Supplementary Material (ESI) for CrystEngComm
This journal is © The Royal Society of Chemistry 2010

Supporting Information: Density, Freezing and Molecular Aggregation in Pyridazine, Pyridine and Benzene

Marcin Podsiadło, Katarzyna Jakóbek and Andrzej Katrusiak*

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

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

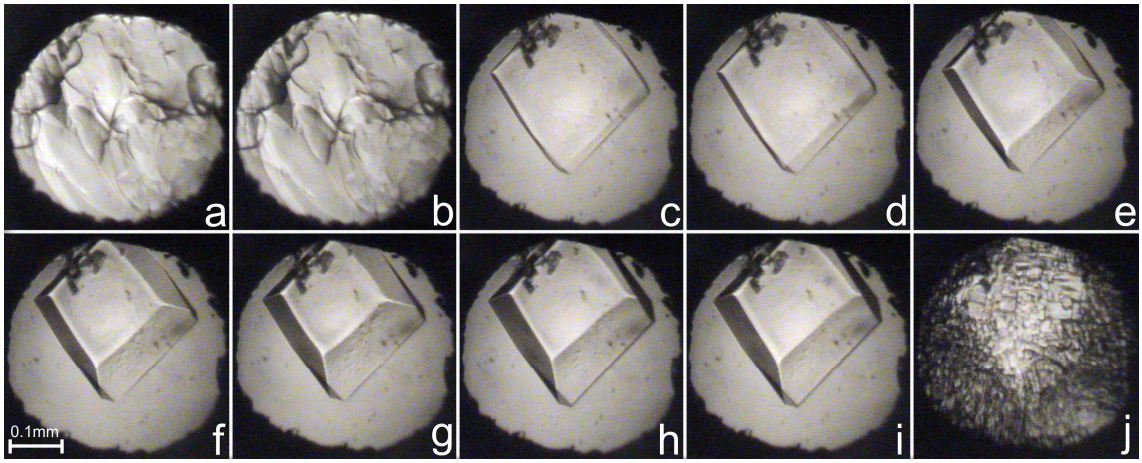

Figure S1. The I/II phase transition of pyridine inside the DAC chamber: (a,b) polycrystalline mass of phase II at 1.20 GPa/295 K; (c) one crystal seed at 350 K; (d-i) single crystal growth during cooling the DAC; (i) single crystal of pyridine phase II just before the phase transition at 310 K; (j) DAC chamber after phase transition filled by polycrystalline mass of pyridine phase I at 0.90 GPa/295 K (the single crystal of pyridine in phase II was damaged when phase transition occurred).

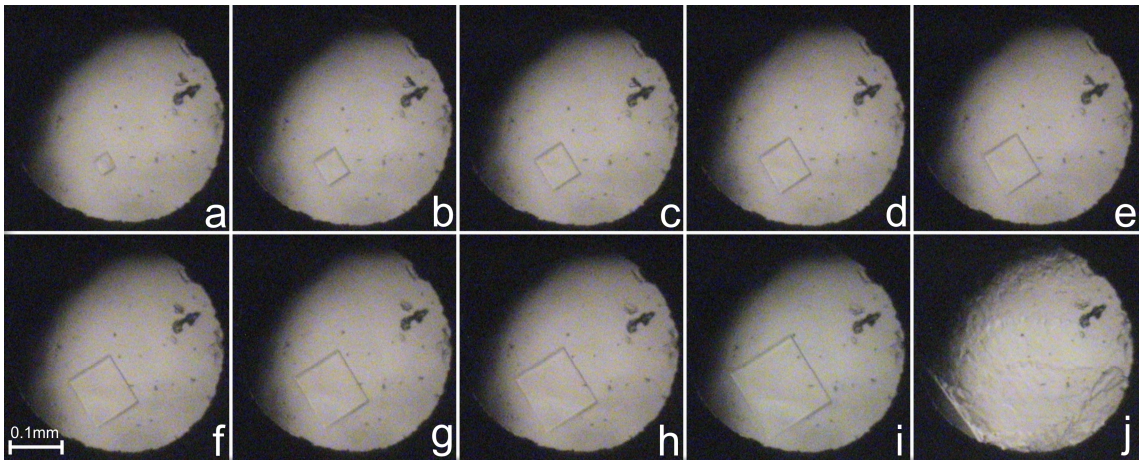

Figure S2. Isochoric freezing of pyridine:methanol 3:1 cocrystal: (a) one crystal grain at *ca.* 450 K; (b-i) isochoric single-crystal growth when the DAC is cooled slowly; (j) the single crystal of pyridine:methanol 3:1 cocrystal at 1.80 GPa/295 K.

