

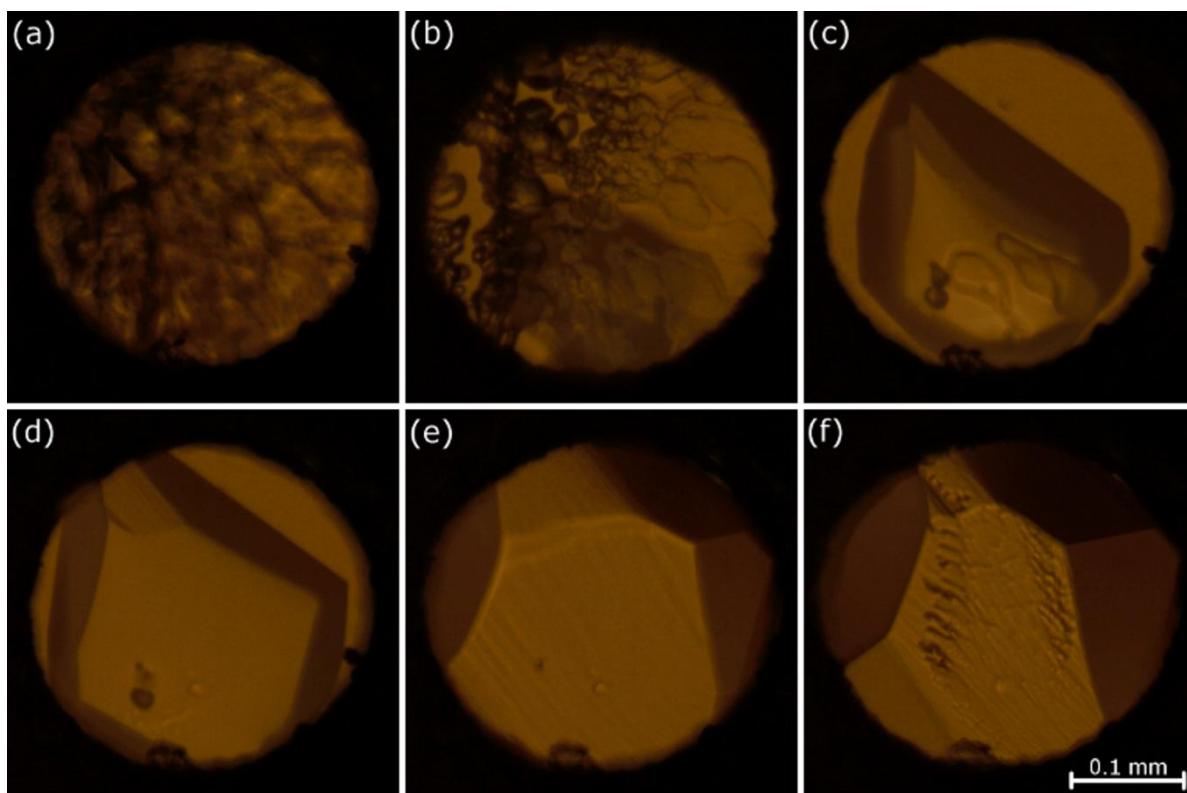
Supporting Information

**Isothermal and isochoric crystallization of highly hygroscopic pyridine N-oxide of aqueous solution**

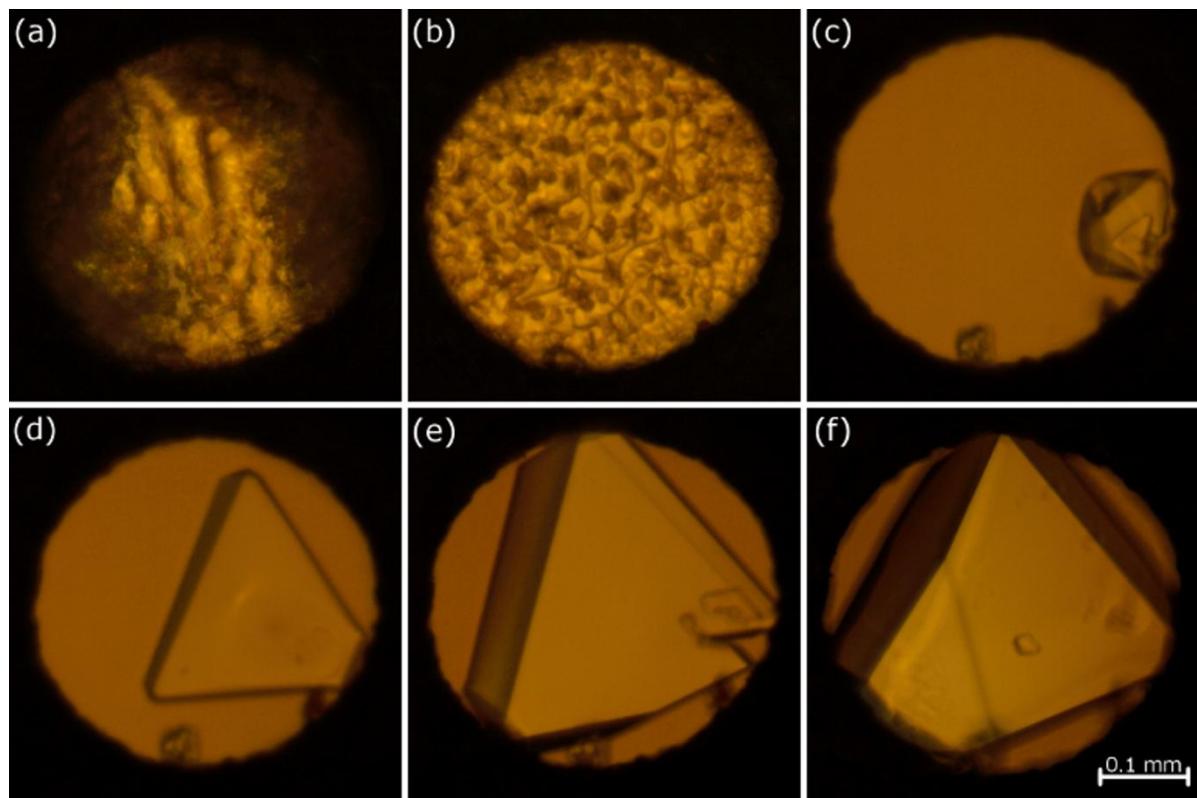
