Supporting Information: Pressure-induced collapse of guanidinium nitrate N−H···O bonded honeycomb layers into a 3-D pattern with varied H-acceptor capacity

Andrzej Katrusiak,[a]* Marek Szafrański[b] and Marcin Podsiadło[a]

[a]*Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*

[b]*Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland*

*E-mail: katran@amu.edu.pl

Diamond-anvil cell X-ray experiment

Guanidinium nitrate (m.p. 486 K, analytical grade without further purification) was dissolved in methanol (the first and the fourth experiment) and in distillate water (the second and the third). Solid guanidinium nitrate was loaded to the modified Merrill-Bassett (Merrill & Bassett, 1974) diamond-anvil cells (DAC) and methanol and saturated aqueous solutions were added to the DAC chambers. Pressure was calibrated by the ruby fluorescence method (Piermarini *et al.*, 1975) with a BETSA PRL spectrometer with the accuracy of 0.05 GPa, before and after the diffraction measurements. The gasket-holes in the 0.3 mm thick steel foil were spark-eroded and pre-indented to *ca.* 0.40 mm in diameter; the initial diameter of the chambers was 0.45 mm.

In the first experiment performed in isochoric conditions in methanol solution (DAC equipped with steel discs), the guanidinium nitrate phase II crystal was obtained: after increasing pressure at 295 K to *ca.* 0.4 GPa, the DAC and the polycrystalline mass inside their chamber were heated using a hot-air gun till all but one grain melted. Then the DAC was slowly cooled and the single crystal grew to fill almost whole volume of the DAC chamber at 295 K. The progress in growing the guanidinium nitrate phase II single crystal is shown in Figure S1.

The single-crystals of guanidinium nitrate in phase IV were obtained from aqueous solution in isochoric conditions: after increasing pressure at 295 K to *ca.* 0.7 GPa (the second experiment with the DAC equipped with beryllium discs) and to *ca.* 0.8 GPa (the third experiment; DAC equipped with steel discs), the DACs and the polycrystalline mass inside their chambers were heated using a hot-air gun till all but one grain melted. Then the DACs were slowly cooled and the single crystals grew to fill *ca.* half of the DACs chamber volumes at 295 K. The progress in growing the guanidinium nitrate phase IV single crystals is shown in Figures S2 and S3.

In the fourth experiment performed in isochoric conditions in methanol solution (DAC equipped with steel discs), the guanidinium nitrate phase IV crystal was obtained: after increasing pressure at 295 K to *ca.* 1.5 GPa, the DAC and the polycrystalline mass inside their chamber were heated using a hot-air gun till all but one grain melted. Then the DAC was slowly cooled and the single crystal grew to fill *ca.* 1/3 volume of the DAC chamber at 295 K. The progress in growing the guanidinium nitrate phase IV single crystal is shown in Figure S4.