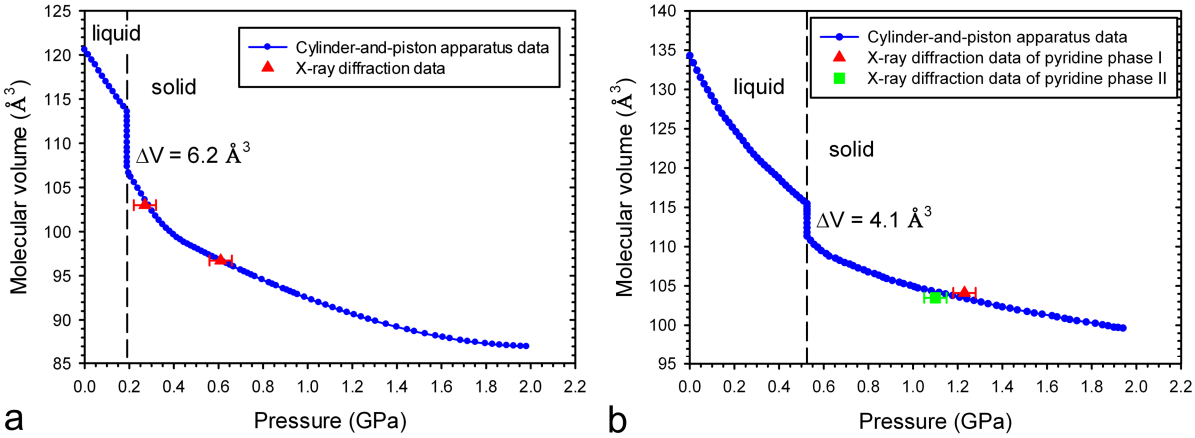

Figure S3. Molecular volume at 295 K of $C_4H_4N_2$ (a) and of C_5H_5N (b) in the function of pressure. The pressure of freezing is marked by the volume jump at 0.19 GPa for pyridazine and at 0.53 GPa for pyridine. Blue circles represent the molecular volume measured in the piston-cylinder press and red triangles mark those from high-pressure X-ray single-crystal diffraction experiments. Green square in (b) represents the molecular volume of pyridine phase II measured at 1.1 GPa/295 K by S. Crawford, M. T. Kirchner, D. Bläser, R. Boese, W. I. F. David, A. Dawson, A. Gehrke, R. M. Ibberson, W. G. Marshall, S. Parsons and O. Yamamuro, *Angew. Chem. Int. Ed.*, 2009, **48**, 755.

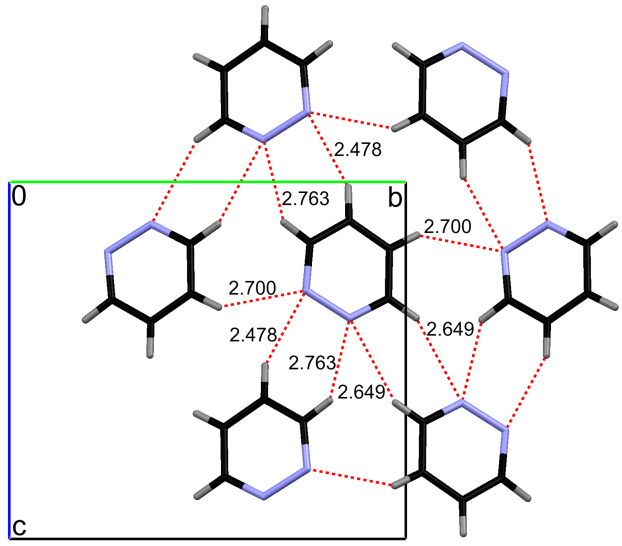

Figure S4. The crystal structure of pyridazine determined at 0.61 GPa/295 K viewed along ***a***. The shortest intermolecular C−H···N hydrogen bonds indicated as red dashed lines.

