

A Combined Experimental Inelastic Neutron Scattering, Raman and *ab initio* Lattice Dynamics Study of α -Lithium Amidoborane – Supplementary Information

Table 1 Geometry optimised atomic coordinates of α -LiNH₂BH₃ used in the DFT calculation. Unit cell parameters $a = 13.932889 \text{ \AA}$, $b = 5.149909 \text{ \AA}$, $c = 7.102219 \text{ \AA}$; space group *Pbca*.

Atom	x/a	y/b	z/c	Wyckoff Positions
H1	0.611029	0.858219	0.172610	1a
H2	0.725859	0.087439	0.177109	1a
H3	0.679709	0.943300	0.933629	1a
H4	0.531589	0.245910	0.983009	1a
H5	0.574639	0.364509	0.178460	1a
Li1	0.677089	0.557659	0.931699	1a
B1	0.653249	0.034329	0.087090	1a
N1	0.594730	0.282559	0.052090	1a

Table 2 Experimental and calculated bond lengths of α -LiNH₂BH₃ with % error.

Bond	Experimental (Å)	Calculated (Å)	% Error
Li-N	1.992	2.013	1.089
B-N	1.541	1.536	-0.292
N-H1	0.989	1.024	3.62
N-H2	0.989	1.030	4.196
B-H3	1.223	1.227	0.376
B-H4	1.223	1.240	1.39
B-H5	1.223	1.242	1.586
Li-B1	2.552	2.515	-1.458
Li-B2	2.686	2.611	-2.777
Li-B3	2.692	2.711	0.747

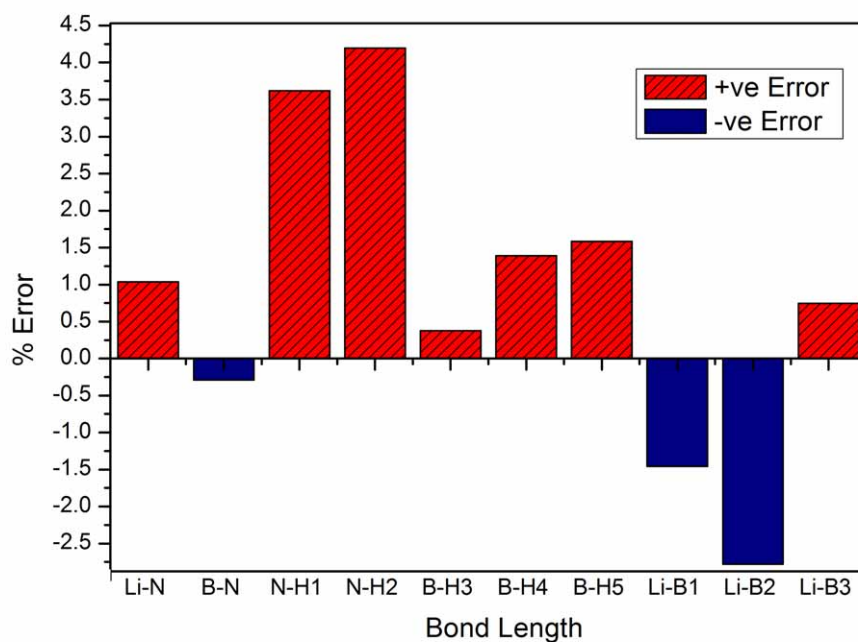


Figure 1 Histogram showing the % error between the experimental and calculated bond lengths of α -LiNH₂BH₃.

Table 3 Wavenumbers and assignments for the observed bands of α -LiNH₂BH₃.

INS (cm ⁻¹)	DFT (cm ⁻¹)	Raman (cm ⁻¹)	DFT (cm ⁻¹)	Assignment	Mulliken group theory labels irreducible representations
-	-0.08			Anharmonic acoustic translation	a
-	-0.07			Anharmonic acoustic translation	b
-	-0.05			Translation	c
39.00w	29.48			Translation	d
-	57.66			Anharmonic translation	e
77.00m	78.76			Anharmonic translation	f
80.00m	88.38			Lattice Libration	a
-	88.92			Lattice Libration	g
-	90.67			Lattice Libration	c
-	93.18			Lattice Libration	d
99.00s	94.42			Lattice Libration	f
113.00m	94.61			Lattice Libration	h
118.00m	117.76			Molecular Libration	e
123.00s	121.44			Molecular Libration	b
	127.05			Molecular Libration	a
-	127.55			Molecular Libration	g
136.00m	130.58			Lattice deformation	f
-	141.24			Lattice deformation	h
-	148.06			Lattice deformation	g
-	150.18			Lattice deformation	c
151.00sh	153.26			Lattice deformation	h
-	155.43			Lattice deformation	b