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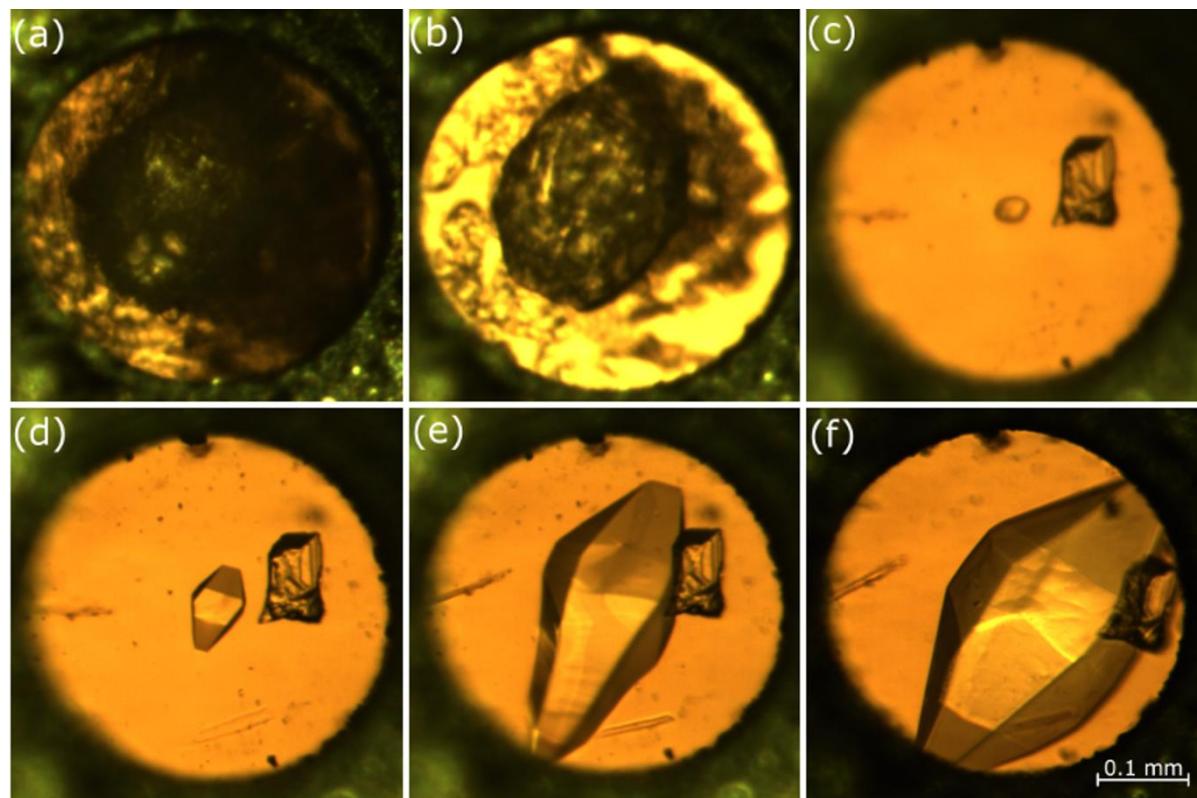
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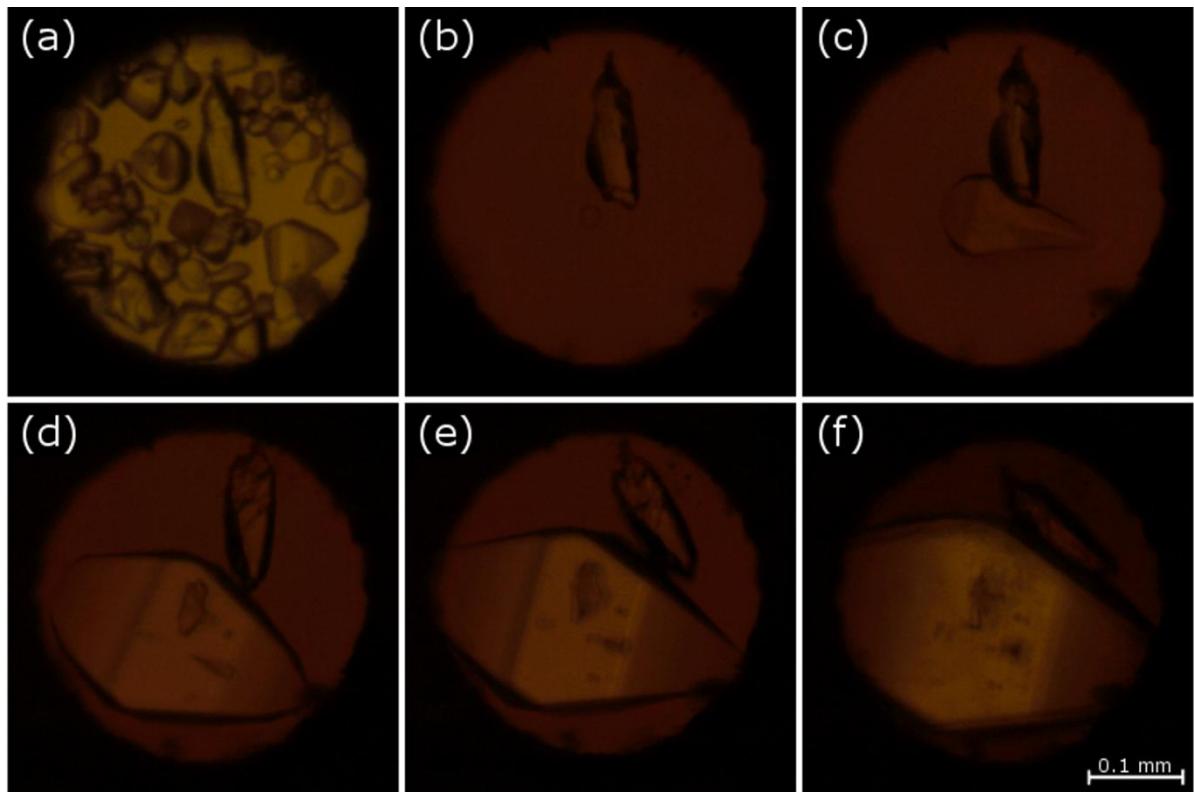
**Figure S1.** Stages of isochoric growth of pyridine N-oxide at 0.71 GPa: (a) polycrystalline mass at 296 K, (b) at 443 K, (c) single crystal at 443 K, (d,e) slow cooling down to 443 K and 373 K, (f) single crystal of pyridine N-oxide at 296 K and 0.71 GPa.