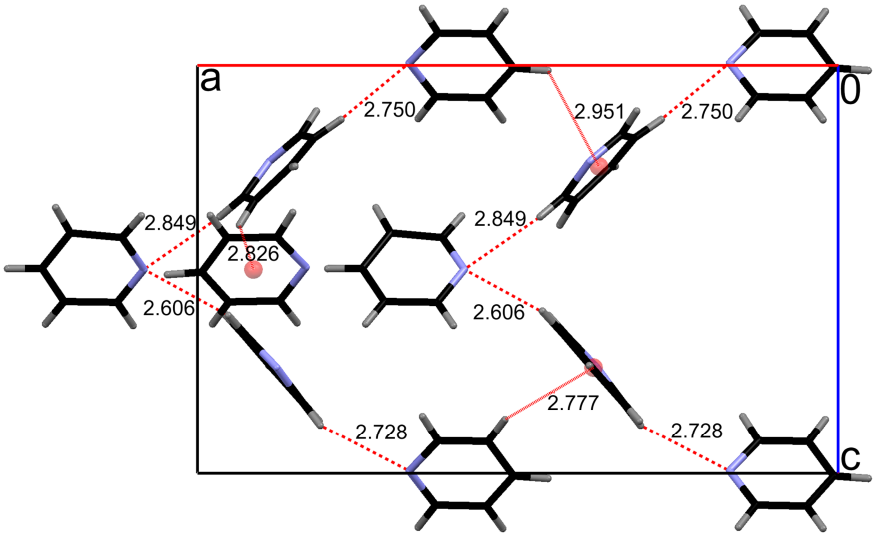

Figure S5. The crystal structure of pyridine I determined at 1.23 GPa/295 K viewed along ***b***. The shortest intermolecular C−H···N hydrogen bonds indicated as red dashed lines, and C−H···π as red solid lines.

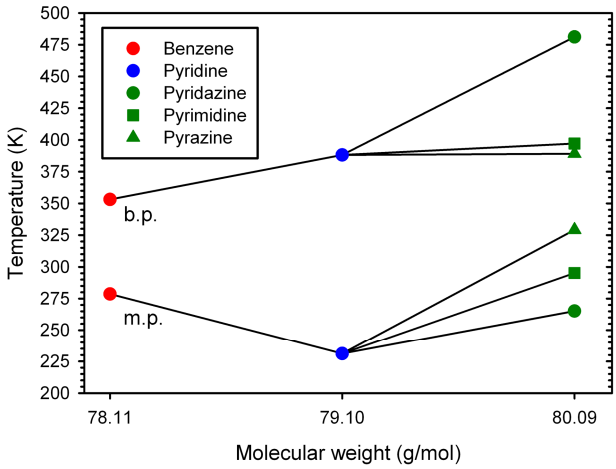

Figure S6. Boiling and melting points (K) in the function of molecular weight (g/mol) for benzene (red dots), pyridine (blue dots), pyridazine (green dots), pyrimidine (green squares) and pyrazine (green triangles).

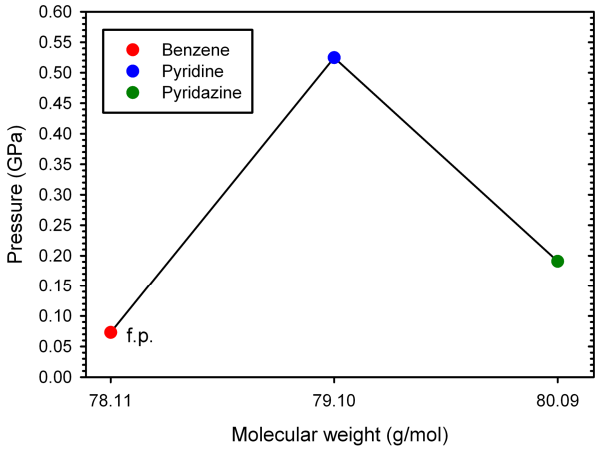

Figure S7. Freezing-pressure (GPa) in the function of molecular weight (g/mol) for benzene (red dot), pyridine (blue dot) and pyridazine (green dot).