-	156.18			Lattice deformation	d
159.00s	158.95			Lattice deformation	g
	161.83			Lattice deformation	h
164.00s	165.42			Lattice deformation	e
	173.77			Lattice deformation	c
-	175.08			Lattice deformation	d
181.00s	182.26			Lattice deformation	c
-	182.47			Lattice deformation	d
	186.78			Lattice deformation	b
-	186.81			Lattice deformation	e
	190.03			Lattice deformation	h
192.00s	191.69			Lattice deformation	g
198.00m	208.67			Lattice deformation	f
204.00m	210.08			Lattice deformation	a
211.00m	211.65			Lattice deformation	a
	217.08			Lattice deformation	f
	219.45			Lattice deformation	b
221.00sh	223.69			Lattice deformation	e
226.00m	227.40			Lattice deformation	c
231.00s	233.19	231.00br	232.00	Lattice deformation	d
-	236.80			Lattice deformation	h
243.00sh	237.57			Lattice deformation	g
247.00sh	240.60			Lattice deformation	d
250.00s	243.32			Lattice deformation	e
260.00s	243.51			Lattice deformation	b
270.00s	247.99			Lattice deformation	c
-	248.47			Lattice deformation	a
279.00s	275.02			Lattice deformation	f
	284.62			Lattice deformation	e
288.00sh	287.63			Lattice deformation	b
294.00m	297.08			Lattice deformation	h
302.00w	297.68			Lattice deformation	a
308.00w	300.80			Lattice deformation	g
315.00w	318.15			Lattice deformation	f
340.00m	343.60			BH ₃ Libration	b
347.00s	347.08			BH ₃ Libration	e
362.00sh	368.70			BH ₃ Libration	f
366.00sh	368.73			BH ₃ Libration	g
	369.06			BH ₃ Libration	a
373.00m	371.96			BH ₃ Libration	h
398.00sh	397.27			BH ₃ Libration	c
402.00w	397.74			BH ₃ Libration	d
416.00w					
425.00w	429.48			NH ₂ Libration	g
450.00sh	442.66			NH ₂ Libration	h
451.00sh	447.81			NH ₂ Libration	b
460.00s	458.73			NH ₂ Libration	e
478.00s	474.81			NH ₂ Libration	c
479.00s	476.19	463.00m	473.00	N-Li stretch	d

480.00s	480.92			NH ₂ Libration	a
481.00s	483.64			NH ₂ Libration	a
-	485.24			NH ₂ Libration	c
489.00sh	488.06			NH ₂ Libration	f
-	490.80			NH ₂ Libration	g
494.00w	494.01			N-Li stretch	d
	496.17			N-Li stretch + NH ₂ Libration	h
	496.18			NH ₂ Libration	b
	499.65			N-Li stretch + NH ₂ Libration	f
529.00w	511.01			N-Li stretch + NH ₂ Libration	e
792.00sh	794.86			NH ₂ Rocking	c
801.00m	797.76			NH ₂ + BH ₃ Rocking	a
808.00m	814.74			NH ₂ + BH ₃ Rocking	g
813.00m	815.22			NH ₂ + BH ₃ Rocking	b
818.00m	821.44			NH ₂ + BH ₃ Rocking	d
824.00m	823.03	820.00m	821.90	NH ₂ + BH ₃ Rocking	f
825.00m	825.79			NH ₂ + BH ₃ Rocking	e
827.00sh	825.96			NH ₂ + BH ₃ Rocking	h
829.00sh	829.91			NH ₂ + BH ₃ Rocking	b
-	831.71			NH ₂ + BH ₃ Rocking	g
834.00sh	836.00			NH ₂ + BH ₃ Rocking	d
	838.04			NH ₂ + BH ₃ Rocking	c
	839.84			NH ₂ + BH ₃ Rocking	a
845.00s	842.74			NH ₂ + BH ₃ Rocking	f
	856.52			NH ₂ + BH ₃ Rocking	e
865.00s	858.63			NH ₂ + BH ₃ Rocking	h
874.00sh				NH ₂ + BH ₃ Rocking	
889.00w	893.72			B-N Stretch	d
889.00w	893.99			B-N Stretch	c
903.00sh	895.09	902.00m	895.80	B-N Stretch	b
914.00w	895.10			B-N Stretch	f
924.00w	895.23			B-N Stretch	a
942.00w	896.69			B-N Stretch	g
985.00w	897.94			NH ₂ + BH ₃ Rocking	e
-	898.86			NH ₂ + BH ₃ Rocking	h
1009.00sh	1013.36			NH ₂ + BH ₃ Rocking	a
	1014.18			NH ₂ + BH ₃ Rocking	c
1021.00s	1021.21			NH ₂ + BH ₃ Rocking	b
-	1023.91			NH ₂ + BH ₃ Rocking	d
-	1024.42			NH ₂ + BH ₃ Rocking	g
	1026.84	1028.00w vbr	1022.00	NH ₂ + BH ₃ Rocking	f
1062.00w	1035.38			NH ₂ + BH ₃ Rocking	e
	1037.72			NH ₂ + BH ₃ Rocking	h
1110.00w	1122.30			NH ₂ + BH ₃ Rocking	h
-	1122.56			NH ₂ + BH ₃ Rocking	e
-	1125.04			NH ₂ + BH ₃ Rocking	b

