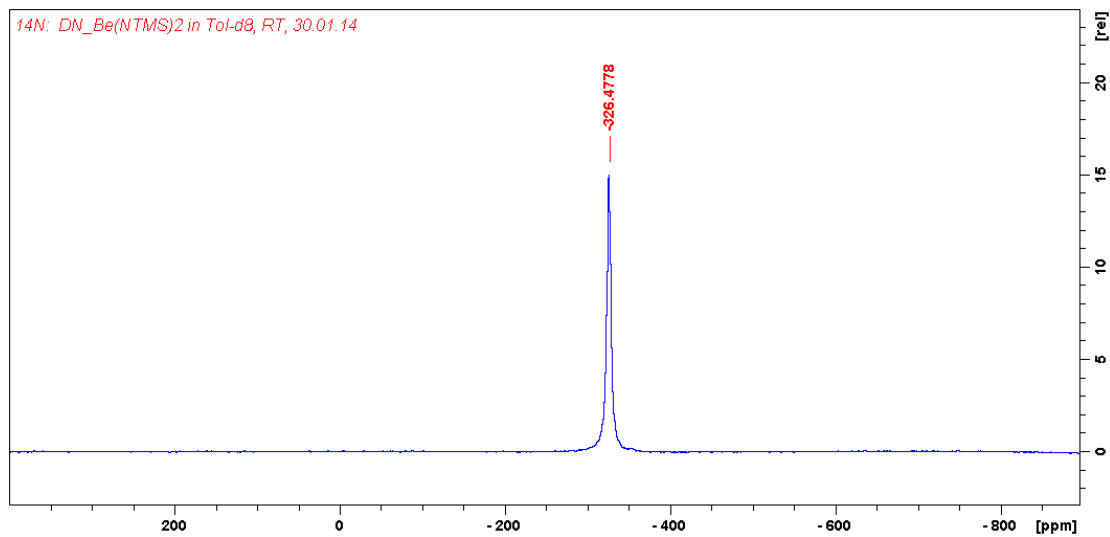
^9Be -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{Tol-}d_8$



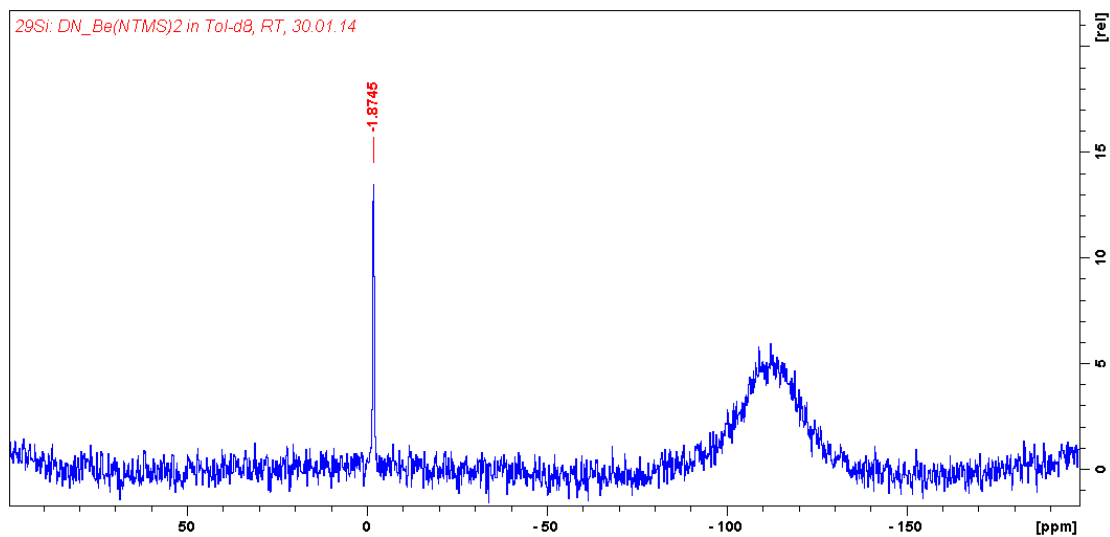
^{13}C -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{Tol-}d_8$



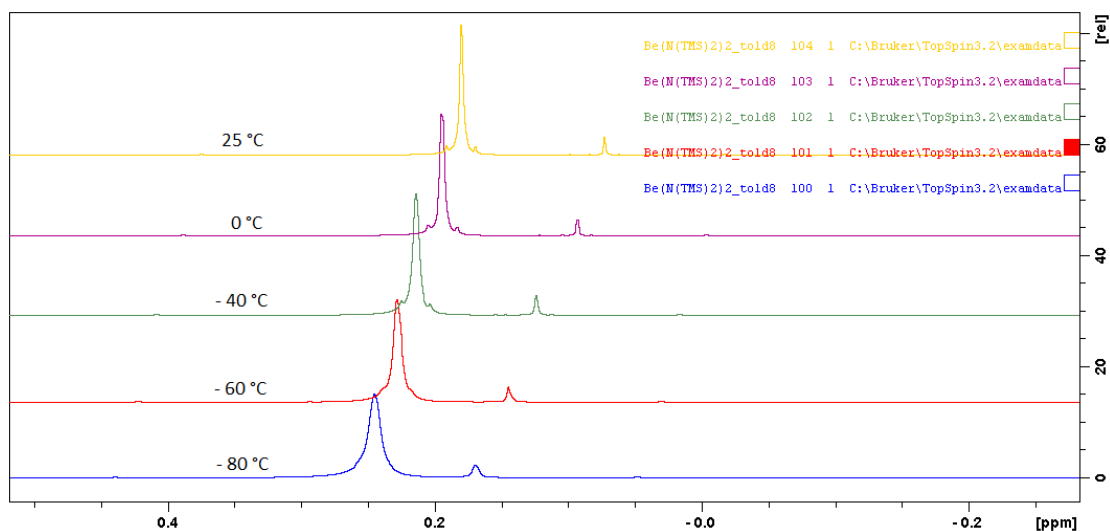
^{14}N -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{Tol-}d_8$



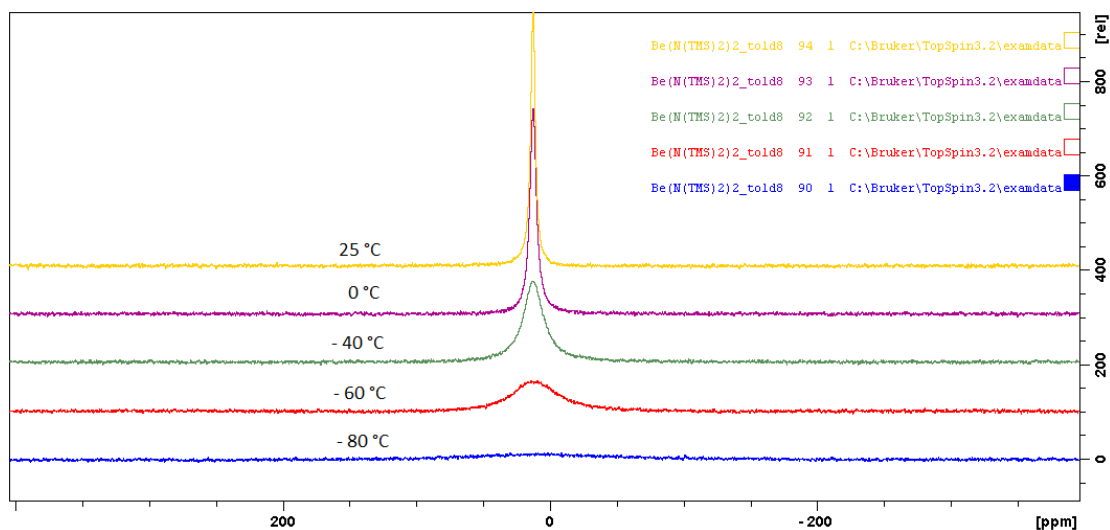
^{29}Si -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{Tol-}d_8$