Table S1. Crystal data and details of the refinements of $C_4H_4N_2$ at 0.27(5) GPa/295 K, and at 0.61(5) GPa/295 K compared with the $C_4H_4N_2$ structure determined at 0.10 MPa/100.0(1) K.

	$C_4H_4N_2$[a]	$C_4H_4N_2$[b]	$C_4H_4N_2$[b]
Temperature (K)	100.0(1)	295(2)	295(2)
Pressure	0.10 MPa	0.27(5) GPa	0.61(5) GPa
Formula weight	80.09	80.09	80.09
Crystal colour	colourless	colourless	colourless
Crystal size (mm)	0.77 x 0.46 x 0.46	0.41 x 0.41 x 0.28	0.40 x 0.40 x 0.25
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions (Å; °) a =	3.7870(6)	3.8432(8)	3.7189(7)
b =	10.7415(29)	10.964(2)	10.748(2)
c =	9.721(6)	9.778(2)	9.6823(19)
β =	91.401(27)	91.13(3)	91.50(3)
Volume (Å^3)	395.32	411.95(15)	386.86(13)
Z	4	4	4
D_x (g cm^{-3})	1.346	1.291	1.375
Wavelength MoKα, λ (Å)	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.08	0.09	0.09
F(000) (e)	168	168	168
2θ max (°)	80	49.98	49.84
Min./Max. indices h,k,l	-6/6, 0/16, 0/17	-4/4, -4/4, -11/11	-4/4, -5/5, -11/11
Reflections collected/unique	–/2431	2829/301	2663/321
R_{int}	–	0.1052	0.0766
Observed reflections (I>4σ(I))	1732	234	250
Data/parameters	2431/71	301/56	321/56
Goodness of fit on F^2	1.139	1.119	1.170
Final R_1 indices (I>4σ(I))	–	0.0587	0.0726
R_1/wR_2 indices (all data)	0.0495/0.0643	0.0779/0.1686	0.0851/0.2330
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0.73, -0.26	0.11, -0.13	0.18, -0.18
Weighting scheme: x; y[c]	0.000321; 0	0.0830; 0.13	0.1544; 0.06
Absorption corrections	None	DAC, gasket and sample crystal	DAC, gasket and sample crystal
DAC transmission min/max	–	0.63 / 0.90	0.63 / 0.88
Gasket shadowing min/max	–	0.43 / 0.94	0.48 / 0.94
Sample transmission min/max	–	0.97 / 0.98	0.97 / 0.98

Extinction method	None	*SHELXL*	*SHELXL*
Extinction coefficient	–	0.81(13)	0.01(5)

[a] A. J. Blake and D. W. H. Rankin, *Acta Cryst.*, 1991, **C47**, 1933;
[b] This work;
[c] $w = 1/(\sigma^2(Fo^2)+x^2P^2+yP)$, where $P=(\mathrm{Max}(Fo^2, 0)+2Fc^2)/3$.

Table S2. Crystal data and details of the refinements of C_5H_5N phase I at 1.23(5) GPa/295 K compared with the C_5H_5N and C_5D_5N structures determined at 0.10 MPa/153 K and at 0.10 MPa/5 K, respectively. Selected crystal data of pyridine:methanol 3:1 cocrystal determined at 1.80 GPa/295 K are also included.