-	1125.20			NH ₂ + BH ₃ Rocking	g
1128.00w	1128.97			NH ₂ + BH ₃ Rocking	d
	1133.52	1131.00w vbr	1128.90	NH ₂ + BH ₃ Rocking	c
1139.00mbr	1134.28			NH ₂ + BH ₃ Rocking	f
1143.00w	1138.44			B-N Stretch + BH ₃ Rocking	a
1151.00mbr	1154.62			B-N Stretch + BH ₃ Rocking	b
1153.00m	1155.28			B-N Stretch + BH ₃ Rocking	g
1174.00sh	1155.68			B-N Stretch + BH ₃ Rocking	a
1197.00m	1157.27			B-N Stretch + BH ₃ Rocking	e
-	1157.66			B-N Stretch + BH ₃ Rocking	h
-	1162.18			B-N Stretch + BH ₃ Rocking	d
-	1164.03			B-N Stretch + BH ₃ Rocking	c
-	1164.57	1167.00w vbr	1158.90	B-N Stretch + BH ₃ Rocking	f
-	1238.00			BH ₃ Wagging	d
-	1238.46			BH ₃ Wagging	c
-	1240.97			BH ₃ Wagging	h
-	1241.09			BH ₃ Wagging	g
-	1243.01			BH ₃ Wagging	a
-	1243.78			BH ₃ Wagging	f
-	1244.07			BH ₃ Wagging	e
-	1244.11			BH ₃ Wagging	b
-	1256.95			BH ₃ Wagging	f
-	1257.79			BH ₃ Wagging	a
-	1257.92			BH ₃ Wagging	d
-	1258.10			BH ₃ Wagging	h
1271.00s	1258.71			BH ₃ Wagging	c
1284.00sh	1258.88			BH ₃ Wagging	g
1405.00w	1261.32	1260.00m	1237.70	BH ₃ Wagging	e
1462.00w	1262.01		1257.90	BH ₃ Wagging	b
1538.00m	1563.13	1536.00w	1571.00	NH ₂ Wagging	g
1559.00sh	1563.20			NH ₂ Wagging	b
1566.00w	1568.04			NH ₂ Wagging	e
-	1568.10			NH ₂ Wagging	h
-	1570.07			NH ₂ Wagging	a
-	1574.49			NH ₂ Wagging	d
-	1574.81			NH ₂ Wagging	f
-	1577.78			NH ₂ Wagging	c
-				NH ₂ Wagging	
1615.00w				NH ₂ Wagging	
1631.00w				NH ₂ Wagging	
1715.00w				NH ₂ Wagging	
1876.00w				Asymmetric B-H stretch	
2148.00b	2190.95	2152.00mbr	2190.10	Asymmetric B-H stretch	a
2160.00w	2191.41			Asymmetric B-H stretch	d
-	2192.77	2190.00mbr	2230.90	Asymmetric B-H stretch	f
-	2197.51			Asymmetric B-H stretch	c