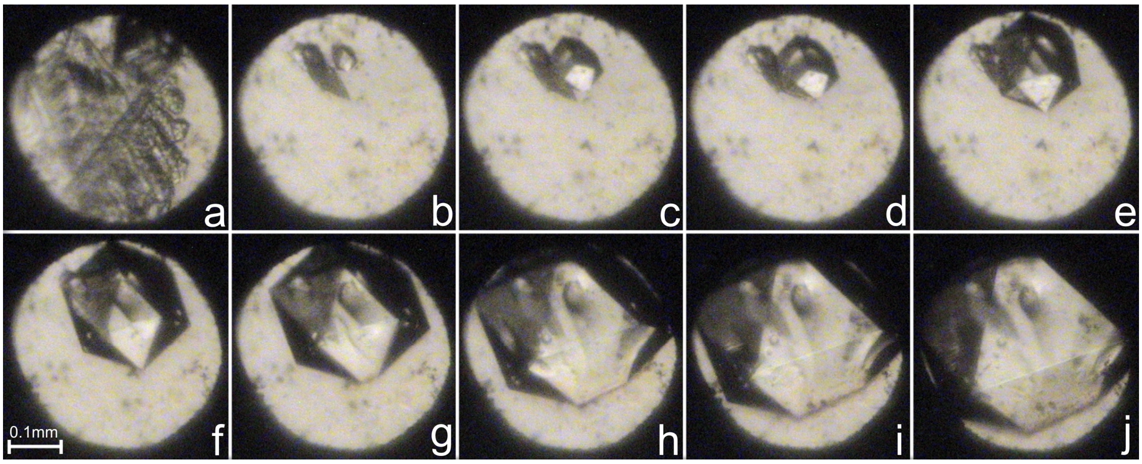

Figure S1. Stages of isochoric guanidinium nitrate phase II single-crystal growth inside the DAC chamber: (a) polycrystalline mass at 400 K; (b) one crystal seed at 420 K; (c-i) the growing crystal on lowering temperature; (j) the guanidinium nitrate single-crystal in CH_3OH solution filling the DAC chamber at 0.36 GPa/295 K. The ruby chip lies in the upper part of the DAC chamber.

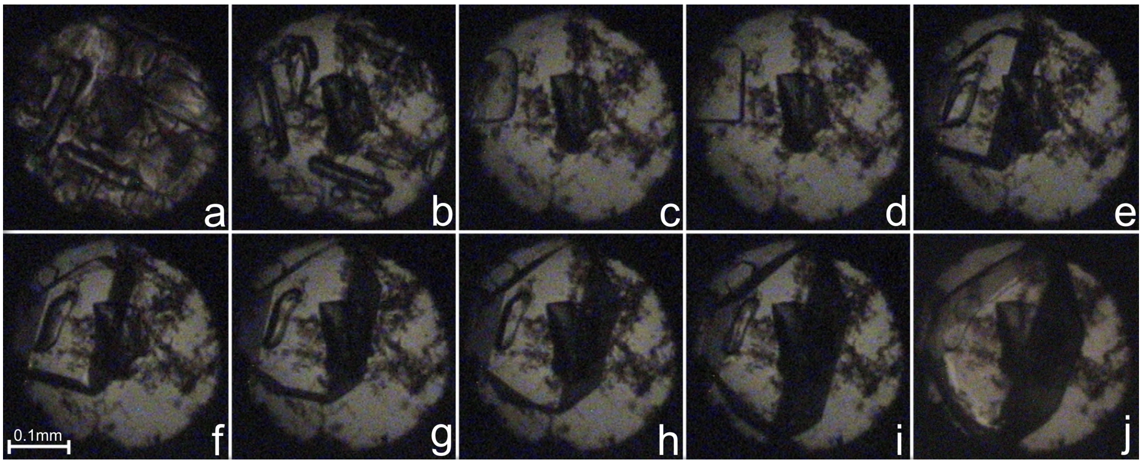

Figure S2. Stages of the guanidinium nitrate isochoric single-crystal growth inside the DAC chamber viewed in a transmission-light mode: (a) polycrystalline mass at 295 K; (b) polycrystalline mass at 330 K; (c) a single-crystal seed at 340 K; (d-i) the single-crystal cooled to 310 K; (j) the DAC chamber filled by the guanidinium nitrate single-crystal in H_2O solution at 295 K and 0.68 GPa. The ruby chip for pressure calibration lies at the central part of the DAC chamber.

