SUPPORTING INFORMATION

Structural Stability, Dihydrogen Bonding, and Pressure-Induced Polymorphic Transformations in Hydrazine Borane

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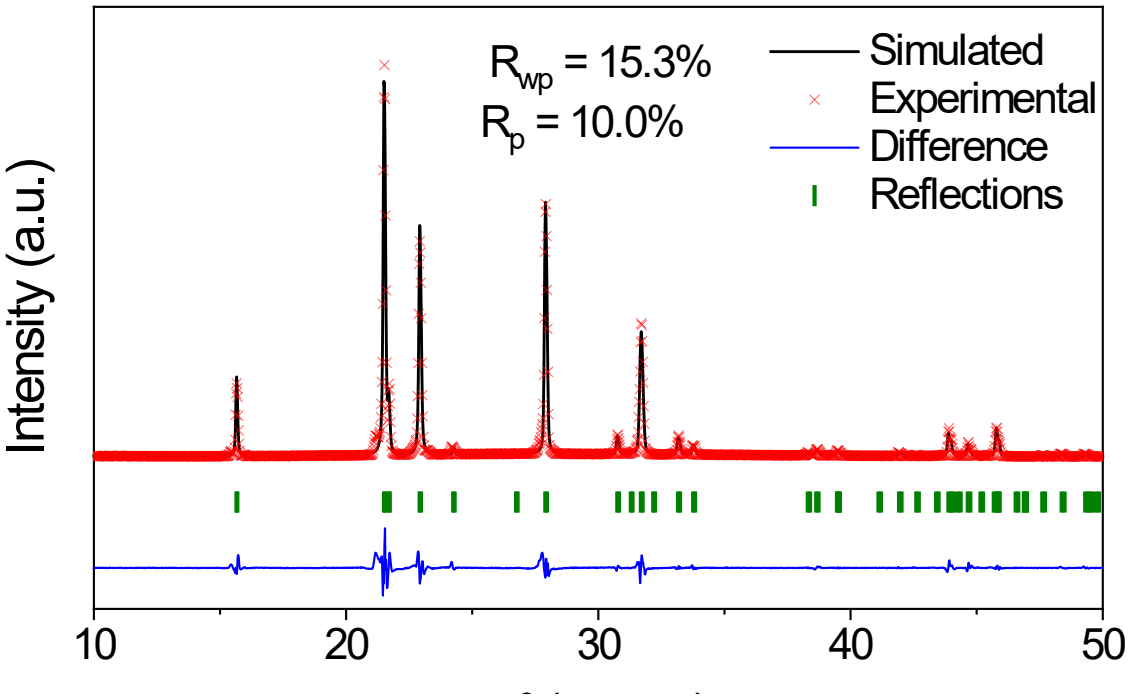


Fig. S1. Calculated XRD patterns in comparison with experimental results under ambient conditions using Rietveld refinements.