-	2199.14			Asymmetric B-H stretch	b
-	2199.97			Asymmetric B-H stretch	e
-	2200.37			Asymmetric B-H stretch	g
-	2200.72			Asymmetric B-H stretch	h
2202.00mb	2231.78			Asymmetric B-H stretch	d
2223.00sh	2232.48			Asymmetric B-H stretch	c
2223.00sh	2233.79			Asymmetric B-H stretch	h
	2234.73			Asymmetric B-H stretch	g
-	2239.28			Symmetric B-H stretch	a
-	2244.17			Symmetric B-H stretch	b
-	2244.32			Asymmetric B-H stretch	e
	2246.10			Asymmetric B-H stretch	f
-	2304.78			Asymmetric B-H stretch	g
-	2306.83	2252.00mbr	2310.00	Symmetric B-H stretch	h
2292.00m	2311.49			Asymmetric B-H stretch	c
-	2311.55			Asymmetric B-H stretch	d
-	2315.23			Asymmetric B-H stretch	a
-	2321.64			Asymmetric B-H stretch	b
2316.00sh	2322.41			Asymmetric B-H stretch	e
2383.00w	2326.91	2372.00w		Asymmetric B-H stretch	f
-	3382.23			Asymmetric B-H stretch	f
	3382.30			Symmetric N-H stretch	d
3279.00w	3382.61		-	Symmetric N-H stretch	a
	3382.98	3303.00s	3381.90	Symmetric N-H stretch	c
-	3384.94			Symmetric N-H stretch	g
-	3384.97			Symmetric N-H stretch	b
-	3385.55			Symmetric N-H stretch	h
-	3385.63			Symmetric N-H stretch	e
-	3453.04			Asymmetric N-H stretch	b
	3453.08			Asymmetric N-H stretch	g
	3453.62			Asymmetric N-H stretch	h
	3453.95			Asymmetric N-H stretch	e
	3454.14			Asymmetric N-H stretch	f
	3454.23			Asymmetric N-H stretch	d
	3454.51			Asymmetric N-H stretch	a
3459.00wbr	3454.99			Asymmetric N-H stretch	c
3520.00w		3360.00s	3453.50	Asymmetric N-H stretch	

s, strong; m,medium; w, weak; sh, shoulder; br, broad; v, very.

	Rep	Mul	E	2	2	2	I	m	m	m
a	B3 _u	24	1	-1	-1	1	-1	1	1	-1
b	B2 _u	24	1	-1	1	-1	-1	1	-1	1
c	B1 _u	24	1	1	-1	-1	-1	-1	1	1
d	A _g	24	1	1	1	1	1	1	1	1
e	B3 _g	24	1	-1	-1	1	1	-1	-1	1
f	B2 _g	24	1	-1	1	-1	1	-1	1	-1
g	A _u	24	1	1	1	1	-1	-1	-1	-1
h	B1 _g	24	1	1	-1	-1	1	1	-1	-1

Table 4 Calculated Born charge tensors for α -LiNH₂BH₃.

Atom	q_{11}	q_{22}	q_{33}	q_{23}	q_{13}	q_{12}
H1	-0.11428	-0.17528	-0.12744	0.06089	0.03972	-0.06006
H2	-0.14906	-0.07380	-0.12364	-0.02856	-0.05881	-0.01488
H3	-0.08683	-0.11426	-0.18155	-0.04977	0.04181	0.02611
H4	0.04859	0.07771	0.09714	-0.02309	-0.02960	0.01423
H5	0.06910	0.09538	0.04320	-0.01739	0.03008	0.04036
Li	0.29166	0.34311	0.36900	0.02631	0.04024	0.00533
B	0.20115	0.28676	0.17458	-0.02807	0.00894	-0.08635
N	-0.26031	-0.43961	-0.25126	-0.07826	0.01836	0.06990

Table 5 Calculated atomic displacements and comparison of they increase with temperature from 100K-300K.

Atom	Atomic Displacement (Å)					Amplitude Increase			
	T=70K	T=100K	T=200K	T=300K	T=370K	T=100K	T=200K	T=300K	T=370K
H1-B	0.026415	0.027729	0.033962	0.042078	0.048428	0.001314	0.007547	0.015663	0.022013
H2-B	0.023803	0.025256	0.031749	0.039916	0.046226	0.001453	0.007946	0.016113	0.022423
H3-B	0.024821	0.025892	0.031564	0.0393	0.045399	0.001071	0.006743	0.014479	0.020578
H4-N	0.023723	0.025379	0.034075	0.045205	0.053612	0.001656	0.010352	0.021482	0.029889
H5-N	0.025293	0.026925	0.036219	0.04827	0.057364	0.001632	0.010926	0.022977	0.032071
Li	0.019168	0.020717	0.028227	0.037594	0.044636	0.001549	0.009059	0.018426	0.025468
B	0.010965	0.012283	0.017972	0.024591	0.029464	0.001318	0.007007	0.013626	0.018499
N	0.010924	0.012379	0.018824	0.026263	0.031691	0.001455	0.0079	0.015339	0.020767