	C_5H_5N[a]	C_5D_5N[b]	C_5H_5N[c]	$C_5H_5N:CH_3OH$ 3:1[c]
Temperature (K)	153	5	295(2)	295(2)
Pressure	0.10 MPa	0.10 MPa	1.23(5) GPa	1.80(5) GPa
Formula weight	79.10	84.11	79.10	269.34
Crystal colour	–	colourless	colourless	colourless
Crystal size (mm)	–	–	0.37 x 0.37 x 0.25	0.40 x 0.40 x 0.25
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic
Space group	$Pna2_1$	$Pna2_1$	$Pna2_1$	Pc
Unit cell dimensions (Å; °) a =	17.524(3)	17.24296(5)	17.267(4)	6.7710(14)
b =	8.969(2)	8.88178(3)	8.7640(18)	5.5910(11)
c =	11.352(2)	11.22288(3)	11.006(2)	18.100(4)
β =				90.40(3)
Volume (Å^3)	1784.2	1718.76(1)	1665.5(6)	685.2(2)
Z	16	16	16	2
D_x (g cm^{-3})	1.18	1.30	1.26	1.31
Wavelength (Å)	–	Neutron, λ = 1.24-5.36	MoKα, λ = 0.71073	MoKα, λ = 0.71073
Absorption coefficient (mm^{-1})	–	–	0.08	0.08
F(000) (e)	–	–	672	288
2θ max (°)	–	–	49.96	49.92
Min./Max. indices h,k,l	–	0/23, 0/12, 0/15	-20/20, -8/8, -12/12	-8/8, -6/6, -7/7
Reflections collected/unique	3364/–	–/2378	12352/2143	4755/907
R_{int}	–	–	0.0985	0.2065
Observed reflections (I>4σ(I))	2762	–	1266	585
Data/parameters	–	2378/93	2143/217	907/27
Goodness of fit on F^2	–	1.749	1.145	2.301
Final R_1 indices (I>4σ(I))	–	–	0.0997	0.3001
R_1/wR_2 indices (all data)	0.044/0.055	0.024/0.030	0.1611/0.2302	0.3587/0.3070
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	–	–	0.16, -0.16	0.40, -0.34
Weighting scheme: x; y[d]	–	–	0.0914; 0	0.0300; 0
Absorption corrections	None	Empirical	DAC, gasket and sample crystal	DAC, gasket and sample crystal
DAC transmission min/max	–	–	0.61 / 0.92	0.63 / 0.90
Gasket shadowing min/max	–	–	0.35 / 0.96	0.46 / 0.95
Sample transmission min/max	–	–	0.97 / 0.98	0.98 / 0.98

[a] D. Mootz and H. G. Wussow, *J. Chem. Phys.*, 1981, **75**, 1517;
[b] S. Crawford, M. T. Kirchner, D. Bläser, R. Boese, W. I. F. David, A. Dawson, A. Gehrke, R. M. Ibberson, W. G. Marshall, S. Parsons and O. Yamamuro, *Angew. Chem. Int. Ed.*, 2009, **48**, 755;
[c] This work;
[d] $w = 1/(\sigma^2(Fo^2)+x^2P^2+yP)$, where $P=(\mathrm{Max}(Fo^2, 0)+2Fc^2)/3$.

Table S3. Atomic coordinates ($\cdot 10^4$), U_{eq} and U_{iso} ($Å^2 \cdot 10^3$) for $C_4H_4N_2$ at 0.27 and 0.61 GPa.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
		0.27 GPa/295 K		
N1	−416(11)	8574(11)	3820(4)	79(4)
N2	−1200(10)	7472(10)	3047(4)	72(4)
C3	−448(12)	7605(10)	1738(5)	59(4)
H3	−1061	6951	1176	70
C4	1073(11)	8549(11)	1104(4)	52(4)
H4	1562	8525	176	63
C5	1854(11)	9533(12)	1885(5)	74(4)
H5	2964	10202	1505	89
C6	989(12)	9539(12)	3256(5)	71(4)
H6	1408	10232	3782	85
		0.61 GPa/295 K		
N1	−452(11)	8585(10)	3818(4)	74(4)
N2	−1267(10)	7483(9)	3041(4)	65(3)
C3	−548(13)	7588(10)	1701(5)	50(4)
H3	−1211	6923	1135	60
C4	1058(12)	8571(11)	1087(4)	58(3)
H4	1586	8549	153	69
C5	1874(13)	9587(11)	1873(5)	66(3)
H5	2977	10279	1491	79
C6	1015(14)	9565(12)	3263(5)	83(4)
H6	1494	10261	3808	99