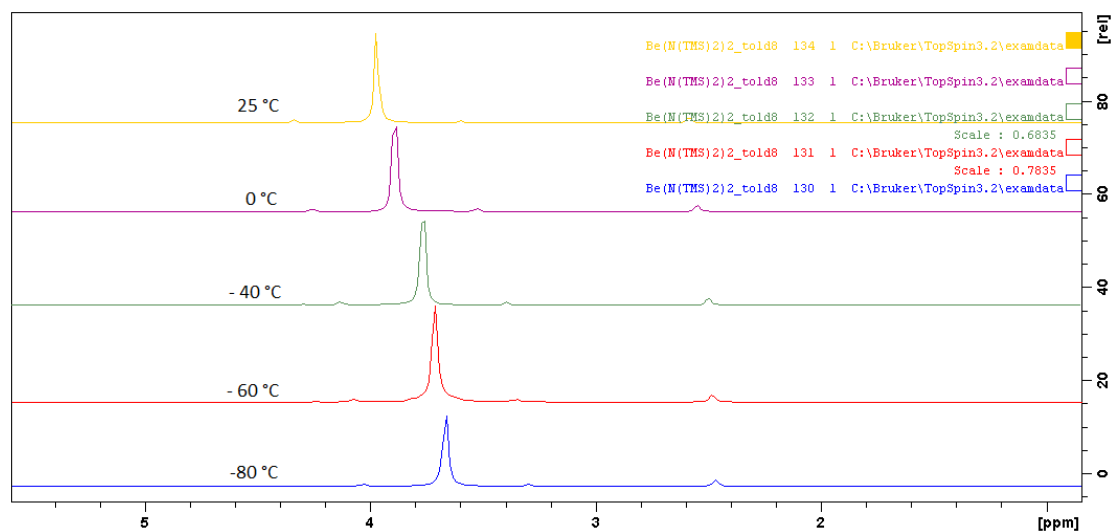
Temperature-dependant ^1H -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{Tol-}d_8$



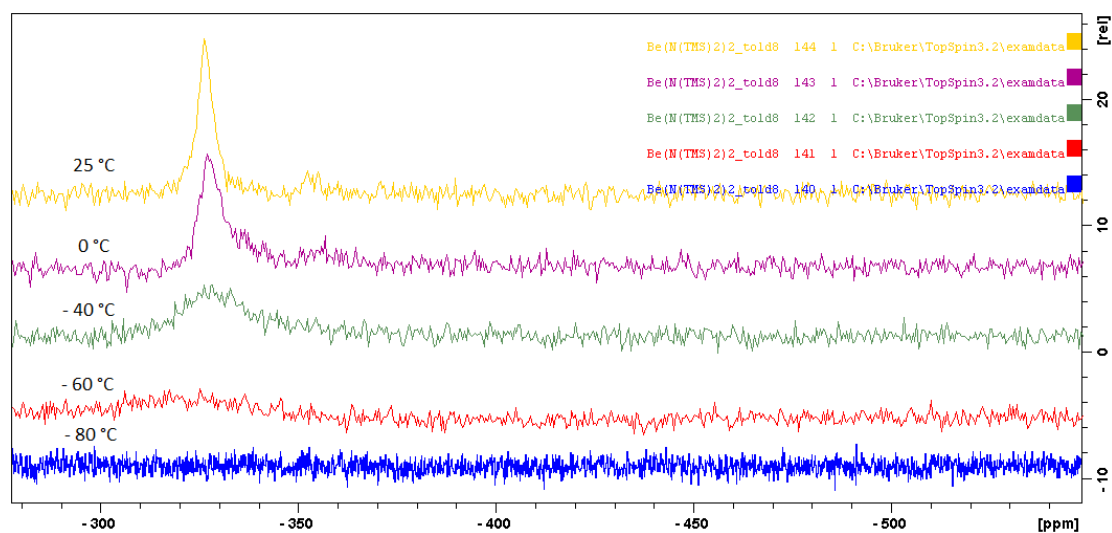
Temperature-dependant ^9Be -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{Tol-}d_8$



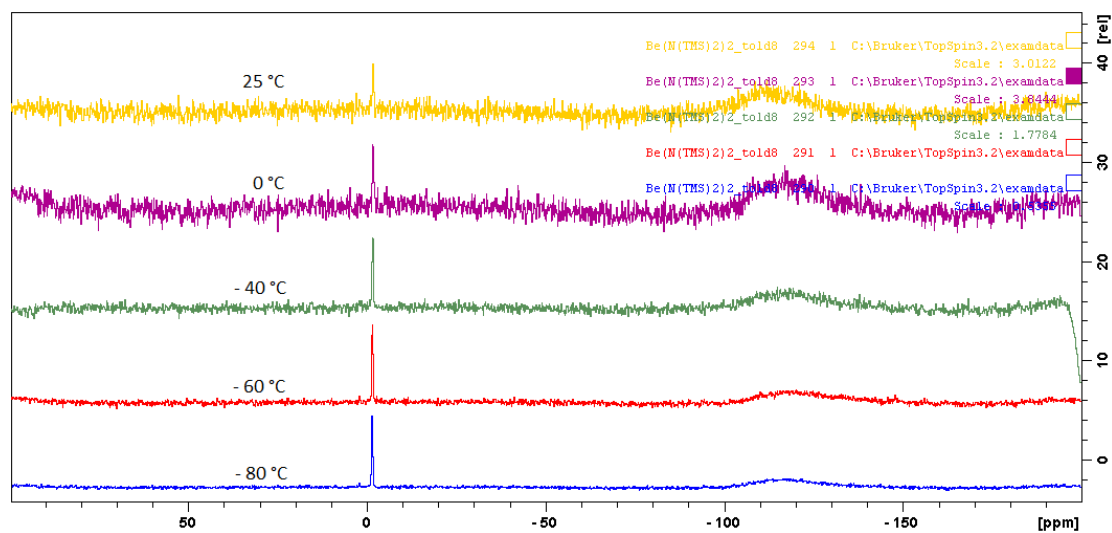
Temperature-dependant ^{13}C -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{Tol-}d_8$



