SUPPORTING INFORMATION

Pressure Mediated Phase Transition and Dihydrogen Bonding Formation in Trimethylamine Borane

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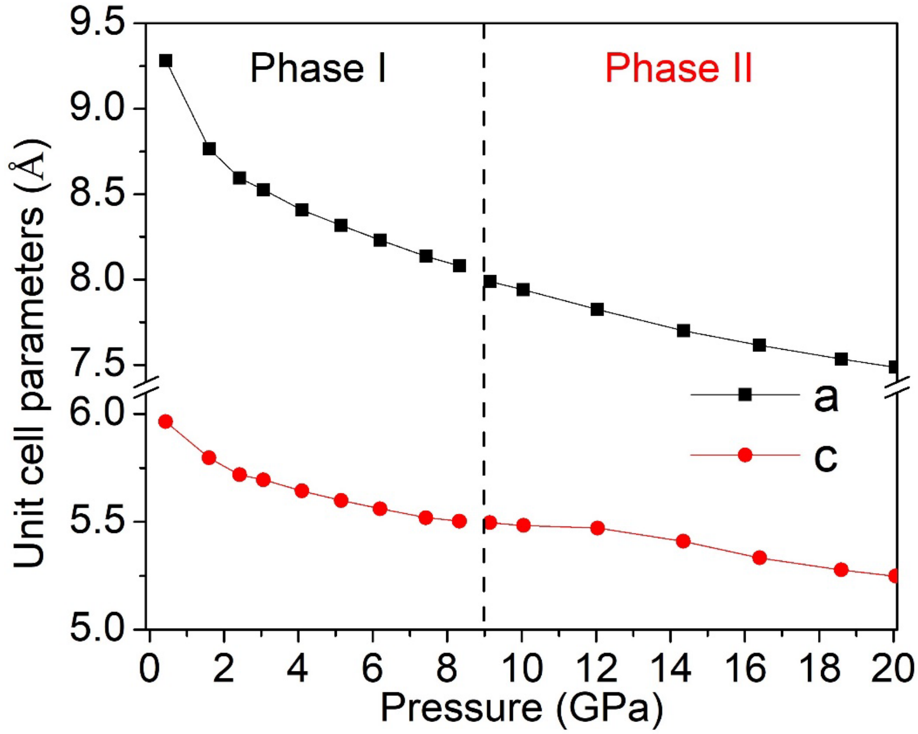


Fig. S1 Unit cell parameters as a function of pressure of TMAB.

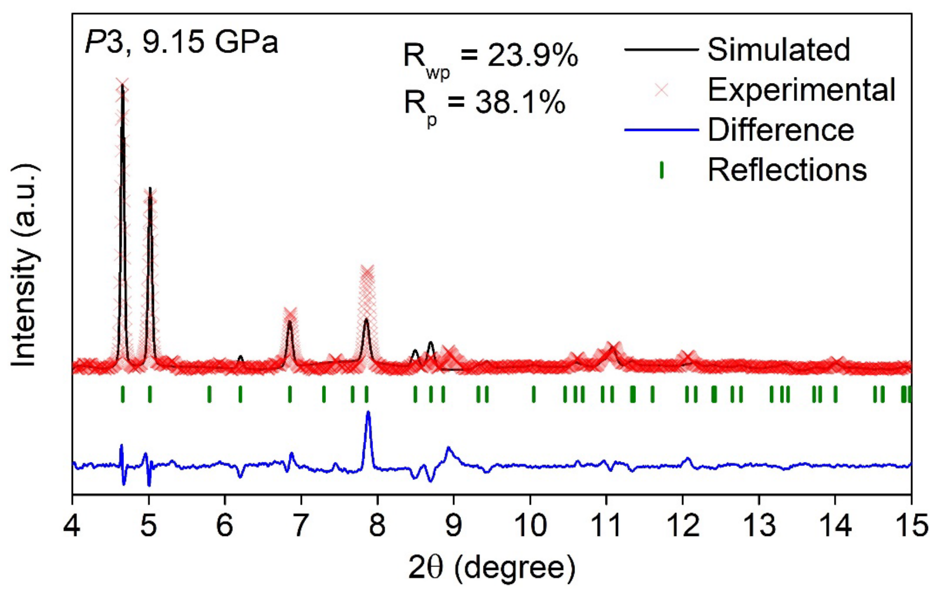


Fig. S2 Experimental and simulated XRD patterns of the *P*3 structures of TMAB at 9.15 GPa obtained by the Rietveld refinement method.