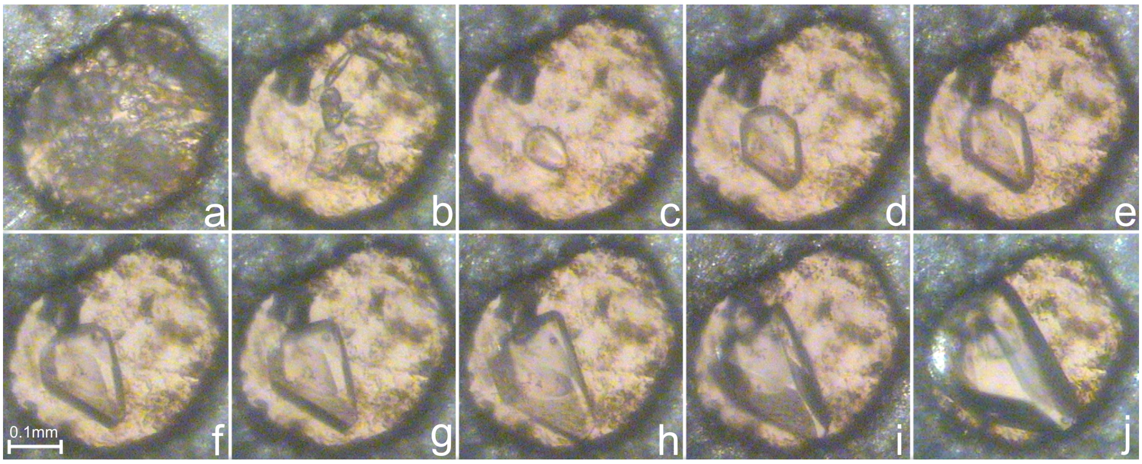

Figure S3. Stages of isochoric guanidinium-nitrate phase IV single-crystal growth inside the DAC chamber: (a) polycrystalline mass at 295 K; (b) a few crystal seeds at 360 K; (c) one crystal seed at 370 K; (d-i) the growing crystal on lowering temperature; (j) the guanidinium nitrate single-crystal in H_2O solution filling the DAC chamber at 0.79 GPa/295 K. The ruby chip lies in the upper part of the DAC chamber.

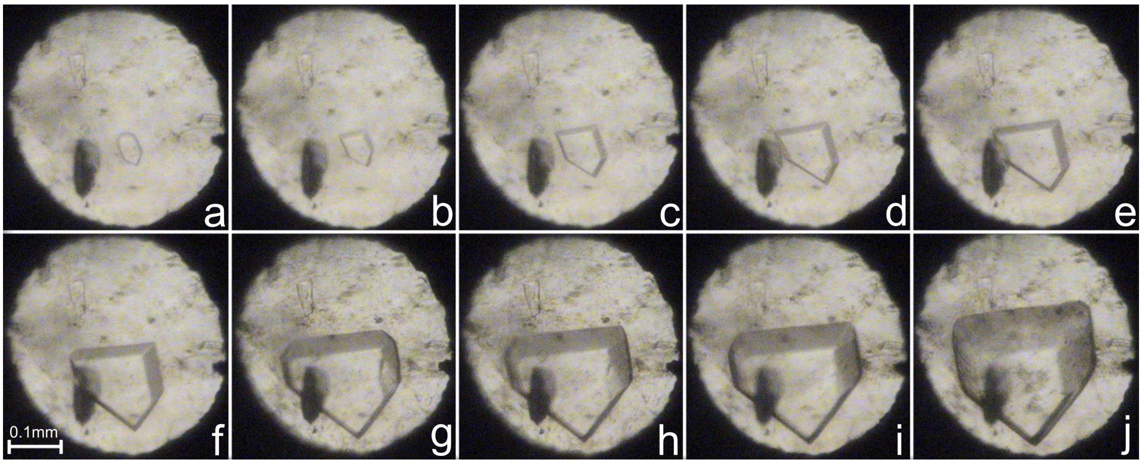

Figure S4. Stages of isochoric guanidinium nitrate phase IV single-crystal growth inside the DAC chamber: (a) one crystal seed at 380 K; (b-i) the growing crystal on lowering temperature; (j) the guanidinium nitrate single-crystal in CH_3OH solution filling *ca.* 1/3 volume of the DAC chamber at 1.51 GPa/295 K. The ruby chip lies in the bottom part of the DAC chamber.

The single-crystals reflection data were collected at 295 K using a KM-4 CCD diffractometer with the graphite-monochromated MoK_α radiation. The DACs were centred by the gasket-shadow method (Budzianowski & Katrusiak, 2004). The reflections were collected with the 40 s exposures at 0.36 GPa, 42 s at 0.68 GPa, 35 s at 0.79 GPa and 28 s at 1.51 GPa; and ω-scan frames of 0.75° in all the measurements (Budzianowski & Katrusiak, 2004).