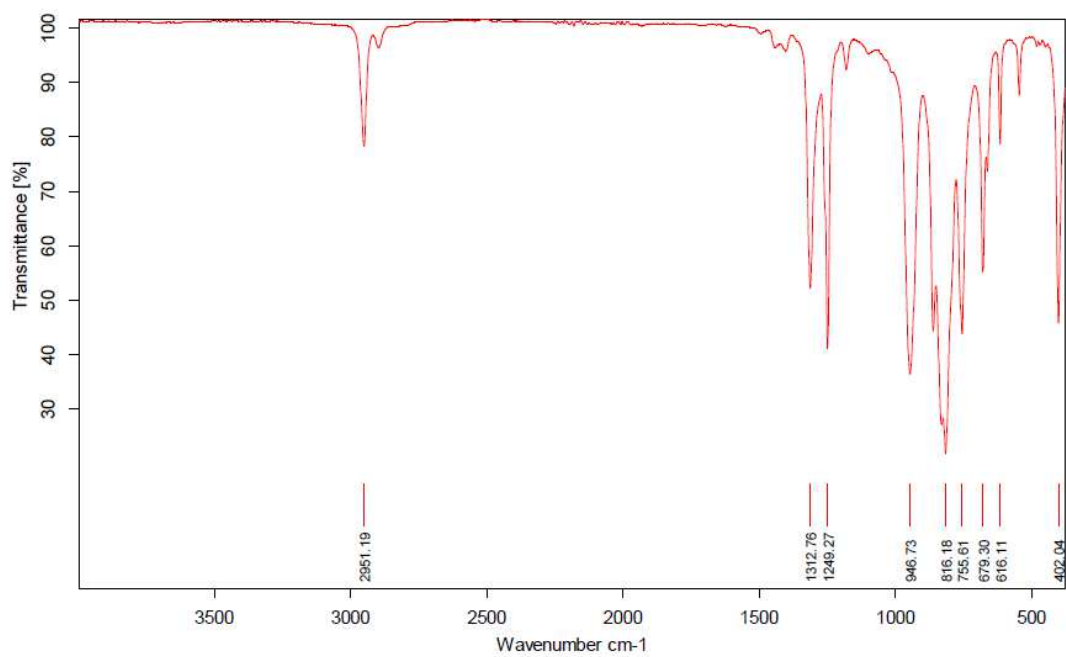
Temperature-dependant ^{14}N -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{Tol-}d_8$



Temperature-dependant ^{29}Si -NMR: $\text{Be}(\text{N}(\text{Tms})_2)_2$ in $\text{Tol-}d_8$



IR spectrum of $\text{Be}(\text{N}(\text{SiMe}_3)_2)_2$



Single-crystal X-ray analysis.

The crystal were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated $\text{Mo}_{K\alpha}$ radiation, $\lambda = 0.71073 \text{ \AA}$) at 100 K. The structure was solved by Direct Methods (SHELXS-97)^[2] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-97).^[3] Absorption corrections was performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2. Hydrogen atoms were refined rigid methyl groups. CCDC 1003578 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1: Crystal structure data of **1**

Identification code	dnp_035m
Empirical formula	$\text{C}_{12} \text{H}_{36} \text{Be N}_2 \text{Si}_4$
Formula weight	329.80
Density (calculated)	$0.966 \text{ g} \cdot \text{cm}^{-3}$
$F(000)$	728
Temperature	100(1) K
Crystal size	$0.300 \times 0.300 \times 0.300 \text{ mm}$
Crystal colour	colourless
Crystal description	cylindric
Wavelength	0.71073 \AA
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a [\AA]	9.8756(5)
b [\AA]	16.6972(8)
c [\AA]	14.5875(7)
α [$^\circ$]	90
β [$^\circ$]	109.492(2)
γ [$^\circ$]	90
Volume	$2267.54(19) \text{ \AA}^3$
Z	4
Cell measurement reflections used	38140
Cell measurement θ min/max	$2.19^\circ/31.54^\circ$
Diffractometer control software	BRUKER D8 KAPPA APEX 2 Vers. 3.0-2009
Diffractometer measurement device	Bruker D8 KAPPA series II with APEX II area detector system
Diffractometer measurement method	Data collection strategy APEX 2/COSMO
θ range for data collection	$1.919^\circ - 31.596^\circ$
Completeness to $\theta = 25.242^\circ$	99.2%
Index ranges	$-14 \leq h \leq 14$
	$-24 \leq k \leq 24$
	$-21 \leq l \leq 21$

Computing data reduction	BRUKER D8 KAPPA APEX 2 Vers. 3.0-2009
Absorption coefficient	0.255 mm ⁻¹
Absorption correction	Semi-empirical from equivalents
Computation absorption correction	BRUKER AXS SMART APEX 2 Vers. 3.0-2009
Max./min. Transmission	0.75/0.64
R_{merg} before/after correction	0.1095 / 0.0785
Computing structure solution	BRUKER D8 KAPPA APEX 2 Vers. 3.0-2009
Computing structure refinement	BRUKER AXS Inc. 2013 Vers. 2013/4
Refinement method	Full-matrix least-squares on F^2
Reflections collected	58472
Independent reflections	7557
R_{int}	0.0507
Data	6284
Restraints	0
Parameter	172
Goof	1.024
Weighting details	$w = 1/[\sigma^2(F_{\text{obs}}^2) + (0.0595P)^2 + 1.6098P]$
	where $P = (F_{\text{obs}}^2 + 2F_{\text{calc}}^2)/3$
$R_1 [I > 2\sigma(I)]$	0.0471
$wR_2 [I > 2\sigma(I)]$	0.1213
R_1 [all data]	0.0588
wR_2 [all data]	0.1326
Absolute structure parameter	
Largest diff. peak and hole	0.766/-0.692

Table 2: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Si(1)	7446(1)	2350(1)	1593(1)	26(1)
Si(2)	4843(1)	3481(1)	1286(1)	31(1)
Si(3)	2942(1)	673(1)	960(1)	24(1)
Si(4)	4191(1)	998(1)	3172(1)	25(1)
N(1)	5730(1)	2577(1)	1575(1)	22(1)
N(2)	4011(1)	1187(1)	1972(1)	22(1)
Be(1)	4881(2)	1880(1)	1786(1)	23(1)
C(1)	7750(2)	1259(1)	1855(2)	36(1)
H(1A)	7638	1137	2483	53
H(1B)	8723	1116	1877	53
H(1C)	7047	950	1342	53
C(2)	8855(2)	2904(2)	2553(2)	64(1)
H(2A)	8726	3481	2431	97
H(2B)	9805	2744	2545	97
H(2C)	8776	2781	3190	97
C(3)	7669(3)	2566(2)	398(2)	72(1)
H(3A)	6877	2321	-124	108
H(3B)	8583	2343	390	108
H(3C)	7663	3146	298	108
C(4)	3080(2)	3388(1)	1494(2)	39(1)
H(4A)	2536	2940	1110	59
H(4B)	2533	3885	1295	59
H(4C)	3249	3290	2186	59
C(5)	5875(3)	4315(1)	2017(3)	95(1)
H(5A)	6001	4225	2705	142
H(5B)	5355	4818	1802	142
H(5C)	6818	4345	1934	142
C(6)	4427(3)	3731(2)	-39(2)	73(1)
H(6A)	5326	3794	-178	109
H(6B)	3879	4232	-189	109
H(6C)	3859	3298	-440	109
C(7)	3584(3)	922(1)	-76(1)	46(1)
H(7A)	3459	1497	-216	69
H(7B)	3026	618	-653	69
H(7C)	4603	783	98	69
C(8)	1031(2)	996(1)	612(2)	47(1)
H(8A)	635	827	1114	71
H(8B)	477	750	-11	71
H(8C)	976	1581	548	71
C(9)	3043(2)	-430(1)	1149(1)	36(1)
H(9A)	4043	-606	1314	54
H(9B)	2452	-698	552	54
H(9C)	2688	-567	1682	54
C(10)	2413(2)	832(1)	3330(1)	37(1)
H(10A)	1826	1316	3139	55
H(10B)	2557	709	4013	55