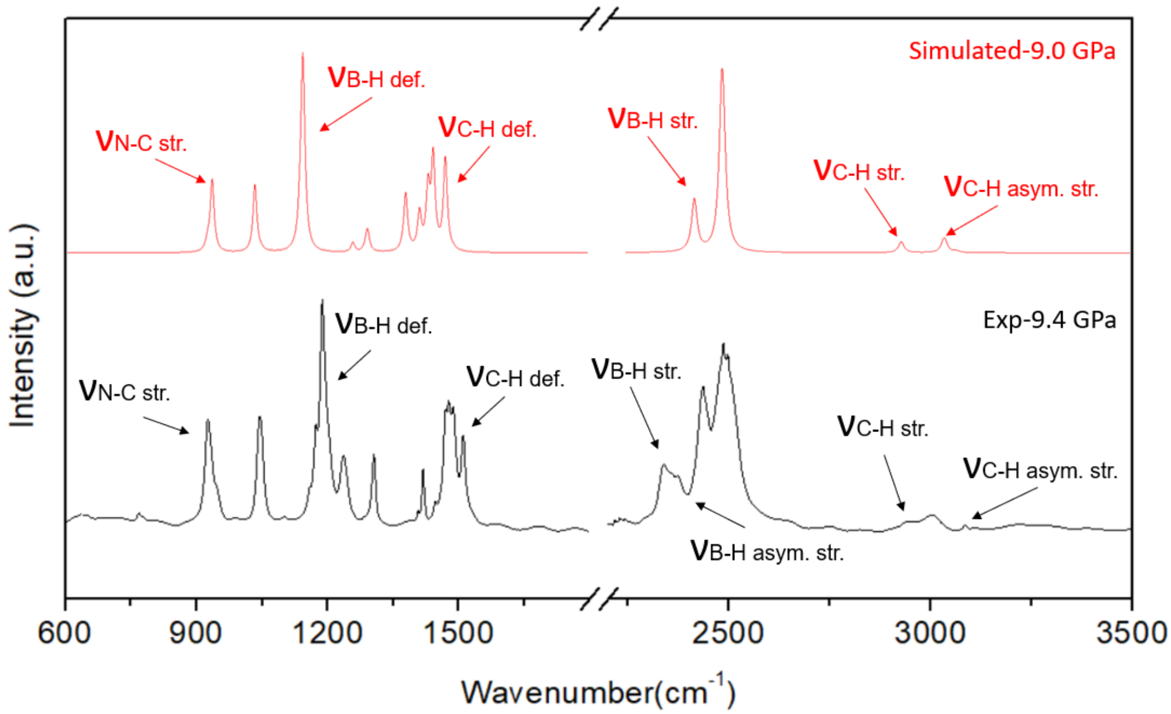


Fig. S3 The comparison between simulated and experimental IR spectra of the $P3_1$ (A) structure of TMAB at 9 GPa.