Program suite *CrysAlis* was used (Xcalibur, 2009) for data collections, determination of the *UB*-matrices, initial data reductions and *Lp* corrections. The reflections intensities have been accounted for the effect of absorption of X-rays by the DAC, shadowing of the beams by the gasket edges, and absorption of the sample crystal itself (Katrusiak, 2003; 2004). The guanidinium nitrate phase II and IV structures were solved by direct methods using program *SHELXS-97* (Sheldrick, 2008), and refined with isotropic displacement parameters (0.36, 0.68 and 1.51 GPa structures) and anisotropic displacement parameters for non-H atoms (0.79 GPa structure) by program *SHELXL-97* (Sheldrick, 2008). The H-atoms were located from geometry assuming the C–H bond length of 0.86 Å (Sheldrick, 2008) and the isotropic displacement parameters 1.2 times $U_{\mathrm{iso}}/U_{\mathrm{eq}}$ of their carriers. Selected details of the guanidinium nitrate phases II and IV structure refinements and crystal data are listed in Table S1. The final atomic parameters are given in Table S2.

Table S1. Crystal data and details of the refinements of guanidinium nitrate phases II and IV at 0.36(5), 0.68(5), 0.79(5) and 1.51(5) GPa (all at 295 K).

$C_1H_6N_4O_3$	**phase II**	**phase IV**	**phase IV**	**phase IV**
Temperature (K)	295(2)	295(2)	295(2)	295(2)
Pressure (GPa)	0.36(5)	0.68(5)	0.79(5)	1.51(5)
Formula weight	122.10	122.10	122.10	122.10
Crystal colour	colourless	colourless	colourless	colourless
Crystal size (mm)	0.34x0.31x0.25	0.25x0.25x0.24	0.36x0.25x0.20	0.34x0.30x0.25
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*m*	*Pc*	*Pc*	*Pc*
Unit cell dimensions (Å; ^{o})	a = 12.340(3)	a = 4.8990(10)	a = 4.8950(10)	a = 4.8670(10)
	b = 7.2110(14)	b = 4.9170(10)	b = 4.8916(10)	b = 4.8450(10)
	c = 7.3900(15)	c = 10.350(2)	c = 10.337(2)	c = 10.140(2)
	β = 125.00(3)	β = 100.80(3)	β = 101.56(3)	β = 102.91(3)
Volume (Å^3)	538.67(19)	244.90(9)	242.49(9)	233.06(8)
Z	4	2	2	2
D_x (g cm^{-3})	1.506	1.656	1.672	1.740
Wavelength MoKα; λ (Å)	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.14	0.16	0.16	0.16
F(000) (e)	256	128	128	128
2θ max (^{o})	54.68	57.86	52.46	51.28
Min./Max. indices h,k,l	-15/15,-9/9,-6/6	-4/4,-6/6,-9/9	-6/6,-5/5,-5/6	-5/5,-5/5,-4/4
Reflections collected/unique	997/100	1866/350	844/254	888/239
R_{int}	0.0359	0.0491	0.0402	0.0597
Observed reflections (I>4σ(I))	82	286	226	206
Data/parameters	100/22	350/34	254/74	239/33
Goodness of fit on F^2	1.160	1.203	1.121	1.198
Final R_1 indices (I>4σ(I))	0.0513	0.0669	0.0324	0.0449
R_1/wR_2 indices (all data)	0.0606/0.0834	0.0902/0.0667	0.0371/0.0781	0.0533/0.0729
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0.08, -0.09	0.10, -0.11	0.08, -0.09	0.11, -0.11
Weighting scheme x; y^a	0; 1.07	0; 0.21	0.0334; 0.15	0; 0.26
Absorption corrections				
DAC transmission min/max	0.92 / 1.00	0.64 / 0.92	0.92 / 1.00	0.92 / 1.00
Gasket shadowing min/max	0.56 / 0.93	0.43 / 0.95	0.58 / 0.93	0.57 / 0.92
Sample transmission min/max	0.96 / 0.97	0.95 / 0.96	0.96 / 0.96	0.96 / 0.96
Extinction method	*SHELXL*	*SHELXL*	*SHELXL*	None
Extinction coefficient	0.38(7)	0.48(3)	0.81(10)	–

[a] $w = 1/(\sigma^2(Fo^2)+x^2P^2+yP)$, where $P=(\mathrm{Max}(Fo^2, 0)+2Fc^2)/3$.