H(10C)	1922	383	2921	55
C(11)	5084(2)	1886(1)	3911(1)	39(1)
H(11A)	6004	1986	3813	58
H(11B)	5252	1779	4600	58
H(11C)	4464	2356	3706	58
C(12)	5342(2)	101(1)	3643(1)	42(1)
H(12A)	4871	-376	3286	63
H(12B)	5485	33	4336	63
H(12C)	6275	176	3554	63

Table 3: Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*U_{11} + \dots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	24(1)	21(1)	38(1)	6(1)	16(1)	2(1)
Si(2)	23(1)	17(1)	49(1)	0(1)	9(1)	1(1)
Si(3)	22(1)	22(1)	27(1)	-3(1)	6(1)	-2(1)
Si(4)	24(1)	30(1)	25(1)	0(1)	13(1)	-1(1)
N(1)	21(1)	17(1)	27(1)	0(1)	9(1)	0(1)
N(2)	21(1)	22(1)	24(1)	-1(1)	10(1)	-2(1)
Be(1)	22(1)	21(1)	26(1)	-1(1)	10(1)	-1(1)
C(1)	33(1)	25(1)	54(1)	9(1)	21(1)	8(1)
C(2)	26(1)	46(1)	107(2)	-15(1)	3(1)	-4(1)
C(3)	83(2)	79(2)	85(2)	51(2)	69(2)	47(1)
C(4)	30(1)	36(1)	54(1)	0(1)	17(1)	9(1)
C(5)	37(1)	34(1)	180(4)	-44(2)	-9(2)	2(1)
C(6)	66(2)	85(2)	78(2)	54(2)	38(1)	38(1)
C(7)	61(1)	52(1)	26(1)	-6(1)	15(1)	-16(1)
C(8)	26(1)	39(1)	64(1)	-11(1)	-2(1)	2(1)
C(9)	38(1)	23(1)	45(1)	-5(1)	12(1)	-2(1)
C(10)	36(1)	41(1)	43(1)	-2(1)	26(1)	-6(1)
C(11)	37(1)	51(1)	31(1)	-12(1)	13(1)	-10(1)
C(12)	45(1)	48(1)	36(1)	14(1)	18(1)	14(1)

Table 4: Bond lengths [\AA] for **1**.

Si(1)-N(1)	1.7286(12)		Si(3)-C(9)	1.8610(17)
Si(1)-C(2)	1.858(2)		Si(3)-C(8)	1.8630(19)
Si(1)-C(3)	1.864(2)		Si(3)-C(7)	1.8703(19)
Si(1)-C(1)	1.8648(16)		Si(3)-Be(1)	2.7633(18)
Si(1)-Be(1)	2.7547(18)		Si(4)-N(2)	1.7270(12)
Si(2)-N(1)	1.7251(12)		Si(4)-C(10)	1.8669(16)
Si(2)-C(5)	1.841(2)		Si(4)-C(12)	1.8673(19)
Si(2)-C(4)	1.8698(18)		Si(4)-C(11)	1.8707(18)
Si(2)-C(6)	1.885(3)		Si(4)-Be(1)	2.7633(19)
Si(2)-Be(1)	2.7680(18)		N(1)-Be(1)	1.525(2)
Si(3)-N(2)	1.7295(12)		N(2)-Be(1)	1.519(2)

Table 5: Bond angles [$^\circ$] for **1**.

N(1)-Si(1)-C(2)	112.67(9)		N(2)-Si(4)-C(12)	111.30(7)
N(1)-Si(1)-C(3)	111.36(9)		C(10)-Si(4)-C(12)	108.50(9)
C(2)-Si(1)-C(3)	108.43(15)		N(2)-Si(4)-C(11)	108.00(7)
N(1)-Si(1)-C(1)	107.92(7)		C(10)-Si(4)-C(11)	109.18(8)
C(2)-Si(1)-C(1)	107.69(11)		C(12)-Si(4)-C(11)	108.13(10)
C(3)-Si(1)-C(1)	108.63(11)		N(2)-Si(4)-Be(1)	29.46(5)
N(1)-Si(1)-Be(1)	29.96(5)		C(10)-Si(4)-Be(1)	129.89(7)
C(2)-Si(1)-Be(1)	123.22(11)		C(12)-Si(4)-Be(1)	115.35(7)
C(3)-Si(1)-Be(1)	123.36(11)		C(11)-Si(4)-Be(1)	79.40(7)
C(1)-Si(1)-Be(1)	77.96(7)		Be(1)-N(1)-Si(2)	116.64(10)
N(1)-Si(2)-C(5)	112.45(10)		Be(1)-N(1)-Si(1)	115.55(10)
N(1)-Si(2)-C(4)	108.18(7)		Si(2)-N(1)-Si(1)	127.70(7)
C(5)-Si(2)-C(4)	109.54(13)		Be(1)-N(2)-Si(4)	116.55(10)
N(1)-Si(2)-C(6)	111.32(10)		Be(1)-N(2)-Si(3)	116.40(10)
C(5)-Si(2)-C(6)	108.39(18)		Si(4)-N(2)-Si(3)	127.05(7)
C(4)-Si(2)-C(6)	106.79(11)		N(2)-Be(1)-N(1)	178.73(16)
N(1)-Si(2)-Be(1)	29.50(5)		N(2)-Be(1)-Si(1)	146.06(11)
C(5)-Si(2)-Be(1)	128.45(13)		N(1)-Be(1)-Si(1)	34.48(6)
C(4)-Si(2)-Be(1)	78.97(7)		N(2)-Be(1)-Si(3)	34.10(6)
C(6)-Si(2)-Be(1)	117.59(11)		N(1)-Be(1)-Si(3)	144.74(11)
N(2)-Si(3)-C(9)	112.12(7)		Si(1)-Be(1)-Si(3)	133.64(7)
N(2)-Si(3)-C(8)	111.30(8)		N(2)-Be(1)-Si(4)	33.99(6)
C(9)-Si(3)-C(8)	109.04(9)		N(1)-Be(1)-Si(4)	147.16(11)
N(2)-Si(3)-C(7)	107.78(7)		Si(1)-Be(1)-Si(4)	133.29(7)

C(9)-Si(3)-C(7)	108.94(10)		Si(3)-Be(1)-Si(4)	68.09(4)
C(8)-Si(3)-C(7)	107.52(11)		N(2)-Be(1)-Si(2)	145.51(11)
N(2)-Si(3)-Be(1)	29.50(5)		N(1)-Be(1)-Si(2)	33.85(6)
C(9)-Si(3)-Be(1)	131.45(7)		Si(1)-Be(1)-Si(2)	68.30(4)
C(8)-Si(3)-Be(1)	113.53(7)		Si(3)-Be(1)-Si(2)	130.00(7)
C(7)-Si(3)-Be(1)	79.51(7)		Si(4)-Be(1)-Si(2)	136.22(7)
N(2)-Si(4)-C(10)	111.65(7)			