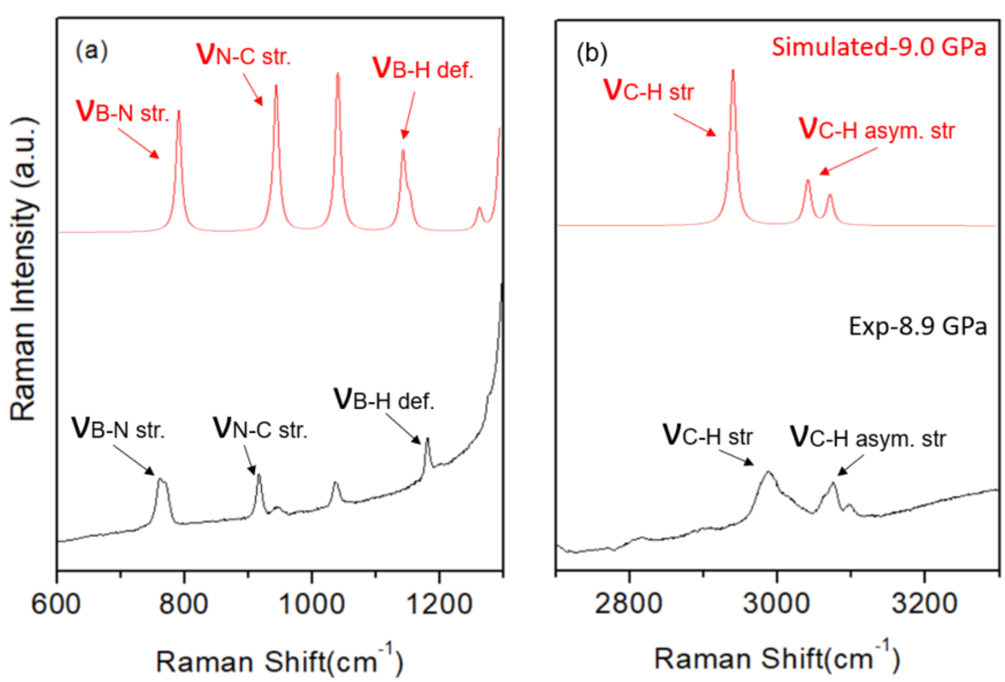


Fig. S4 The comparison between simulated and experimental Raman spectra of $P3_1$ (A) structure of TMAB at 9 GPa.

Table S1 Partial assignments and vibrational frequencies (cm^{-1}) of TMAB at ambient pressure.

Description	This work		Durig *et al.*[50]	
	Raman	IR	Raman	IR
asym. C–H stretching	3025	3019	3019	3018
	3013	3003	3004	3002
sym. C–H stretching	2961	2952	2953	2954
asym. B–H stretching	2377	2371	2373	2360
sym. B–H stretching	2270	2263	2266	2264
B–H deformation	1174	1168	1168	1168
C–H deformation	1468	1474	1475	1473
B–N stretching	691	–	680	680
N–C stretching	865	856	860	859

Table S2 Pressure dependence of the selected IR modes of TMAB on compression [a].

Assignment	Frequency (cm^{-1})	dν/dP ($cm^{-1}\cdot GPa^{-1}$)	
		Phase I (0–9.4 GPa)	Phase II (>9.4 GPa)
ν B-H def.	1168.6	2.23	1.43
ν C-H def.	1446.5	4.56	1.35
ν C-H def.	1474.3	4.28	–
ν B-H str.	2315.8	6.19	–
ν B-H str.	2370.8	11.64	3.63
ν C-H asym. str.	3019.6	8.86	–

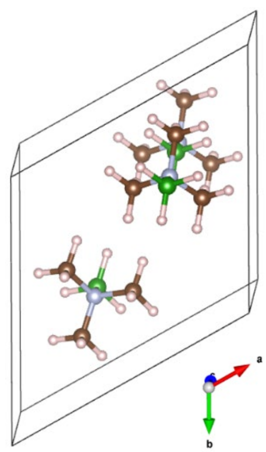
[a] Measured at ambient pressure and room temperature.

Table S3 Pressure dependence of the selected Raman modes of TMAB on compression.

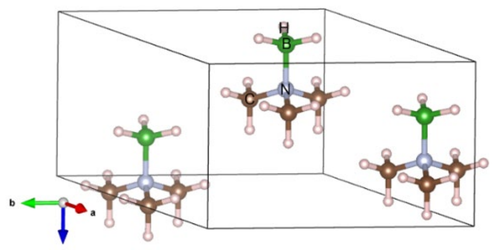
Assignment	Frequency (cm^{-1})	dν/dP ($cm^{-1}\cdot GPa^{-1}$)	
		Phase I (0–8.9 GPa)	Phase II (>8.9 GPa)
ν_1	352.4	7.28	–
ν_2	442.2	5.58	–
ν_3	448.8	5.28	–
ν B-N str.	691.7	8.14	5.27
ν B-N str.	729.2	7.91	–
ν B-H def.	1160.5	2.19	3.02
ν B-H str.	2374.0	10.50	–
ν C-H str.	2930.0	7.09	3.68
ν C-H str.	2958.4	5.91	–
ν C-H asym. str.	3008.5	7.39	6.53