Table S2. Atomic coordinates ($\cdot 10^4$), U_{eq} and U_{iso} ($Å^2 \cdot 10^3$) for guanidinium nitrate phases II and IV at 0.36, 0.68, 0.79 and 1.51 GPa (all at 295 K).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
phase II at 0.36 GPa/295 K				
C1	8933(21)	0	2459(54)	61(3)
N1	9817(19)	0	2211(46)	63(3)
H1	10162	−1031	2196	75
N2	8520(14)	1480(6)	2692(33)	67(2)
H2	7889	1477	2869	80
H3	8864	2512	2677	80
N3	5687(23)	0	2804(55)	70(2)
O1	4454(19)	0	2272(46)	95(3)
O2	6167(9)	1520(5)	2836(22)	72(2)
phase IV at 0.68 GPa/295 K				
C1	−2087(39)	1069(13)	484(20)	29(2)
N1	−3253(25)	3244(10)	59(13)	36(2)
H11	−4657	3831	367	44
H12	−2651	4149	−541	44
N2	−2622(31)	−26(12)	1497(15)	42(2)
H21	−1631	−1369	1853	51
H22	−3980	562	1838	51
N3	−79(33)	−96(12)	175(18)	50(2)
H31	698	−1431	641	61
H32	547	427	−508	61
N4	2336(29)	−5580(14)	2656(16)	37(2)
O1	261(26)	−4480(11)	3220(14)	53(2)
O2	2761(25)	−4662(11)	1779(13)	41(2)
O3	3613(26)	−7565(8)	3274(13)	41(1)
phase IV at 0.79 GPa/295 K				
C1	−2001(17)	1000(15)	613(14)	34(4)
N1	−3264(15)	3270(15)	47(15)	51(8)
H11	−4646	3963	333	61
H12	−2689	4028	−600	61
N2	−2869(16)	−88(13)	1562(17)	38(11)
H21	−2155	−1600	1895	46
H22	−4176	683	1876	46
N3	15(17)	−155(11)	112(13)	50(13)
H31	750	−1667	434	60
H32	585	610	−535	60
N4	2273(14)	−5604(15)	2728(15)	34(4)
O1	358(13)	−4542(9)	3192(11)	62(8)
O2	2890(13)	−4652(11)	1690(12)	58(9)
O3	3459(14)	−7629(10)	3273(17)	58(8)
phase IV at 1.51 GPa/295 K				
C1	−2044(17)	1115(14)	644(19)	20(2)
N1	−3305(15)	3381(11)	42(17)	37(2)
H11	−4759	4044	282	44
H12	−2662	4177	−585	44
N2	−2823(14)	−207(14)	1575(17)	31(2)
H21	−1911	−1653	1918	37
H22	−4263	342	1864	37
N3	−18(13)	−88(12)	118(16)	35(2)
H31	664	−1662	419	42
H32	587	722	−516	42
N4	2288(16)	−5713(13)	2647(17)	26(2)
O1	300(11)	−4667(10)	3229(13)	42(2)
O2	2949(12)	−4616(15)	1736(18)	44(2)
O3	3495(12)	−7817(8)	3263(12)	32(2)

Differential thermal analysis and dielectric spectroscopy methods

The hydrostatic pressure exerted to the sample by the compressed helium was calibrated by means of a manganin gauge with an accuracy of ±2 MPa. The temperature was measured inside the cell using a copper-constantan thermocouple. The transition temperatures were determined as the onsets of the thermal or dielectric anomalies. The DTA heating/cooling runs were recorded at a temperature rate of 2 K·min^{-1}, whereas the electric permittivity was measured at a rate of 1 K·min^{-1}.