Table S4. Atomic coordinates ($\cdot 10^4$), U_{eq} and U_{iso} ($Å^2 \cdot 10^3$) for C_5H_5N phase I at 1.23 GPa.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
		1.23 GPa/295 K		
N1	1235(4)	2834(8)	2400(7)	56(2)
C11	780(4)	2106(11)	1651(7)	49(2)
H11	480	2690	1124	59
C12	708(4)	575(12)	1579(8)	67(2)
H12	382	108	1018	81
C13	1142(4)	−238(10)	2376(9)	74(2)
H13	1114	−1297	2353	89
C14	1601(4)	410(12)	3185(9)	77(3)
H14	1899	−176	3712	93
C15	1627(4)	2000(12)	3225(8)	61(2)
H15	1916	2487	3824	73
N2	834(3)	6934(11)	4997(7)	66(2)
C21	1254(4)	7745(13)	5803(9)	73(3)
H21	1005	8357	6373	88
C22	2082(4)	7666(13)	5785(10)	82(3)
H22	2373	8232	6334	98
C23	2429(4)	6771(12)	4972(9)	65(2)
H23	2965	6664	4980	78
C24	1985(4)	5992(11)	4103(8)	70(3)
H24	2213	5427	3484	84
C25	1180(3)	6110(12)	4217(8)	62(3)
H25	877	5543	3684	74
N3	1121(3)	1103(8)	7356(7)	54(2)
C31	719(4)	1929(13)	8215(9)	71(3)
H31	348	1474	8709	85
C32	895(4)	3483(14)	8311(9)	81(3)
H32	656	4063	8911	97
C33	1442(4)	4209(12)	7497(9)	68(3)
H33	1522	5258	7471	81

C34	1821(4)	3214(12)	6781(7)	59(2)
H34	2239	3557	6325	71
C35	1612(3)	1734(11)	6704(6)	43(2)
H35	1856	1139	6117	52
N4	1695(3)	7001(10)	9942(7)	58(2)
C41	1283(4)	6072(10)	10768(7)	55(2)
H41	1555	5450	11303	66
C42	490(4)	6070(11)	10793(8)	62(2)
H42	237	5424	11333	75
C43	67(4)	6972(12)	10065(9)	65(2)
H43	−470	7013	10125	78
C44	464(4)	7833(10)	9224(7)	51(2)
H44	199	8449	8677	61
C45	1242(4)	7766(11)	9207(7)	53(3)
H45	1487	8330	8604	63

Table S5. Bond lengths (Å), valency and torsion angles (º) of pyridazine observed at 0.27 and 0.61 GPa compared with those of $C_4H_4N_2$ structure determined at 0.10 MPa/100.0 K.

