Supporting Information

Anti and Gauche Conformers of an Inorganic Butane Analogue, $NH_3BH_2NH_2BH_3$

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X-Ray Crystallography

Details of X-ray single crystal diffraction data and a summary of the intensity data collection parameters for the *anti* and two *gauche* conformers of DDAB are listed in Table S1. Crystal structure data of one of *gauche* conformer (chunk shaped crystals) were reported in our previous communication[1] and crystal structure data of another gauche conformer (needle shaped crystals) were also collected on a Nonius Kappa CCD diffractometer, which employs graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). Single crystals were mounted on the tips of glass fibers coated with Fomblin oil (perfluoropolyether). Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the DENZOSMN package (Nonius BV, 1999).[2] An absorption correction for the structures was accounted for using SCALEPACK. The structures were solved by direct methods and refined using the SHELXTL-97 (full-matrix least-squares refinements) structure solution package.[3] Hydrogen atoms bonded to nitrogen and boron were located and refined isotropically and all non-hydrogen atoms were located and refined anisotropically. The hydrogen atoms of the 18-crown-6 ether were calculated assuming standard geometries.

The crystal structure data of the *anti* conformer was collected on a Bruker APEXII CCD system equipped with a Cu ImuS micro-focus source with Quazar MX optics (λ = 1.54178 Å). A total of 5796 frames were collected. The total exposure time was 16.10 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 1719 reflections to a maximum θ angle of 66.26° (0.84 Å resolution), of which 693 were independent (average

redundancy 2.481, completeness = 96.8%, R_{int} = 2.43%, R_{sig} = 2.85%) and 662 (95.53%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.3061(8) Å, b = 4.4678(5) Å, c = 7.3183(8) Å, β = 117.245(7)°, volume = 212.38(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 1310 reflections above 20 σ(I) with 14.18° < 2θ < 132.5°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.823.

The structure was solved and refined using the Bruker SHELXTL software package, using the space group Pn, with Z = 2 for the formula unit, $H_{10}B_2N_2$.The final anisotropic full-matrix least-squares refinement on F^2 with 50 variables converged at R1 = 3.66%, for the observed data and wR2 = 9.90% for all data. The goodness-of-fit was 1.105. The largest peak in the final difference electron density synthesis was 0.172 $e^-/Å^3$ and the largest hole was -0.147 $e^-/Å^3$ with an RMS deviation of 0.033 $e^-/Å^3$. The data set contains merohedral twinning and the twin law [001,0 $\bar{1}$ 0, 100] was applied during refinement. The fractional contribution of the minor component of the twin refined to a value of 0.276(3).

Table S1. Crystallographic data and structure refinement details for *anti* conformer and two *gauche* conformers (For comparison, the reported crystallographic data[1] of chunk shaped crystal are listed here).

	$C_{12}H_{34}B_2N_2O_6$ (gauche)	$C_{12}H_{34}B_2N_2O_6$ (gauche)	$H_{10}B_2N_2$ (anti)
	Chunk-shaped[1]	Needle-shaped	
fw	324.03	324.03	59.72
T (K)	150 (2)	150(2)	100(2) K
λ (Å)	0.71073	0.71073	1.54178
cryst syst	Orthorhombic	Orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	Pn
a, (Å)	8.8717(1)	8.3112(1)	7.3061(8)
b, (Å)	11.6178(1)	13.0955(2)	4.4678(5)
c, (Å)	18.2118(2)	16.7666(3)	7.3183(8)
α, (deg)	90	90	90
β, (deg)	90	90	117.245(7)
γ, (deg)	90	90	90
V, (Å^3)	1877.08(3)	1824.87(5)	212.38 (4)
Z	4	4	2
D_{calc}, (g/cm^3)	1.147	1.179	0.934
μ (mm^{-1})	0.087	0.089	0.410
F(000)	712	712	68
cryst size (mm)	0.35 × 0.27 × 0.27	0.31× 0.08 × 0.08	0.069 × 0.074 × 0.103
2θ range, (deg)	5.10-50.02	5.48-50.08	13.60-132.52
reflns collected	51930	28432	1719
indep reflns/R_{int}	3319/0.031	3225/0.066	693/0.0243
params	240	239	50
GOF on F^2	1.032	1.006	1.105
R_1, wR_2 [I>2σ(I)]	0.0314, 0.0799	0.0356, 0.0656	0.0366, 0.0966
R_1, wR_2 (all data)	0.0370, 0.0832	0.0631, 0.0720	0.0386, 0.0990

Table S2. Selected bond distances (Å) and angles (°) for three crystal structures.