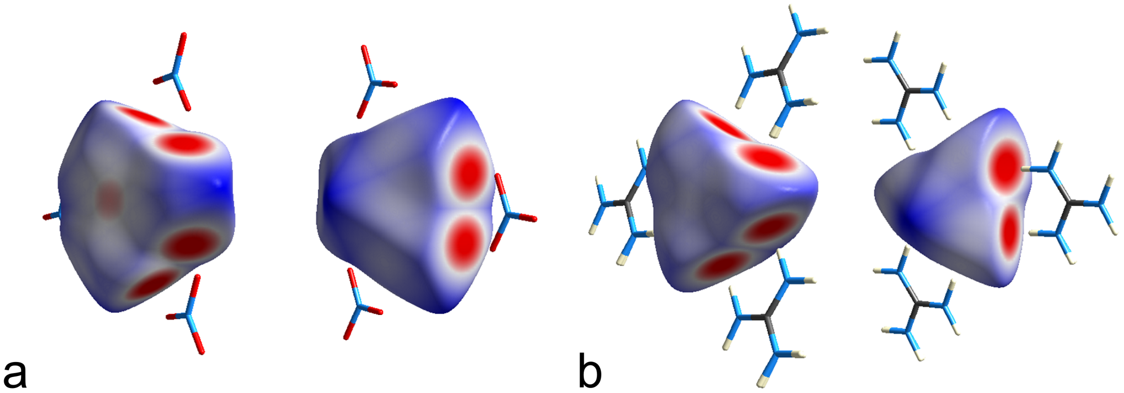

Figure S5. The Hirshfeld surfaces (Grimwood *et al.,* 2008) for the guanidinium nitrate phase II determined at 0.36 GPa/295 K: (a) guanidinium cations and (b) nitrate anions. The colour scale describes distances longer (shades of navy-blue), equal (white) and shorter (red) than van der Waals radii. The colour scale ranges from -0.5 to 1.5.

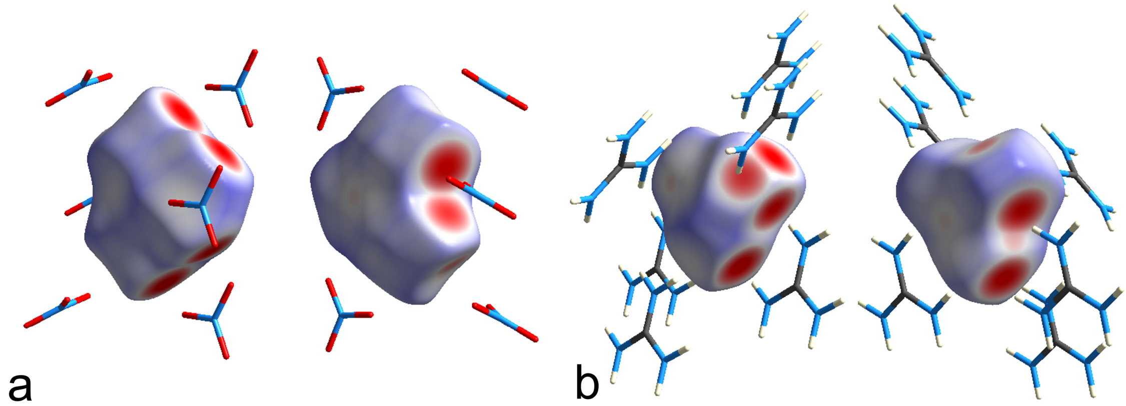

Figure S6. The Hirshfeld surfaces (Grimwood *et al.,* 2008) for the guanidinium nitrate phase IV determined at 0.79 GPa/295 K: (a) guanidinium cations and (b) nitrate anions. The colour scale describes distances longer (shades of navy-blue), equal (white) and shorter (red) than van der Waals radii. The colour scale ranges from -0.5 to 1.5.