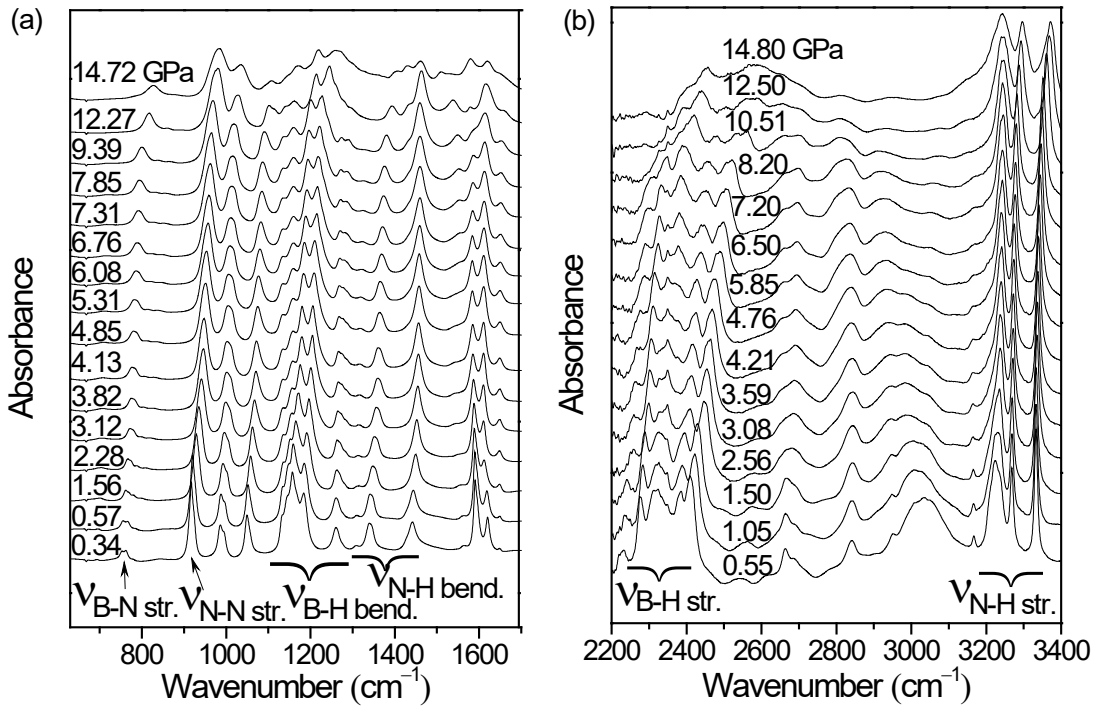


Fig. S2. Selected IR spectra of $N_2H_4BH_3$ collected at room temperature on compression in the region of 630−3400 cm^{-1}. The pressures in GPa are labeled for each spectrum and the assignments are labeled for selected IR modes.