References

- [1] H. Bürger, C. Forker and J. Goubeau, *Monatsh.*, 1965, **96**, 597.
- [2] G. M. Sheldrick, *Acta Crystallogr.* 1990, **A46**, 467
- [3] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures University of Göttingen, Göttingen (Germany) **1997**. (see also: G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112)

Computational Studies

All geometries were fully optimized using tightened convergence criteria and improved integration grids at the density functional theory level, employing the BP86 exchange-correlation functional [1] including a third-generation dispersion correction [2] as implemented in the Turbomole V6.3 quantum chemistry program package [3]. A triple -zeta valence quality Gaussian type function basis set termed def2-TZVP [4] has been used throughout. The resolution-of-the-identity approximation was employed, making use of an appropriate auxiliary basis set [5]. Vibrational frequencies were determined from central numerical differences of analytical gradients. Atom coordinates, energies and the electron localization function (ELF) [6] of the optimized geometry are given below.

References

- 1 a) A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098; b) J. P. Perdew, *Phys. Rev. B* 1986, **33**, 8822.
- 2 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.
- 3 a) TURBOMOLE V6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>; b) R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Letters* 1989, **162**, 165; c) M. Häser and R. Ahlrichs, *J. Comput. Chem.* 1989, **10**, 104; d) O. Treutler and R. Ahlrichs, *J. Chem. Phys.* 1995, **102**, 346; e) M. v. Arnim and R. Ahlrichs, *J. Chem. Phys.* 1999, **111**, 9183.
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- 5 F. Weigend, *Phys. Chem. Chem. Phys.* 2006, **8**, 1057.
- 6 a) A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.* 1990, **92**, 5397; b) A. Savin and B. Silvi, *Nature* 1994, **371**, 683.

Be[N(SiMe₃)₂]₂**Energy (in Hartree) and atomic coordinates (in Å):** Energy = -1762.005517557

Si	-1,565556	-0,1015462	2,2844377
Si	1,565556	0,1015462	2,2844377
Si	0,1015462	-1,565556	-2,2844377
Si	-0,1015462	1,565556	-2,2844377
N	0	0	1,5250395
N	0	0	-1,5250395
Be	0	0	0
C	-2,8467518	0,3183826	0,9612718
C	-1,713281	1,1165967	3,7143417
C	-1,8881378	-1,8447041	2,9209687
C	2,8467518	-0,3183826	0,9612718
C	1,8881378	1,8447041	2,9209687
C	1,713281	-1,1165967	3,7143417
C	-0,3183826	-2,8467518	-0,9612718
C	1,8447041	-1,8881378	-2,9209687
C	-1,1165967	-1,713281	-3,7143417
C	1,1165967	1,713281	-3,7143417
C	0,3183826	2,8467518	-0,9612718
C	-1,8447041	1,8881378	-2,9209687
H	-2,7118113	1,3470514	0,5938985
H	-3,8701629	0,2318871	1,3552993
H	-2,7660371	-0,3556118	0,0937788
H	-1,5220099	2,1459207	3,3781
H	-0,9935224	0,8831183	4,5131195
H	-2,7208808	1,0818754	4,1552858
H	-1,7989365	-2,5738366	2,1019757
H	-2,895388	-1,937103	3,3545602
H	-1,158577	-2,1219893	3,6956618
H	2,7660371	0,3556118	0,0937788
H	2,7118113	-1,3470514	0,5938985
H	3,8701629	-0,2318871	1,3552993
H	1,7989365	2,5738366	2,1019757
H	2,895388	1,937103	3,3545602
H	1,158577	2,1219893	3,6956618
H	1,5220099	-2,1459207	3,3781
H	0,9935224	-0,8831183	4,5131195
H	2,7208808	-1,0818754	4,1552858
H	-0,2318871	-3,8701629	-1,3552993
H	-1,3470514	-2,7118113	-0,5938985
H	0,3556118	-2,7660371	-0,0937788
H	2,1219893	-1,158577	-3,6956618
H	1,937103	-2,895388	-3,3545602
H	2,5738366	-1,7989365	-2,1019757
H	-0,8831183	-0,9935224	-4,5131195
H	-2,1459207	-1,5220099	-3,3781
H	-1,0818754	-2,7208808	-4,1552858
H	0,8831183	0,9935224	-4,5131195
H	2,1459207	1,5220099	-3,3781

H	1,0818754	2,7208808	-4,1552858
H	0,2318871	3,8701629	-1,3552993
H	1,3470514	2,7118113	-0,5938985
H	-0,3556118	2,7660371	-0,0937788
H	-2,1219893	1,158577	-3,6956618
H	-1,937103	2,895388	-3,3545602
H	-2,5738366	1,7989365	-2,1019757

Vibrational frequencies:

mode	symmetry	wave number	IR intensity	selection rules	
		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
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3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	b	5.62	0.00833	YES	YES
8	e	28.35	0.03419	YES	YES
9	e	28.35	0.03419	YES	YES
10	a	41.52	0.00000	NO	YES
11	e	42.52	0.02380	YES	YES
12	e	42.52	0.02380	YES	YES
13	b	50.49	0.00000	YES	YES
14	a	73.79	0.00000	NO	YES
15	e	92.84	0.08072	YES	YES
16	e	92.84	0.08072	YES	YES
17	b	108.80	0.26501	YES	YES
18	e	153.29	0.11306	YES	YES
19	e	153.29	0.11306	YES	YES
20	a	157.91	0.00000	NO	YES
21	b	159.12	0.00300	YES	YES
22	a	163.49	0.00000	NO	YES
23	b	165.77	0.00406	YES	YES
24	a	166.58	0.00000	NO	YES
25	b	174.36	0.03368	YES	YES
26	a	177.09	0.00000	NO	YES
27	e	178.87	0.21105	YES	YES
28	e	178.87	0.21105	YES	YES
29	e	181.21	0.08703	YES	YES
30	e	181.21	0.08703	YES	YES
31	b	181.79	0.00720	YES	YES
32	a	185.04	0.00000	NO	YES
33	e	186.70	0.02064	YES	YES
34	e	186.70	0.02064	YES	YES
35	b	191.99	0.49720	YES	YES
36	a	196.32	0.00000	NO	YES
37	e	198.64	0.74984	YES	YES
38	e	198.64	0.74984	YES	YES
39	b	209.00	5.43670	YES	YES
40	e	219.84	2.46496	YES	YES
41	e	219.84	2.46496	YES	YES
42	a	230.64	0.00000	NO	YES