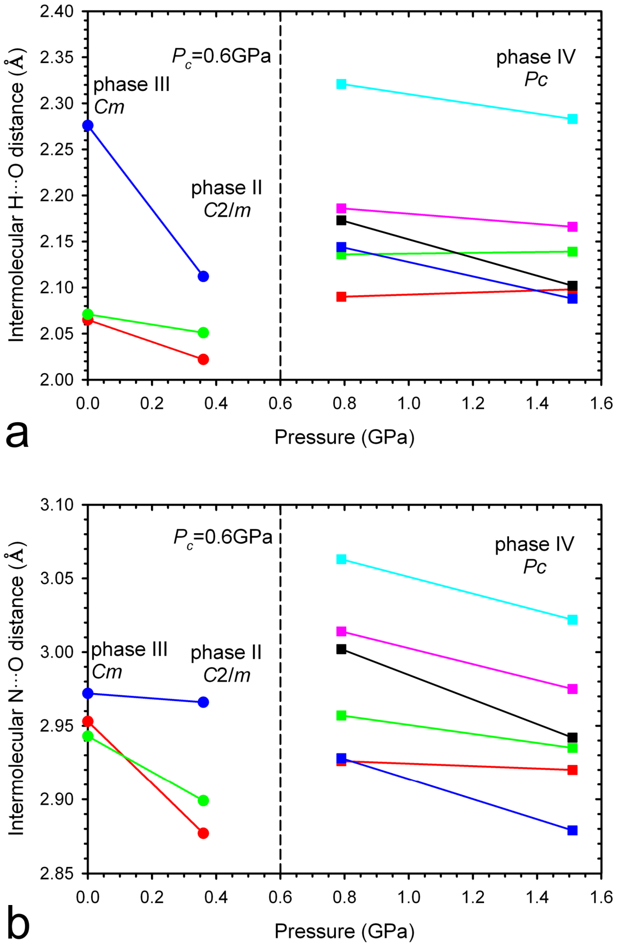

Figure S7. Hydrogen bond lengths (a) H···O and (b) N···O in the structures of phase III (0.1 MPa/153 K), phase II (0.36 GPa/295 K) and phase IV (0.79 and 1.51 GPa all at 295 K). The vertical dashed line marks the magnitude of pressure of transition between phases II and IV. The lines joining the points have been drawn to guide the eye only.

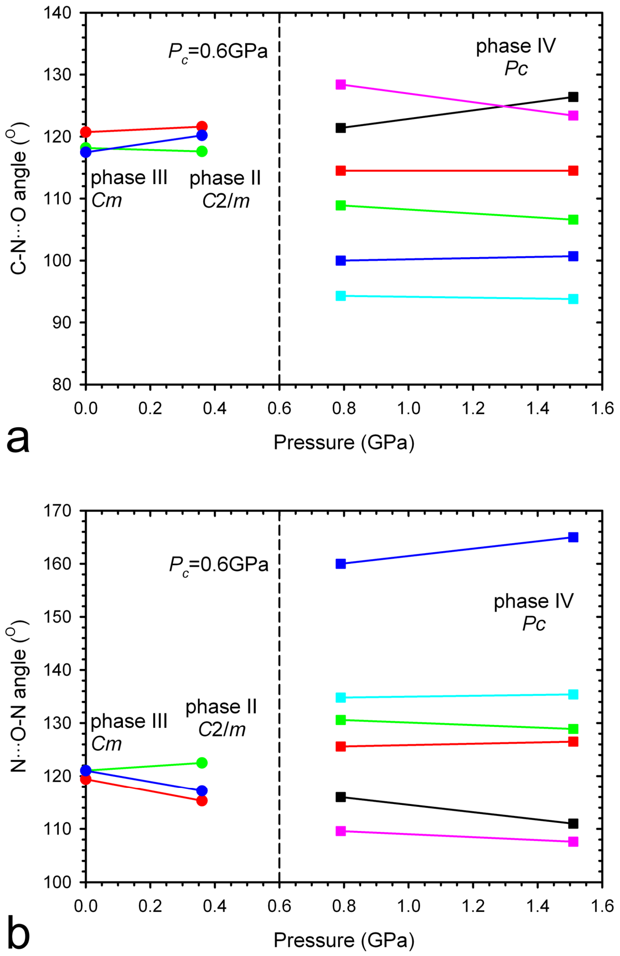

Figure S8. Angular dimensions of the hydrogen bonds in GN phases II, III and IV: (a) C−N···O, and (b) N···O−N angles. The colours used in this figure correspond to those in Figure S7.

Table S3. Dimensions of the shortest intermolecular N−H···O contacts observed in guanidinium nitrate phases II and IV. The symmetry codes of the acceptor atoms are given.