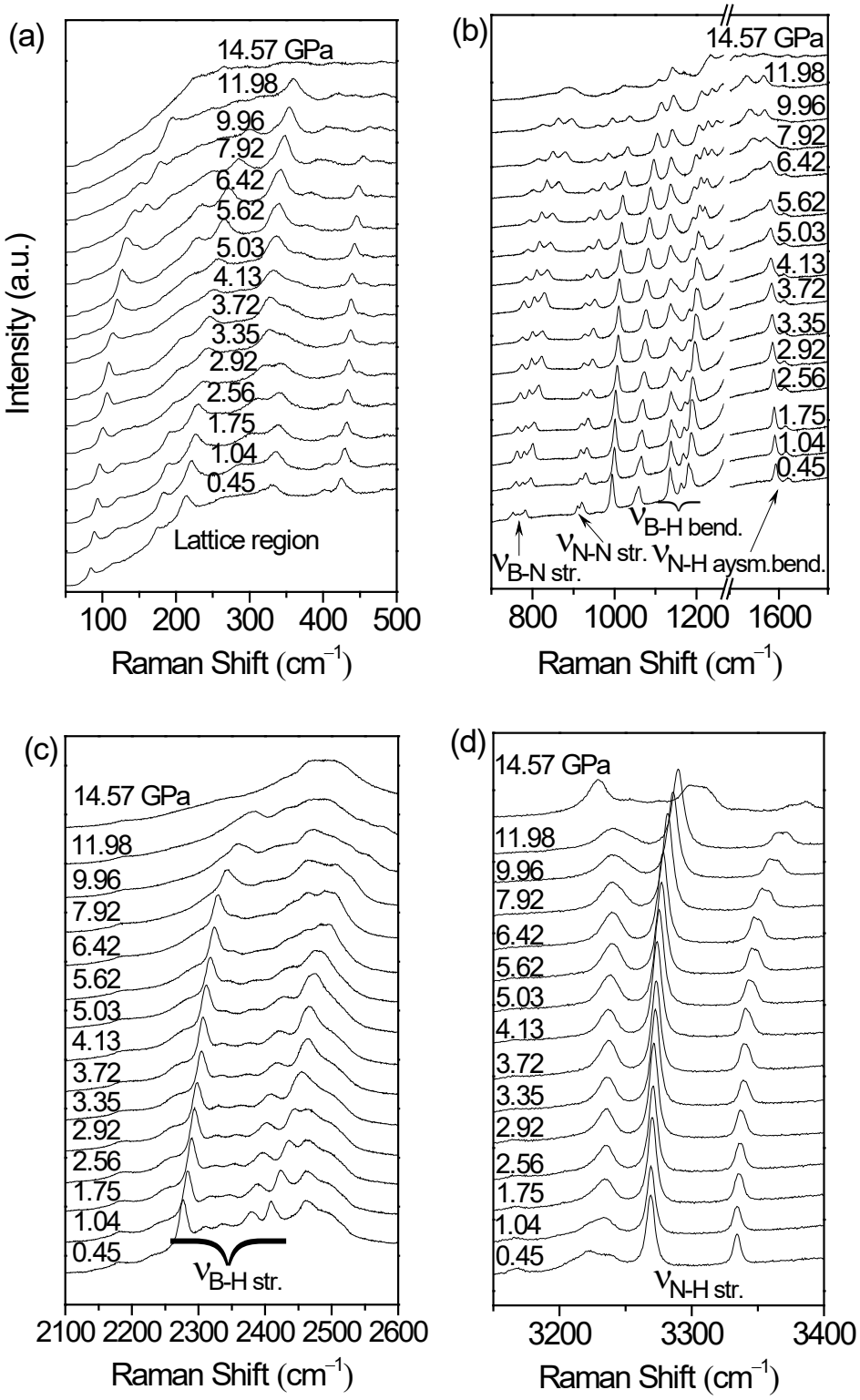


Fig. S3. Selected Raman spectra of $N_2H_4BH_3$ collected at room temperature on compression in the region of 5−3400 cm^{-1}. The pressures in GPa are labeled for each spectrum and the assignments are labeled for selected Raman modes.