Distances (Å)					
Gauche conformer (chunk)		Gauche conformer (needle)		Anti conformer	
N1-B1	1.5881(18)	N1-B1	1.579(3)	N1-B1	1.596(4)
B1-N2	1.563(2)	B1-N2	1.576(3)	B1-N2	1.545(3)
N2-B2	1.600(2)	N2-B2	1.603(3)	N2-B2	1.601(4)
N1-HN1	0.89(2)	N1-HN1	0.94(2)		
N1-HN2	0.858(18)	N1-HN2	0.85(2)		
N1-HN3	0.97(2)	N1-HN3	0.859(19)		
B1-HB1	1.086(17)	B1-HB1	1.128(17)		
B1-HB2	1.127(16)	B1-HB2	1.077(16)		
N2-HN4	0.89(2)	N2-HN4	1.02(2)		
N2-HN5	0.97(2)	N2-HN5	1.00(3)		
B2-HB3	1.098(19)	B2-HB3	1.15(2)		
B2-HB4	1.03(2)	B2-HB4	1.138(19)		
B2-HB5	1.06(2)	B2-HB5	1.15(2)		
Angles (°)					
N1-B1-N2	108.36(12)	N1-B1-N2	108.27(17)	N1-B1-N2	110.2(2)
B1-N2-B2	118.03(13)	B1-N2-B2	117.10(17)	B1-N2-B2	112.7(2)
N1-B1-N2-B2	-59.66(2)	N1-B1-N2-B2	76.42(2)	N1-B1-N2-B2	-179.94(19)

Table S3. A total of 24 dihydrogen bond distances (Å) in the *anti* conformer structure (after normalization).

H1NA-H2BA	2.09	H1BA-H1NC	2.32	H2NB-H2BC	2.23
H1NA-H2BB	2.04	H1BA-H1NB	2.18	H2BA-H1NA	2.09
H1NA-H2BC	2.38	H1BB-H2NA	2.30	H2BA-H1NC	2.12
H1NB-H1BA	2.18	H1BB-H1NB	2.02	H2BB-H1NA	2.04
H1NB-H1BB	2.02	H1BB-H1NC	2.37	H2BB-H2NB	2.15
H1NC-H1BA	2.32	H2NA-H1BB	2.30	H2BC-H1NA	2.38
H1NC-H1BB	2.37	H2NA-H2BC	2.27	H2BC-H2NA	2.37
H1NC-H2BA	2.12	H2NB-H2BB	2.15	H2BC-H2NB	2.23

Table S4. Dihedral angles of B-N-B-N in structures of Me_2NHBH_2-$NHMe_2BH_3$ (I), (1,4-C_4H_8)NH BH_2N(1,4-C_4H_8)BH_3 (II), $MeNH_2BH_2NH_2MeBH_3$ (III), and [Ir(PCy_3)$_2$(H)$_2$(η^2-$H_3BNHMeBH_2$ NH_2Me)][$BAr^F{}_4$] (IV) in literatures, and anti and gauche forms in this work.

structures	I	II	III	IV	gauche form (chunk)	gauche form (needle)	anti form
dihedrals	45.36	49.73	179.9	59.9	-59.66(2)	76.42(2)	-179.94(19)