N−H···O	H···O (Å)	N···O (Å)	N−H···O (°)	symmetry code
phase II at 0.36 GPa/295 K				
N2−H3···O1	2.022	2.877(6)	172.78	0.5+*x*, 0.5+*y*, *z*
N1−H1···O2	2.051	2.899(7)	168.41	0.5+*x*, −0.5+*y*, *z*
N2−H2···O2	2.112	2.966(6)	172.25	*x*, *y*, *z*
phase IV at 0.68 GPa/295 K				
N3−H31···O2	2.118	2.978(10)	177.80	*x*, *y*, *z*
N1−H11···O2	2.231	3.057(30)	160.90	−1+*x*, 1+*y*, *z*
N1−H12···O1	2.096	2.861(28)	147.90	*x*, −*y*, −0.5+*z*
N2−H21···O1	2.170	3.004(8)	163.30	*x*, *y*, *z*
N2−H22···O3	2.259	3.086(35)	161.26	−1+*x*, 1+*y*, *z*
N3−H32···O1	2.379	3.051(17)	135.37	*x*, −*y*, −0.5+*z*
phase IV at 0.79 GPa/295 K				
N3−H31···O2	2.090	2.926(13)	163.76	*x*, *y*, *z*
N1−H11···O2	2.136	2.957(15)	159.60	−1+*x*, 1+*y*, *z*
N1−H12···O1	2.144	2.928(17)	151.44	*x*, −*y*, −0.5+*z*
N2−H21···O1	2.173	3.002(13)	162.00	*x*, *y*, *z*
N2−H22···O3	2.186	3.014(18)	161.32	−1+*x*, 1+*y*, *z*
N3−H32···O1	2.321	3.063(12)	144.64	*x*, −*y*, −0.5+*z*
phase IV at 1.51 GPa/295 K				
N3−H31···O2	2.098	2.920(14)	159.72	*x*, *y*, *z*
N1−H11···O2	2.139	2.935(22)	153.78	−1+*x*, 1+*y*, *z*
N1−H12···O1	2.088	2.879(20)	152.79	*x*, −*y*, −0.5+*z*
N2−H21···O1	2.102	2.942(12)	165.15	*x*, *y*, *z*
N2−H22···O3	2.166	2.975(18)	156.75	−1+*x*, 1+*y*, *z*
N3−H32···O1	2.283	3.022(12)	144.14	*x*, −*y*, −0.5+*z*

Table S4. Angular dimensions of the N−H···O hydrogen bonds in GN phases II and IV.

C−N−H···O−N	C−N···O* (º)	N···O*−N* (º)	*symmetry code
phase II at 0.36 GPa/295 K			
C1−N2−H3···O1−N3	121.6(4)	115.3(6)	$0.5+x, 0.5+y, z$
C1−N1−H1···O2−N3	117.6(4)	122.5(5)	$0.5+x, -0.5+y, z$
C1−N2−H2···O2−N3	120.2(4)	117.2(4)	x, y, z
phase IV at 0.68 GPa/295 K			
C1−N3−H31···O2−N4	121.2(19)	130.3(16)	x, y, z
C1−N1−H11···O2−N4	112.5(13)	126.9(11)	$-1+x, 1+y, z$
C1−N1−H12···O1−N4	97.1(13)	162.0(9)	$x, -y, -0.5+z$
C1−N2−H21···O1−N4	131.6(17)	109.7(12)	x, y, z
C1−N2−H22···O3−N4	125.0(12)	107.2(11)	$-1+x, 1+y, z$
C1−N3−H32···O1−N4	88.6(13)	135.1(5)	$x, -y, -0.5+z$
phase IV at 0.79 GPa/295 K			
C1−N3−H31···O2−N4	114.5(9)	125.6(4)	x, y, z
C1−N1−H11···O2−N4	108.9(9)	130.6(5)	$-1+x, 1+y, z$
C1−N1−H12···O1−N4	100.0(5)	160.0(9)	$x, -y, -0.5+z$
C1−N2−H21···O1−N4	121.4(5)	116.0(7)	x, y, z
C1−N2−H22···O3−N4	128.4(6)	109.6(12)	$-1+x, 1+y, z$
C1−N3−H32···O1−N4	94.3(6)	134.8(7)	$x, -y, -0.5+z$
phase IV at 1.51 GPa/295 K			
C1−N3−H31···O2−N4	114.5(12)	126.5(9)	x, y, z
C1−N1−H11···O2−N4	106.6(13)	128.9(8)	$-1+x, 1+y, z$
C1−N1−H12···O1−N4	100.7(10)	165.0(9)	$x, -y, -0.5+z$
C1−N2−H21···O1−N4	126.4(8)	111.0(10)	x, y, z
C1−N2−H22···O3−N4	123.4(8)	107.6(10)	$-1+x, 1+y, z$
C1−N3−H32···O1−N4	93.8(8)	135.4(4)	$x, -y, -0.5+z$

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