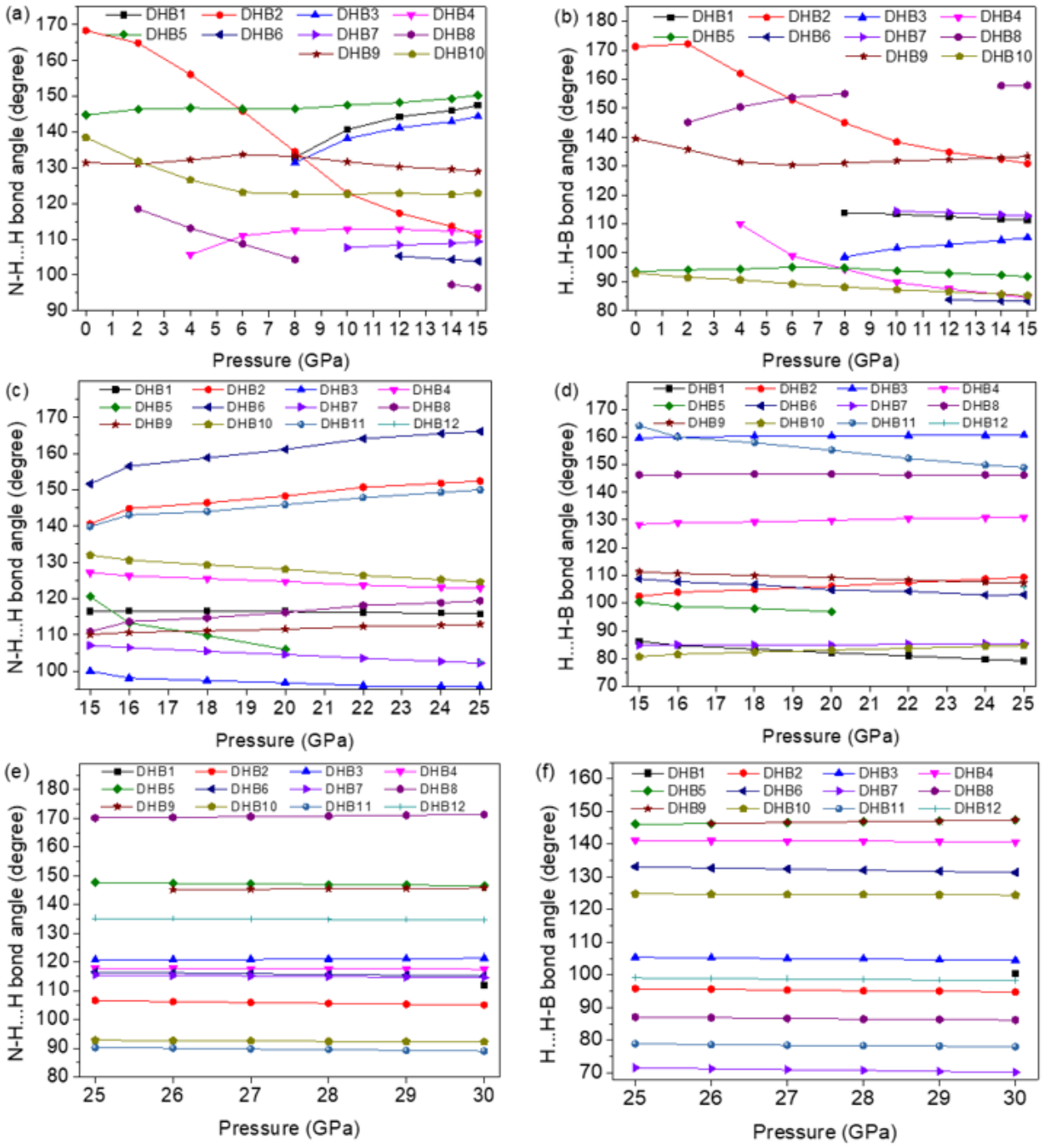


Figure S4. The N-H…H and H…H-B angles versus pressure in phase I (a) (b), phase II (c) (d), and phase III (e) (f).

Table S1. Assignments and vibrational frequencies (cm^{-1}) of $N_2H_4BH_3$ at ambient pressure.

	IR (cm^{-1})	Raman (cm^{-1})
Lattice modes		81
		107
		156
		178
		330
B–N stretching	749	749
	755	773
N–N stretching	913	907
N–H rocking	987	992
	1050	1053
B–H bending	1155	1137
	1183	1178
	1260	1269
N–H bending	1337	1341
	1436	1444
N−H asymmetric bending	1591	1594
	1622	1623
B–H stretching	2271	2272
	2300	2303
	2376	2373
	2398	2399
N–H stretching	3168	3170
	3223	3216
	3268	3269
	3333	3334

Table S2. The pressure dependence of characteristic IR modes of HB on compression.

Assignment	Frequency (cm^{-1})	dν/dp ($cm^{-1}\cdot GPa^{-1}$)
N-N stretching	913	4.6
N-H rocking	986	3.3
B-N bending	1133	0.4
	1156	4.3
	1260	1.5
N-H bending	1337	4.2
	1436	1.3
N-H asym. bending	1591	−0.8
B-H stretching	2271	5.6
N-H stretching	3268	3.0

Table S3. The pressure dependence of characteristic Raman modes of HB on compression.

Assignment	Frequency (cm^{-1})	dν/dp ($cm^{-1}\cdot GPa^{-1}$)
Lattice modes	84	6.8
	288	5.7
	425	3.7
B-N stretching	752	6.1
	783	9.4
N-N stretching	909	4.3
	920	6.2
N-H rocking	994	3.6
B-H stretching	2277	8.7
N-H stretching	3269	1.9

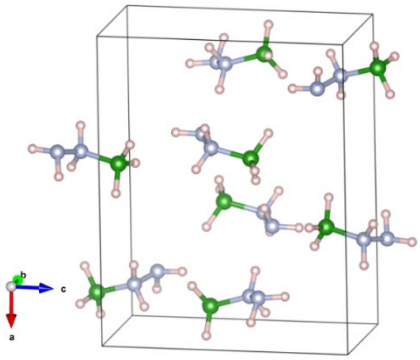
Table S4. Refined cell parameters and volume[a] of $N_2H_4BH_3$ at selected pressures.

Pressure (GPa)	a (Å)	b (Å)	c (Å)	V (Å^3)
0.82	13.000	4.947	9.451	607.9
1.53	12.981	4.905	9.429	600.4
1.88	12.951	4.867	9.399	592.5
2.47	12.863	4.810	9.339	577.8
3.39	12.765	4.712	9.265	557.3
3.89	12.741	4.689	9.246	552.4
4.45	12.696	4.668	9.249	548.2
5.32	12.623	4.620	9.191	535.9
6.28	12.473	4.569	9.086	517.8
7.22	12.397	4.534	9.008	506.3
8.52	12.294	4.493	8.922	492.8
10.41	12.175	4.401	8.922	478.1
12.50	11.985	4.368	8.662	453.4
16.50	11.798	4.317	8.529	434.4
19.86	11.663	4.287	8.445	422.3

a. The uncertainties of all unit cell parameters from refinement are less than 0.003 Å and less than 0.7 Å^3 for unit cell volume.