$C_4H_4N_2$ at:	**0.10 MPa/100.0 K[a]**	**0.27 GPa/295 K[b]**	**0.61 GPa/295 K[b]**
bond lengths (Å)			
N1−N2	1.3456(9)	1.454(13)	1.431(12)
N1−C6	1.3298(10)	1.313(15)	1.308(15)
N2−C3	1.3252(10)	1.327(7)	1.336(6)
C3−C4	1.3950(11)	1.346(13)	1.358(14)
C4−C5	1.3712(11)	1.353(15)	1.362(15)
C5−C6	1.3897(11)	1.388(7)	1.392(7)
C3−H3	0.978(15)	0.93	0.93
C4−H4	0.933(12)	0.93	0.93
C5−H5	0.945(13)	0.93	0.93
C6−H6	0.988(15)	0.93	0.93
angles (º)			
N2−N1−C6	119.28(6)	122.3(5)	122.4(5)
N1−N2−C3	118.90(7)	111.3(8)	113.3(7)
N1−C6−C5	123.85(7)	120.7(9)	121.3(9)
N2−C3−C4	123.91(7)	129.4(9)	126.3(8)
C4−C5−C6	116.93(7)	119.6(9)	118.3(9)
C3−C4−C5	117.12(7)	116.6(6)	118.3(5)
N1−C6−H6	116.1(9)	119.7	119.4
N2−C3−H3	115.5(9)	115.3	116.8
C6−C5−H5	119.3(8)	120.2	120.9
C5−C4−H4	122.8(8)	121.7	120.9
C4−C3−H3	120.6(9)	115.3	116.8
C5−C6−H6	120.0(9)	119.7	119.4
C4−C5−H5	123.8(8)	120.2	120.9
C3−C4−H4	120.1(8)	121.7	120.9
torsion angles (º)			
C6−N1−N2−C3	−0.30(11)	−2.5(9)	−3.2(8)
N2−N1−C6−C5	−0.46(11)	−1.3(10)	−0.1(10)
N2−N1−C6−H6	−178.7(10)	178.7	179.9
N1−N2−C3−C4	1.20(11)	4.8(9)	5.1(9)
N1−N2−C3−H3	−179.0(10)	−175.3	−174.9
N2−C3−C4−C5	−1.27(12)	−2.8(10)	−3.7(10)
N2−C3−C4−H4	179.1(9)	177.2	176.3
H3−C3−C4−C5	179.0(10)	177.2	176.3
H3−C3−C4−H4	−0.6(14)	−2.8	−3.7
C3−C4−C5−C6	0.48(11)	−1.7(9)	−0.1(10)
C3−C4−C5−H5	179.2(10)	178.3	179.9

H4−C4−C5−C6	−179.9(9)	178.3	179.9
H4−C4−C5−H5	−1.2(13)	−1.7	−0.1
C4−C5−C6−N1	0.36(11)	3.5(10)	1.8(10)
C4−C5−C6−H6	178.6(10)	−176.5	−178.2
H5−C5−C6−N1	−178.5(9)	−176.5	−178.2
H5−C5−C6−H6	−0.3(14)	3.5	1.8

[a] A. J. Blake and D. W. H. Rankin, *Acta Cryst.*, 1991, **C47**, 1933;
[b] This work.

Table S6. The geometry of shortest intermolecular distances (Å) and angles (º) of pyridazine structure observed at 0.27 and 0.61 GPa compared with those of $C_4H_4N_2$ structure determined at 0.10 MPa/100.0 K.

$C_4H_4N_2$ at:	**0.10 MPa/100.0 K[a]**	**0.27 GPa/295 K[b]**	**0.61 GPa/295 K[b]**
C4···N2^{i} (Å)	3.366	3.377(8)	3.335(8)
H4···N2^{i} (Å)	2.510	2.517	2.478
C4−H4···N2^{i} (º)	152.58	153.78	153.37
C6···N1^{j} (Å)	3.506	3.540(10)	3.467(10)
H6···N1^{j} (Å)	2.609	2.720	2.649
C6−H6···N1^{j} (º)	150.98	147.59	147.02
C5···N2^{k} (Å)	3.572	3.629(16)	3.515(16)
H5···N2^{k} (Å)	2.709	2.812	2.700
C5−H5···N2^{k} (º)	152.20	147.26	146.81
N1···N2^{l} (Å)	3.757	3.832(8)	3.711(7)
N1···N1^{l} (Å)	3.787	3.843(1)	3.719(1)
C4···N2^{i} (Å)	3.366	3.377(8)	3.335(8)
C6···N1^{l} (Å)	3.428	3.502(9)	3.373(9)
C4···N1^{i} (Å)	3.432	3.513(13)	3.468(11)
C6···N1^{j} (Å)	3.506	3.540(10)	3.467(10)
C3···N1^{m} (Å)	3.550	3.639(8)	3.528(8)

[a] A. J. Blake and D. W. H. Rankin, *Acta Cryst.*, 1991, **C47**, 1933;
[b] This work.
Symmetry codes: (^{i}) 0.5+*x*, 1.5–*y*, –0.5+*z*; (^{j}) –*x*, 2–*y*, 1–*z*; (^{k}) 0.5–*x*, 0.5+*y*, 0.5–*z*; (^{l}) 1+*x*, *y*, *z*; (^{m}) –0.5+*x*, 1.5–*y*, –0.5+*z*.