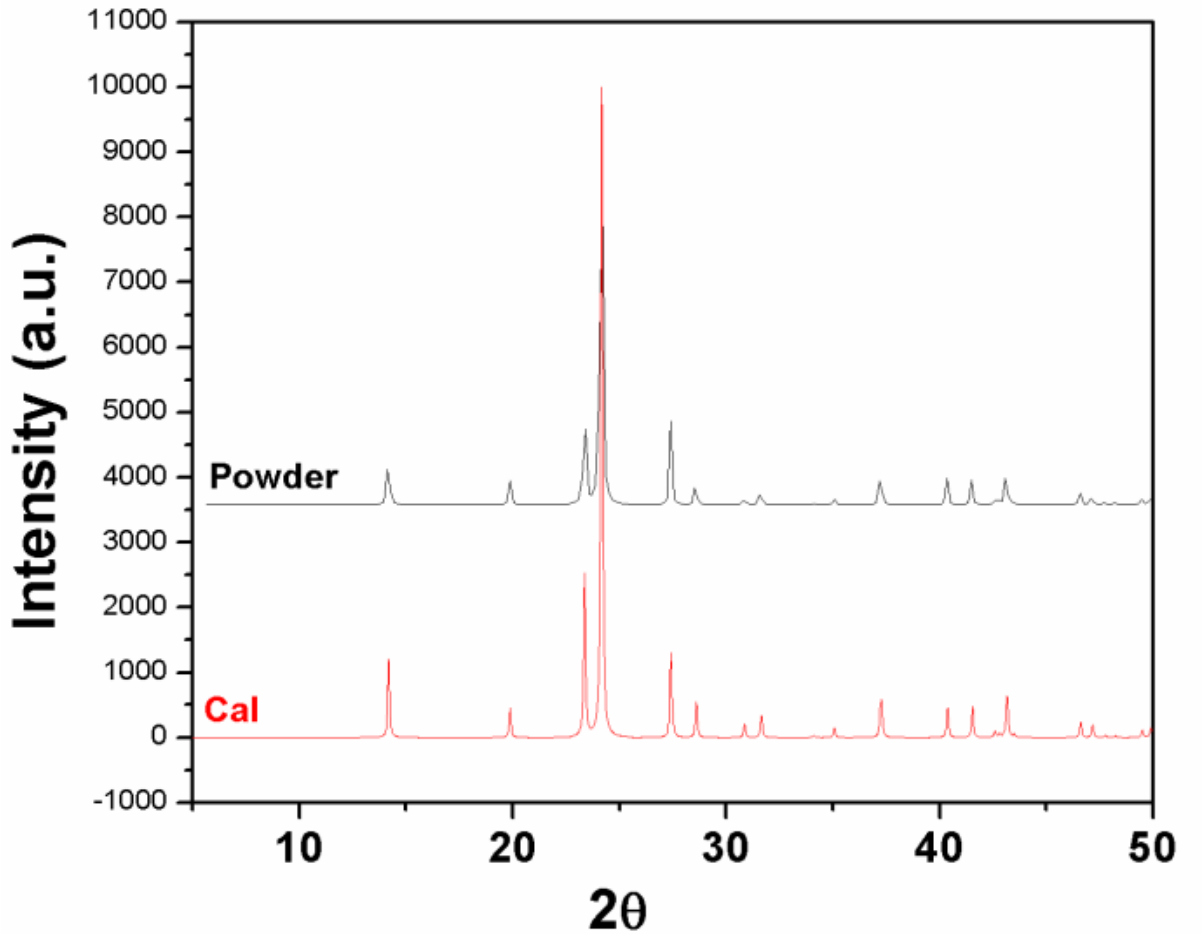

Figure S1. Comparison of XRD powder pattern with the simulated pattern from single crystal structure determination.

References:

1. X. Chen, J.-C. Zhao, S. G. Shore *J. Am. Chem. Soc.* **2010**, *132*, 10658.
2. Z. Otwinowski, W. Minor *Processing of X-Ray Diffraction Data Collected in Oscillation Mode.* In *Macromolecular Crystallography, Part A*, Carter, Jr., C.W.; Sweet, R. M., Eds. *Methods in Enzymology 276*, Academic Press, New York, 1997, p. 307.
3. G. M. Sheldrick, *SHELXTL-97: Acta Cryst.,* **2008***, A64,* 112-122.