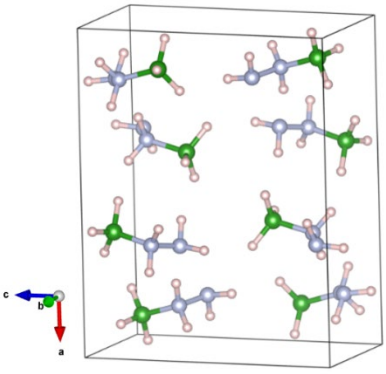
Table S5. Crystal structures, cell parameters (*a*, *b*, *c* in Å; α, β, γ in degrees) and Wyckoff positions for the unit cells of the phase I, phase II and phase III of $N_2H_4BH_3$ optimized at ambient pressure.

phase I-*Pbcn*



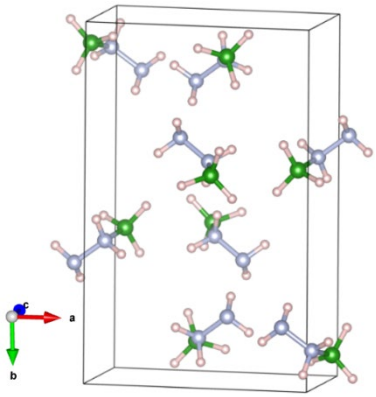
a, *b*, *c*	12.355	5.326	9.787
α, β, γ	90.000	90.000	90.000
H(8*d*)	0.9764	0.2819	0.3979
H(8*d*)	0.9112	−0.0579	0.3588
H(8*d*)	0.8206	0.2563	0.3402
H(8*d*)	0.7883	0.0219	0.5695
H(8*d*)	0.9217	0.0288	0.6085
H(8*d*)	0.8363	0.3379	0.7269
H(8*d*)	0.9091	0.4762	0.6048
B(8*d*)	0.8938	0.1543	0.4014
N(8*d*)	0.8609	0.1256	0.5572
N(8*d*)	0.8413	0.3667	0.6226

phase II-*Pbca*



a, *b*, *c*	12.359	5.351	9.711
α, β, γ	90.000	90.000	90.000
H(8*c*)	0.9783	0.4838	0.8528
H(8*c*)	0.9079	0.8159	0.8896
H(8*c*)	0.8222	0.4959	0.9112
H(8*c*)	0.7849	0.7228	0.6806
H(8*c*)	0.9168	0.7269	0.6382
H(8*c*)	0.8332	0.4120	0.5220
H(8*c*)	0.9131	0.2821	0.6400
B(8*c*)	0.8937	0.6024	0.8486
N(8*c*)	0.8590	0.6245	0.6919
N(8*c*)	0.8423	0.3827	0.6267

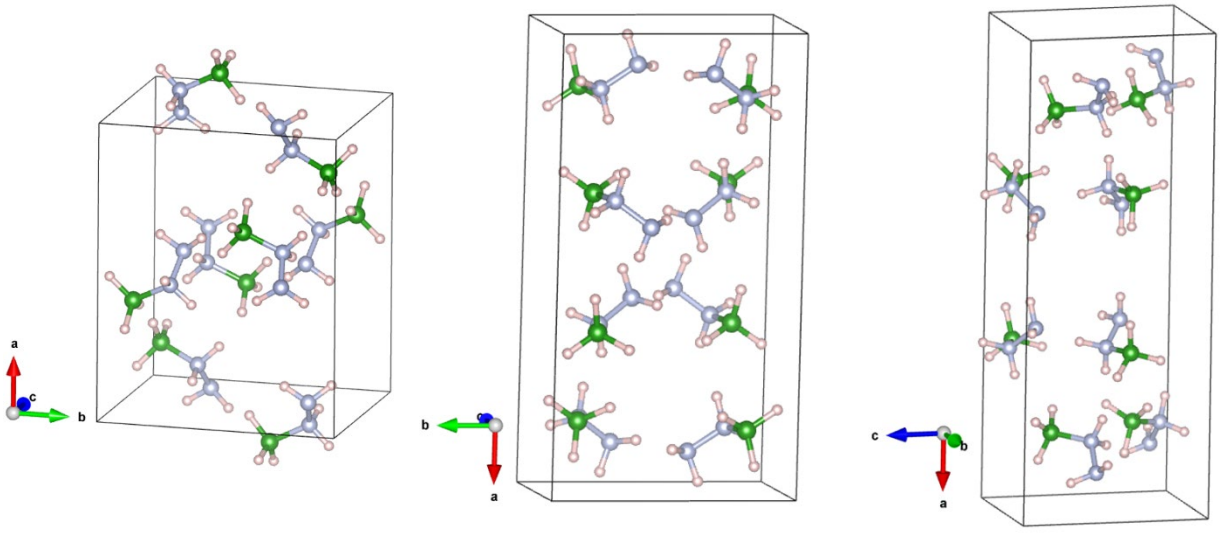
phase III-*Pccn* (A)