Table S4 Cell parameters (*a*, *b*, *c* in Å; α, β, γ in degrees) and Wyckoff positions for the unit cells of the top-ranked candidate strutures of TMAB optimized at ambient pressure.

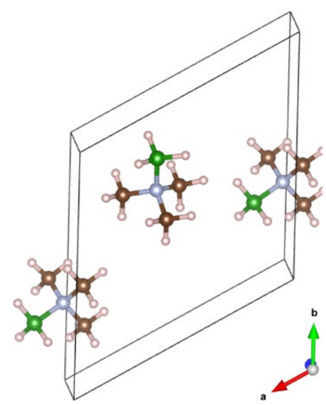
*P*3



$P3_1$ (A)



$P3_1$ (B)



*P*3

a, *b*, *c*	9.577	9.577	5.833
α, β, γ	90.000	90.000	120.000
H(3*d*)	0.9654	1.2008	0.7475
H(3*d*)	0.7847	1.0098	0.7553
H(3*d*)	0.9056	1.0733	0.4988
H(3*d*)	1.0590	1.1402	1.1136
H(3*d*)	1.2857	0.7833	0.1897
H(3*d*)	1.3634	0.9004	0.4482
H(3*d*)	1.1595	0.7399	0.4376
H(3*d*)	1.4304	0.8037	0.8045
H(3*d*)	0.5133	0.3162	1.3302
H(3*d*)	0.4129	0.1923	1.0858
H(3*d*)	0.4906	0.4044	1.0697
H(3*d*)	0.5568	0.2022	0.7152
C(3*d*)	0.9076	1.0760	0.6871
C(3*d*)	1.2822	0.7804	0.3779
C(3*d*)	0.5103	0.3101	1.1421
B(3*d*)	1.0000	1.0000	1.0522
B(3*d*)	1.3333	0.6667	0.7435
B(3*d*)	0.6667	0.3333	0.7764
N(3*d*)	1.0000	1.0000	0.7748
N(3*d*)	1.3333	0.6667	0.4657
N(3*d*)	0.6667	0.3333	1.0540

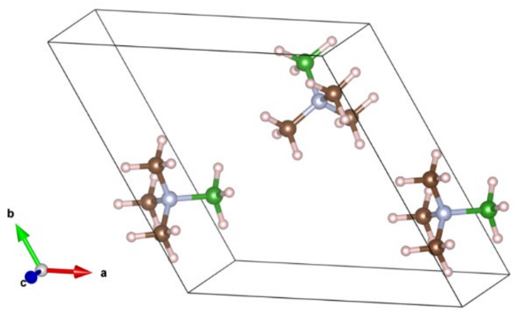
$P3_1$ (A)

a, *b*, *c*	9.405	9.405	5.938
α, β, γ	90.000	90.000	120.000
H(3*a*)	0.5680	0.3559	0.4001
H(3*a*)	0.1213	0.0988	0.4001
H(3*a*)	0.3109	0.5453	0.4002
H(3*a*)	0.5676	0.5457	0.4001
H(3*a*)	0.1210	0.0990	0.3999
H(3*a*)	0.3114	0.0990	0.3999
H(3*a*)	0.5043	0.4189	0.6477
H(3*a*)	0.2481	0.1623	0.6477
H(3*a*)	0.2475	0.4184	0.6477
H(3*a*)	0.4053	0.4768	0.0434
H(3*a*)	0.4050	0.2614	0.0434
H(3*a*)	0.1899	0.2617	0.0433
B(3*a*)	0.3334	0.3333	0.1033
C(3*a*)	0.5050	0.4193	0.4628
C(3*a*)	0.2473	0.4189	0.4627
C(3*a*)	0.2477	0.1617	0.4628
N(3*a*)	0.3333	0.3333	0.3760