**Figure S2.** Stages of isochoric growth of pyridine N-oxide at 0.78 GPa: (a) melting polycrystalline mass at 423 K, (b) at 473 K, (c) single crystal at 543 K, (d,e) slow cooling down to 533 K and 473 K, (f) single crystal of pyridine N-oxide at 296 K and 0.78 GPa.



**Figure S3.** Stages of isochoric growth of pyridine N-oxide at 1.18 GPa: (a) melting polycrystalline mass at 453 K, (b) at 473 K, (c) single crystal at 543 K, (d,e) slow cooling down to 463 K and 443 K, (f) single crystal of pyridine N-oxide at 296 K and 1.18 GPa.



**Figure S4.** Stages of isochoric growth of pyridine N-oxide at 2.0 GPa: (a) melting polycrystalline mass at 503 K, (b) single crystal at 473 K, (c,d,e) slow cooling down to 453 K , 433 K and 373 K, (f) single crystal of pyridine N-oxide at 296 K and 2.0 GPa.

**Table S1.** Geometric parameters for C-H···O contacts in pyridine N-oxide crystal structure. Values for structure at 0.0001 GPa are cited after Marsh. [1]

	p[GPa]	C···O	H···O	H <sup>n</sup> ···O	C-H···O	C-H <sup>n</sup> ···O	C···O-N
C1-H1···O1 <sup>i</sup>	0.0001	3.257	2.471	2.471	134.0	134.0	123.0
	0.71	3.208(5)	2.400	2.275	145.3	143.1	122.1(1)
	0.78	3.211(4)	2.403	2.278	145.2	143.1	121.9(1)
	1.05	3.161(3)	2.344(26)	2.295	136.8(19)	135.5	121.4(1)
	1.18	3.160(4)	2.330(26)	2.253	141.7(23)	140.0	121.3(1)
	2.00	3.110(7)	2.255(46)	2.219	138.7(41)	138.1	121.0(1)
C2-H2···O1 <sup>ii</sup>	0.0001	3.387	2.939	2.939	105.3	105.3	102.8
	0.71	3.247(5)	2.777	2.722	112.4	109.4	101.3(1)
	0.78	3.239(3)	2.760	2.704	113.1	110.1	101.3(1)
	1.05	3.192(3)	2.718(33)	2.657	112.8(21)	109.8	100.9(1)
	1.18	3.170(3)	2.699(28)	2.679	107.8(17)	107.0	100.5(1)
	2.00	3.119(6)	2.604(53)	2.564	113.5(36)	110.9	100.0(2)
C3-H3···O1 <sup>iii</sup>	0.0001	4.151	3.284	3.068	180	180.0	180.0
	0.71	3.941(8)	3.011	2.858	180.0	180.0	180.0(3)
	0.78	3.935(5)	3.005	2.852	180.0	180.0	180.0(1)
	1.05	3.844(5)	3.024(49)	2.761	180.0(43)	180.0	180.0(2)
	1.18	3.796(6)	2.714(47)	2.713	180.0(34)	180.0	180.0(2)

	2.00	3.692(10)	2.783(83)	2.610	180.0(70)	180.0	180.0(3)
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n-normalized carbon-hydrogen bond length (1.083Å) [2]

i-Symmetry operation:  $\frac{1}{2} -y, x -\frac{1}{2}, \frac{1}{4} +z$

ii-Symmetry operation:  $x, y-1, z$

iii- Symmetry operation:  $x-1, y-1, z$

**Table S2.** Bond lengths in pyridine N-oxide (highlighted are the dimensions involving ideally located H-atoms..

Bond \ Pressure	0.71GPa	0.78 GPa	1.05 GPa	1.18 GPa	2.00 GPa
O1-N1	1.314(6)	1.318(3)	1.305(4)	1.306(4)	1.305(7)
N1-C1	1.357(5)	1.352(3)	1.357(4)	1.355(3)	1.367(7)
C1-C2	1.383(5)	1.373(3)	1.356(4)	1.369(4)	1.361(8)
C2-C3	1.372(5)	1.371(3)	1.374(4)	1.383(4)	1.377(6)
C1-H1	0.9300	0.9300	1.01(2)	0.98(3)	1.037(5)
C2-H2	0.9300	0.9300	0.92(3)	1.03(3)	0.967(6)
C3-H3	0.9300	0.9300	0.82 (5)	1.08(4)	0.909(8)

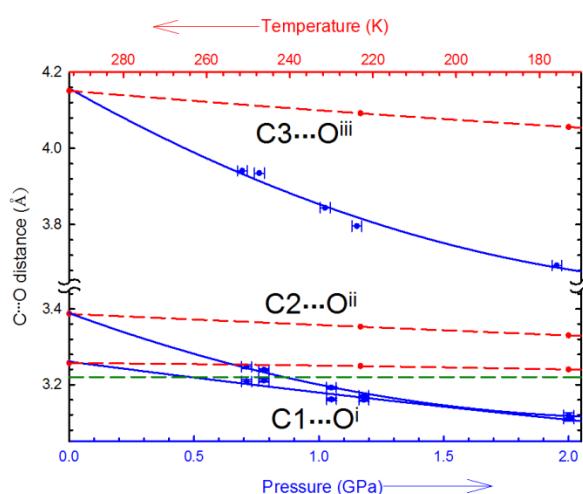
Fixed H-C distances are highlighted.