43	b	231.73	0.00814	YES	YES
44	a	238.03	0.00000	NO	YES
45	e	249.19	8.56024	YES	YES
46	e	249.19	8.56024	YES	YES
47	e	308.51	0.31507	YES	YES
48	e	308.51	0.31507	YES	YES
49	b	314.21	0.79343	YES	YES
50	e	382.85	35.49114	YES	YES
51	e	382.85	35.49114	YES	YES
52	a	386.41	0.00000	NO	YES
53	b	527.46	8.61359	YES	YES
54	e	595.08	6.58964	YES	YES
55	e	595.08	6.58964	YES	YES
56	a	616.31	0.00000	NO	YES
57	b	643.85	15.40855	YES	YES
58	e	653.98	0.01710	YES	YES
59	e	653.98	0.01710	YES	YES
60	a	654.71	0.00000	NO	YES
61	b	656.88	0.61021	YES	YES
62	a	664.22	0.00000	NO	YES
63	e	664.27	3.66748	YES	YES
64	e	664.27	3.66748	YES	YES
65	a	665.11	0.00000	NO	YES
66	b	665.17	0.42111	YES	YES
67	e	667.08	11.29361	YES	YES
68	e	667.08	11.29361	YES	YES
69	b	667.74	25.41248	YES	YES
70	a	721.67	0.00000	NO	YES
71	a	734.79	0.00000	NO	YES
72	b	735.51	0.03567	YES	YES
73	e	736.89	0.88205	YES	YES
74	e	736.89	0.88205	YES	YES
75	e	746.80	26.66734	YES	YES
76	e	746.80	26.66734	YES	YES
77	b	754.81	50.71870	YES	YES
78	e	816.24	78.41716	YES	YES
79	e	816.24	78.41716	YES	YES
80	a	822.77	0.00000	NO	YES
81	b	825.46	0.77023	YES	YES
82	e	825.56	29.79258	YES	YES
83	e	825.56	29.79258	YES	YES
84	a	827.80	0.00000	NO	YES
85	e	833.82	148.49108	YES	YES
86	e	833.82	148.49108	YES	YES
87	b	836.72	142.45380	YES	YES
88	a	854.40	0.00000	NO	YES
89	b	857.27	412.81146	YES	YES
90	a	930.23	0.00000	NO	YES
91	e	961.26	486.56939	YES	YES
92	e	961.26	486.56939	YES	YES
93	b	1230.08	1.14796	YES	YES
94	a	1230.08	0.00000	NO	YES
95	e	1230.95	13.03287	YES	YES
96	e	1230.95	13.03287	YES	YES

97	e	1231.86	68.14648	YES	YES
98	e	1231.86	68.14648	YES	YES
99	b	1234.04	109.59327	YES	YES
100	a	1236.92	0.00000	NO	YES
101	e	1241.08	40.19040	YES	YES
102	e	1241.08	40.19040	YES	YES
103	b	1242.54	13.74825	YES	YES
104	a	1244.70	0.00000	NO	YES
105	b	1353.06	697.24345	YES	YES
106	e	1398.78	0.35666	YES	YES
107	e	1398.78	0.35666	YES	YES
108	a	1401.10	0.00000	NO	YES
109	b	1402.28	4.65487	YES	YES
110	a	1404.20	0.00000	NO	YES
111	b	1405.00	2.07603	YES	YES
112	a	1405.48	0.00000	NO	YES
113	e	1406.05	2.80421	YES	YES
114	e	1406.05	2.80421	YES	YES
115	b	1407.37	7.71069	YES	YES
116	e	1408.05	1.68486	YES	YES
117	e	1408.05	1.68486	YES	YES
118	e	1414.36	5.78335	YES	YES
119	e	1414.36	5.78335	YES	YES
120	a	1416.18	0.00000	NO	YES
121	e	1417.95	1.47527	YES	YES
122	e	1417.95	1.47527	YES	YES
123	b	1418.90	0.08112	YES	YES
124	a	1419.74	0.00000	NO	YES
125	b	1421.64	13.41823	YES	YES
126	e	1425.34	15.07420	YES	YES
127	e	1425.34	15.07420	YES	YES
128	a	1426.06	0.00000	NO	YES
129	b	1428.02	20.49569	YES	YES
130	a	2951.54	0.00000	NO	YES
131	e	2951.78	3.24059	YES	YES
132	e	2951.78	3.24059	YES	YES
133	b	2952.07	23.54197	YES	YES
134	e	2957.07	16.62376	YES	YES
135	e	2957.07	16.62376	YES	YES
136	a	2957.34	0.00000	NO	YES
137	b	2957.36	1.14825	YES	YES
138	e	2958.55	3.95459	YES	YES
139	e	2958.55	3.95459	YES	YES
140	b	2958.76	21.87940	YES	YES
141	a	2958.80	0.00000	NO	YES
142	b	3024.64	8.41058	YES	YES
143	e	3024.70	15.97828	YES	YES
144	e	3024.70	15.97828	YES	YES
145	a	3024.76	0.00000	NO	YES
146	e	3032.56	13.95543	YES	YES
147	e	3032.56	13.95543	YES	YES
148	a	3033.12	0.00000	NO	YES
149	b	3033.13	1.98291	YES	YES
150	a	3034.22	0.00000	NO	YES

151	e	3034.35	5.99897	YES	YES
152	e	3034.35	5.99897	YES	YES
153	b	3034.59	2.14155	YES	YES
154	b	3036.24	34.72206	YES	YES
155	e	3036.29	49.42136	YES	YES
156	e	3036.29	49.42136	YES	YES
157	a	3036.66	0.00000	NO	YES
158	e	3040.04	21.14281	YES	YES
159	e	3040.04	21.14281	YES	YES
160	b	3040.47	53.50711	YES	YES
161	a	3040.56	0.00000	NO	YES
162	e	3040.96	8.26495	YES	YES
163	e	3040.96	8.26495	YES	YES
164	a	3041.25	0.00000	NO	YES
165	b	3041.26	0.10463	YES	YES

Electron localization function:

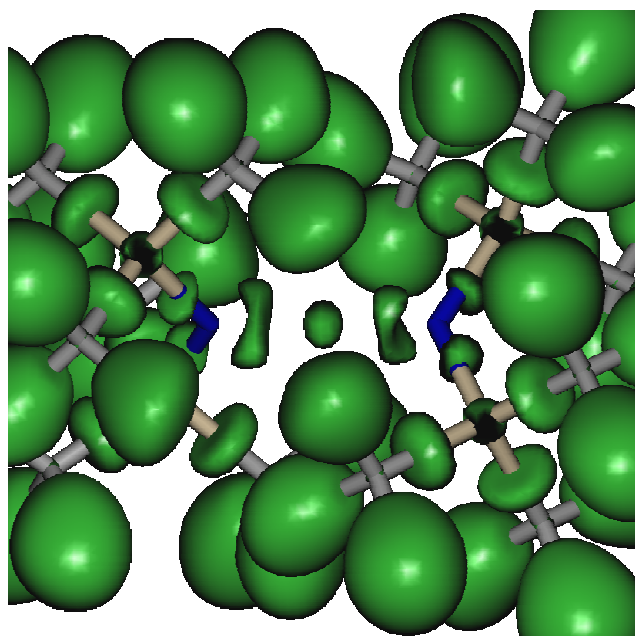


Fig. S1 ELF isosurfaces of $\text{Be}[\text{N}(\text{SiMe}_3)_2]_2$ (isovalue 0.850, Be atom in the centre).