$P3_1$ (B)

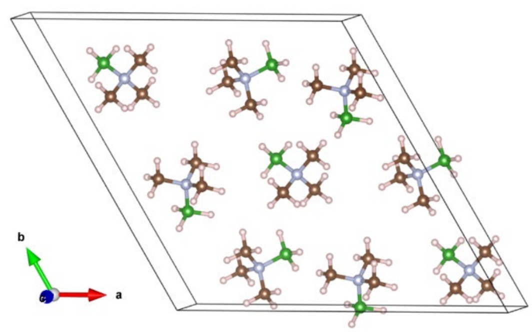
a, *b*, *c*	10.298	10.298	5.775
α, β, γ	90.000	90.000	120.000
H(3*a*)	0.5207	0.5236	0.2547
H(3*a*)	0.4224	0.5979	0.0982
H(3*a*)	0.5657	0.7136	0.3000
H(3*a*)	0.6852	0.5902	−0.3227
H(3*a*)	0.4911	0.5169	−0.2559
H(3*a*)	0.5990	0.4551	−0.0939
H(3*a*)	0.8240	0.8128	0.2058
H(3*a*)	0.8776	0.7606	−0.0554
H(3*a*)	0.7916	0.6259	0.1726
H(3*a*)	0.5232	0.7737	−0.2245
H(3*a*)	0.7411	0.8520	−0.3066
H(3*a*)	0.6871	0.9171	−0.0081
B(3*a*)	0.6493	0.8174	−0.1512
C(3*a*)	0.5308	0.6241	0.1714
C(3*a*)	0.6019	0.5508	−0.1834
C(3*a*)	0.7939	0.7212	0.0830
N(3*a*)	0.6441	0.6761	−0.0175

$P3_2$



a, *b*, *c*	10.249	10.249	5.775
α, β, γ	90.000	90.000	120.000
H(3*a*)	0.3356	1.1505	1.1052
H(3*a*)	0.1884	0.9604	1.1522
H(3*a*)	0.1624	1.0766	0.9481
H(3*a*)	0.4529	0.9079	0.8012
H(3*a*)	0.3468	0.8585	1.0626
H(3*a*)	0.5032	1.0453	1.0263
H(3*a*)	0.3129	1.1546	0.5944
H(3*a*)	0.4325	1.0786	0.5296
H(3*a*)	0.4833	1.2161	0.7564
H(3*a*)	0.1050	0.7536	0.8469
H(3*a*)	0.2246	0.8172	0.5483
H(3*a*)	0.0855	0.8975	0.6285
B(3*a*)	0.1676	0.8532	0.7028
C(3*a*)	0.2441	1.0495	1.0227
C(3*a*)	0.4091	0.9493	0.9381
C(3*a*)	0.3893	1.1198	0.6679
N(3*a*)	0.3050	0.9953	0.8355

*R*3



a, *b*, *c*	17.344	17.344	5.753
α, β, γ	90.000	90.000	120.000
H(9*b*)	0.3032	0.5595	0.4717
H(9*b*)	0.2256	0.4950	0.2469
H(9*b*)	0.3186	0.4800	0.3092
H(9*b*)	0.1053	0.3920	0.7811
H(9*b*)	0.1055	0.4470	0.5178
H(9*b*)	0.1810	0.5086	0.7482
H(9*b*)	0.3178	0.4033	0.6671
H(9*b*)	0.2301	0.3730	0.8732
H(9*b*)	0.3094	0.4880	0.8233
H(9*b*)	0.1177	0.3337	0.2701
H(9*b*)	0.1181	0.2724	0.5689
H(9*b*)	0.2215	0.3156	0.3457
B(9*b*)	0.1631	0.3278	0.4229
C(9*b*)	0.2691	0.4944	0.3841
C(9*b*)	0.1470	0.4442	0.6573
C(9*b*)	0.2716	0.4220	0.7419
N(9*b*)	0.2134	0.4237	0.5542