**Table S3.** Bonds angles in pyridine N-oxide.

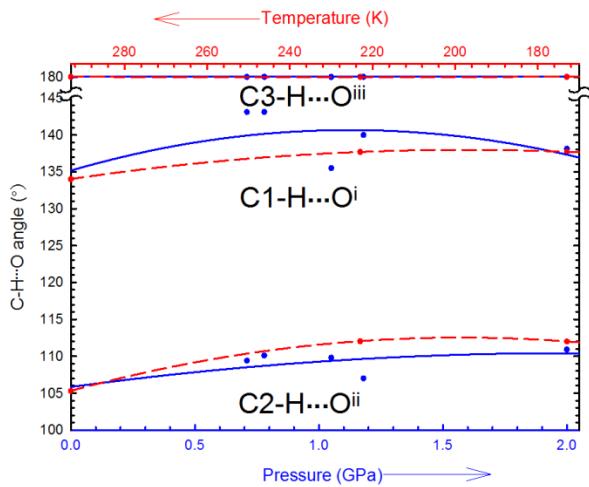
Angle \ Pressure	0.71GPa	0.78 GPa	1.05 GPa	1.18 GPa	2.00 GPa
O1-N1-C1	119.71(21)	120.10 (17)	120.55(28)	120.21 (21)	119.89 (43)
N1-C1-C2	119.78(46)	120.47 (26)	120.92(36)	120.63(31)	119.03 (60)
C1-C2-C3	120.55(54)	120.40 (28)	120.67(35)	120.95 (31)	123.11 (66)
C1-N1-C1'	120.57 (43)	119.81 (35)	118.90 (56)	119.59 (41)	120.22 (86)
C2-C3-C2'	118.76(57)	118.44 (37)	117.92 (54)	117.25 (40)	115.50 (86)
H1-C1-C2	120.11	119.77	129.43 (164)	124.54 (183)	128.91 (333)
H1-C1-N1	120.11	119.77	109.38 (169)	114.70 (180)	111.67 (334)
H2-C2-C1	119.72	119.80	117.16 (202)	118.86 (154)	110.14 (295)
H2-C2-C3	119.72	119.80	122.17 (207)	120.17 (155)	126.71 (286)
H3-C3-C2	120.62	120.78	121.04 (27)	121.37 (20)	122.25 (43)

Angles including fixed H atoms are highlighted.

' atoms generated by symmetry operation y, x, -z



**Figure S5.** The C···O distances of C-H···O contacts in PNO in the function of pressure (solid blue curves) and temperature (dashed red curves), for carbon-hydrogen distances normalized to 1.083Å. [2] The dashed green line indicates the sum of van der Waals radii for carbon and oxygen atoms equal 3.22Å. [3] Superscripts represent symmetry operations (i)  $\frac{1}{2} -y, x -\frac{1}{2}, \frac{1}{4} +z$ ; (ii)  $x, y-1, z$ ; (iii)  $x-1, y-1, z$ .



**Figure S6.** The C-H...O angles of C-H...O contacts in PNO in the function of pressure (solid blue curves) and temperature (dashed red curves), for carbon-hydrogen distances normalized to 1.083 Å. [2] Superscripts represent symmetry operations (i)  $\frac{1}{2} -y, x -\frac{1}{2}, \frac{1}{4} +z$ ; (ii)  $x, y-1, z$ ; (iii)  $x-1, y-1, z$ .

## References

1. Marsh, R.E., Kapon, M., Shengzhi Hu, Herbstein, F.H. (2002). *Acta Crystallogr. Sect. B-Struct. Sci.*, **58**, 62–77.
2. Allen, F. H., Bruno, I. J. (2010). *Acta Crystallogr B.*, **66**, 380–386.
3. Bondi, A. (1964). *J. Phys. Chem.*, **68**, 441–451.