Be[N(SiH₃)₂]₂

Energy (in Hartree) and atomic coordinates (in Å):

Energy = -1289.830208033

Si	-1.0831094	1.0831094	2.3604091
Si	1.0831094	-1.0831094	2.3604091
Si	-1.0831094	-1.0831094	-2.3604091
Si	1.0831094	1.0831094	-2.3604091
N	0.0000000	0.0000000	1.5280684
N	0.0000000	0.0000000	-1.5280684
Be	0.0000000	0.0000000	0.0000000
H	-1.8455720	1.8455720	1.3239748
H	-0.3368391	2.0473607	3.2268435
H	-2.0473607	0.3368391	3.2268435
H	1.8455720	-1.8455720	1.3239748
H	2.0473607	-0.3368391	3.2268435
H	0.3368391	-2.0473607	3.2268435
H	-1.8455720	-1.8455720	-1.3239748
H	-0.3368391	-2.0473607	-3.2268435
H	-2.0473607	-0.3368391	-3.2268435
H	2.0473607	0.3368391	-3.2268435
H	1.8455720	1.8455720	-1.3239748
H	0.3368391	2.0473607	-3.2268435

Vibrational frequencies:

mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	selection rules RAMAN
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3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	b1	10.63	0.00000	NO	YES
8	e	50.03	0.16586	YES	YES
9	e	50.03	0.16586	YES	YES
10	a2	89.74	0.00000	NO	NO
11	b1	90.03	0.00000	NO	YES
12	e	90.85	0.14541	YES	YES
13	e	90.85	0.14541	YES	YES
14	a1	104.79	0.00000	NO	YES
15	e	142.72	0.00222	YES	YES
16	e	142.72	0.00222	YES	YES
17	b2	161.24	3.18192	YES	YES
18	e	344.58	10.82588	YES	YES
19	e	344.58	10.82588	YES	YES
20	a1	373.54	0.00000	NO	YES
21	b2	580.61	4.62333	YES	YES
22	a1	649.66	0.00000	NO	YES
23	a2	665.56	0.00000	NO	NO
24	b1	669.12	0.00000	NO	YES

25	e	673.16	0.04472	YES	YES
26	e	673.16	0.04472	YES	YES
27	e	709.14	62.55074	YES	YES
28	e	709.14	62.55074	YES	YES
29	b2	755.31	82.05481	YES	YES
30	e	912.28	114.35520	YES	YES
31	e	912.28	114.35520	YES	YES
32	a2	914.28	0.00000	NO	NO
33	b1	915.19	0.00000	NO	YES
34	e	919.36	655.66417	YES	YES
35	e	919.36	655.66417	YES	YES
36	e	936.80	7.47080	YES	YES
37	e	936.80	7.47080	YES	YES
38	a1	937.92	0.00000	NO	YES
39	b2	939.29	0.13509	YES	YES
40	a1	946.07	0.00000	NO	YES
41	b2	956.49	620.06464	YES	YES
42	e	976.66	50.64752	YES	YES
43	e	976.66	50.64752	YES	YES
44	a1	981.25	0.00000	NO	YES
45	b2	1363.05	796.00678	YES	YES
46	a2	2149.67	0.00000	NO	NO
47	b1	2150.01	0.00000	NO	YES
48	e	2153.64	39.73609	YES	YES
49	e	2153.64	39.73609	YES	YES
50	e	2154.26	140.71023	YES	YES
51	e	2154.26	140.71023	YES	YES
52	e	2158.26	192.09204	YES	YES
53	e	2158.26	192.09204	YES	YES
54	a1	2159.95	0.00000	NO	YES
55	b2	2160.21	474.49528	YES	YES
56	b2	2162.72	30.47511	YES	YES
57	a1	2165.38	0.00000	NO	YES

Electron localization function:

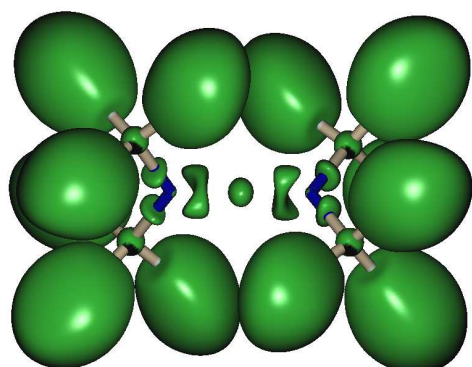


Fig. S2 ELF isosurfaces of $\text{Be}[\text{N}(\text{SiH}_3)_2]_2$ (isovalue 0.850, Be atom in the centre).

Be[N(CH₃)₂]₂

Energy (in Hartree) and atomic coordinates (in Å):

Energy = -284.0657271656

C	-0.8543001	0.8543001	2.3247129
C	0.8543001	-0.8543001	2.3247129
C	-0.8543001	-0.8543001	-2.3247129
C	0.8543001	0.8543001	-2.3247129
N	0.0000000	0.0000000	1.5169187
N	0.0000000	0.0000000	-1.5169187
Be	0.0000000	0.0000000	0.0000000
H	-1.4871900	1.4871900	1.6857076
H	-0.2638636	1.5238653	2.9815261
H	-1.5238653	0.2638636	2.9815261
H	1.4871900	-1.4871900	1.6857076
H	1.5238653	-0.2638636	2.9815261
H	0.2638636	-1.5238653	2.9815261
H	-1.4871900	-1.4871900	-1.6857076
H	-0.2638636	-1.5238653	-2.9815261
H	-1.5238653	-0.2638636	-2.9815261
H	1.5238653	0.2638636	-2.9815261
H	1.4871900	1.4871900	-1.6857076
H	0.2638636	1.5238653	-2.9815261

Vibrational frequencies:

mode	symmetry	wave number	IR intensity	selection rules	
		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	b1	63.10	0.00000	NO	YES
8	e	77.80	0.01265	YES	YES
9	e	77.80	0.01265	YES	YES
10	e	175.33	1.84963	YES	YES
11	e	175.33	1.84963	YES	YES
12	a2	232.75	0.00000	NO	NO
13	b1	232.85	0.00000	NO	YES
14	a1	276.12	0.00000	NO	YES
15	e	280.57	2.64770	YES	YES
16	e	280.57	2.64770	YES	YES
17	b2	400.31	0.40412	YES	YES
18	e	429.21	30.95165	YES	YES
19	e	429.21	30.95165	YES	YES
20	a1	545.23	0.00000	NO	YES
21	b2	892.04	24.80729	YES	YES
22	a1	998.33	0.00000	NO	YES
23	e	1057.35	5.67031	YES	YES
24	e	1057.35	5.67031	YES	YES
25	a2	1074.64	0.00000	NO	NO