a, *b*, *c*	8.854	14.072	5.051
α, β, γ	90.000	90.000	90.000
H(8*e*)	1.1835	0.5344	0.3333
H(8*e*)	1.1406	0.6693	0.2208
H(8*e*)	0.9757	0.5716	0.1998
H(8*e*)	1.0141	0.5585	0.7163
H(8*e*)	1.1270	0.6517	0.7180
H(8*e*)	0.9124	0.7317	0.4900
H(8*e*)	0.8151	0.6400	0.6014
B(8*e*)	1.0887	0.5971	0.3199
N(8*e*)	1.0385	0.6210	0.6144
N(8*e*)	0.9065	0.6828	0.6455

Table S6. Crystal structures, cell parameters (*a*, *b*, *c* in Å; α, β, γ in degrees) and Wyckoff positions for the unit cells of the top-ranked candidate structures of $N_2H_4BH_3$ optimized at ambient pressure.

Pccn (B) | *Pcca* | *Pmc*2_1



a, *b*, *c*	11.004	8.820	7.662
α, β, γ	90.000	90.000	90.000
H(8*e*)	1.2209	0.4374	0.2232
H(8*e*)	1.1779	0.4395	0.4798
H(8*e*)	1.0608	0.5222	0.3028
H(8*e*)	1.0434	0.2594	0.1793
H(8*e*)	1.1409	0.1818	0.3230
H(8*e*)	0.9322	0.3423	0.4411
H(8*e*)	0.9267	0.1568	0.3891
B(8*e*)	1.1402	0.4289	0.3313
N(8*e*)	1.0775	0.2679	0.3078
N(8*e*)	0.9817	0.2428	0.4363

a, *b*, *c*	15.408	8.213	5.187
α, β, γ	90.000	90.000	90.000
H(8*f*)	0.9288	0.1663	0.0642
H(8*f*)	0.8216	0.3054	0.0302
H(8*f*)	0.8105	0.0688	0.1269
H(8*f*)	0.7978	0.2619	0.5082
H(8*f*)	0.8805	0.1397	0.5491
H(8*f*)	0.9775	0.3356	0.4796
H(8*f*)	0.9047	0.4613	0.3551
B(8*f*)	0.8549	0.1901	0.1422
N(8*f*)	0.8598	0.2375	0.4386
N(8*f*)	0.9146	0.3777	0.5035

a, *b*, *c*	18.602	5.764	7.209
α, β, γ	90.000	90.000	90.000
H(4*c*)	0.2055	0.4693	0.7313
H(4*c*)	0.1089	0.5706	0.8281
H(4*c*)	0.1982	0.7581	0.8877
H(4*c*)	0.2045	0.8554	0.5486
H(4*c*)	0.1404	0.6722	0.4837
H(4*c*)	0.1258	1.1208	0.5776
H(4*c*)	0.0825	0.9630	0.7374
H(4*c*)	0.7050	0.0770	0.9857
H(4*c*)	0.6813	0.1900	0.7286
H(4*c*)	0.6017	0.1201	0.9122
H(4*c*)	0.6521	0.4497	1.1076
H(4*c*)	0.7166	0.5184	0.9497
H(4*c*)	0.5676	0.5283	0.8736
H(4*c*)	0.6188	0.7634	0.9144
B(4*c*)	0.1681	0.6347	0.7741
B(4*c*)	0.6635	0.1894	0.8900
N(4*c*)	0.1559	0.7823	0.5906
N(4*c*)	0.1011	0.9637	0.6026
N(4*c*)	0.6657	0.4480	0.9654
N(4*c*)	0.6183	0.5978	0.8582