26	b1	1079.28	0.00000	NO	YES
27	e	1129.66	2.40382	YES	YES
28	e	1129.66	2.40382	YES	YES
29	b2	1148.23	97.43242	YES	YES
30	e	1158.05	54.22564	YES	YES
31	e	1158.05	54.22564	YES	YES
32	a1	1274.50	0.00000	NO	YES
33	e	1399.80	1.91206	YES	YES
34	e	1399.80	1.91206	YES	YES
35	b2	1413.31	213.72428	YES	YES
36	a2	1422.53	0.00000	NO	NO
37	b1	1423.57	0.00000	NO	YES
38	a1	1427.47	0.00000	NO	YES
39	e	1432.55	7.98400	YES	YES
40	e	1432.55	7.98400	YES	YES
41	b2	1441.50	45.27087	YES	YES
42	e	1455.40	14.96888	YES	YES
43	e	1455.40	14.96888	YES	YES
44	a1	1474.74	0.00000	NO	YES
45	b2	1526.63	293.42087	YES	YES
46	e	2871.29	71.40073	YES	YES
47	e	2871.29	71.40073	YES	YES
48	b2	2875.49	375.06151	YES	YES
49	a1	2880.01	0.00000	NO	YES
50	e	2896.57	128.69278	YES	YES
51	e	2896.57	128.69278	YES	YES
52	a2	2907.97	0.00000	NO	NO
53	b1	2908.10	0.00000	NO	YES
54	e	3008.44	30.64839	YES	YES
55	e	3008.44	30.64839	YES	YES
56	b2	3009.99	62.65424	YES	YES
57	a1	3010.06	0.00000	NO	YES

Electron localization function:

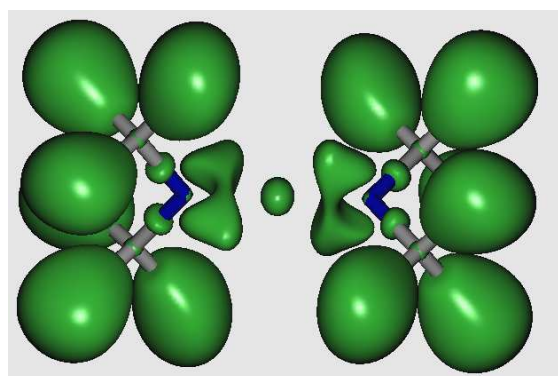


Fig. S3 ELF isosurfaces of $\text{Be}[\text{N}(\text{CH}_3)_2]_2$ (isovalue 0.850, Be atom in the centre).

Be(NH₂)₂

Energy (in Hartree) and atomic coordinates (in Å):

Energy = -126.7941708946

H	-0.5869150	-0.5869150	-2.1094516
H	0.5869150	0.5869150	-2.1094516
H	-0.5869150	0.5869150	2.1094516
H	0.5869150	-0.5869150	2.1094516
N	0.0000000	0.0000000	-1.5216276
N	0.0000000	0.0000000	1.5216276
Be	0.0000000	0.0000000	0.0000000

Vibrational frequencies:

mode	symmetry	wave number	IR intensity	selection rules	
		cm ^{**} (-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	e	260.33	7.61132	YES	YES
8	e	260.33	7.61132	YES	YES
9	e	376.37	152.86698	YES	YES
10	e	376.37	152.86698	YES	YES
11	b1	389.49	0.00000	NO	YES
12	a1	667.15	0.00000	NO	YES
13	e	691.77	61.76165	YES	YES
14	e	691.77	61.76165	YES	YES
15	b2	1373.63	218.35647	YES	YES
16	a1	1534.16	0.00000	NO	YES
17	b2	1542.47	206.21765	YES	YES
18	b2	3473.62	39.15021	YES	YES
19	a1	3474.57	0.00000	NO	YES
20	e	3550.13	19.06097	YES	YES
21	e	3550.13	19.06097	YES	YES

Electron localization function:

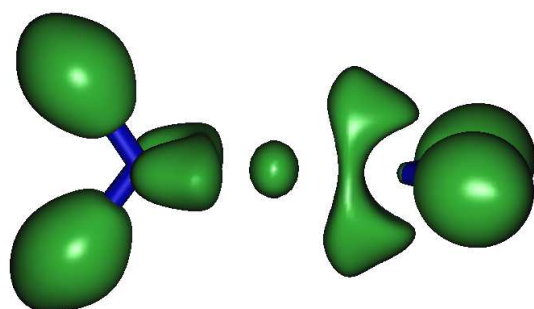


Fig. S4 ELF isosurfaces of Be(NH₂)₂ (isovalue 0.850, Be atom in the centre).

BeMe₂

Energy (in Hartree) and atomic coordinates (in Å):

Energy = -94.60648543539

Be	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.6915401
C	0.0000000	0.0000000	-1.6915401
H	0.8840420	0.5104019	2.1115851
H	0.0000000	-1.0208038	2.1115851
H	-0.8840420	0.5104019	2.1115851
H	-0.8840420	-0.5104019	-2.1115851
H	0.8840420	-0.5104019	-2.1115851
H	0.0000000	1.0208038	-2.1115851

Vibrational frequencies:

mode	symmetry	wave number cm**(-1)	IR intensity km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a1u	84.46	0.00000	NO	NO
8	eu	215.25	4.75436	YES	NO
9	eu	215.25	4.75436	YES	NO
10	a1g	533.73	0.00000	NO	YES
11	eg	558.66	0.00000	NO	YES
12	eg	558.66	0.00000	NO	YES
13	eu	739.34	105.29125	YES	NO
14	eu	739.34	105.29125	YES	NO
15	a2u	1076.72	67.45628	YES	NO
16	a1g	1198.78	0.00000	NO	YES
17	a2u	1221.73	148.85917	YES	NO
18	eg	1400.41	0.00000	NO	YES
19	eg	1400.41	0.00000	NO	YES
20	eu	1403.20	1.63336	YES	NO
21	eu	1403.20	1.63336	YES	NO
22	a2u	2935.12	5.47014	YES	NO
23	a1g	2936.72	0.00000	NO	YES
24	eu	3000.27	26.24979	YES	NO
25	eu	3000.27	26.24979	YES	NO
26	eg	3000.83	0.00000	NO	YES
27	eg	3000.83	0.00000	NO	YES

Be(OH)₂

Energy (in Hartree) and atomic coordinates (in Å):

Energy = -166.5929384782

H	0.5661304	-2.0346567	0.2904894
H	-0.5661304	2.0346567	0.2904894
O	0.0005603	-1.4394278	-0.2134190
O	-0.0005603	1.4394278	-0.2134190
Be	0.0000000	0.0000000	-0.1541408

Vibrational frequencies:

mode	symmetry	wave number	IR intensity	selection rules
		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	214.59	124.92073	YES YES
8	b	296.86	68.51329	YES YES
9	a	300.98	28.48539	YES YES
10	b	571.30	316.55005	YES YES
11	a	576.84	74.23207	YES YES
12	a	715.28	1.73302	YES YES
13	b	1484.40	356.99605	YES YES
14	b	3844.10	150.45562	YES YES
15	a	3845.22	21.28893	YES YES

BeF₂

Energy (in Hartree) and atomic coordinates (in Å):

Energy = -214.6838272174

Be	0.0000000	0.0000000	0.0000000
F	0.0000000	0.0000000	1.3918334
F	0.0000000	0.0000000	-1.3918334

Vibrational frequencies:

mode	symmetry	wave number	IR intensity	selection rules
		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6	e1u	334.15	142.25521	YES NO
7	e1u	334.15	142.25521	YES NO
8	a1g	694.81	0.00000	NO YES
9	a2u	1510.45	351.33301	YES NO