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**Supporting information for article:**

**High-pressure sapphire capillary cell for synchrotron single-crystal X-ray diffraction measurements to 1500 bar**

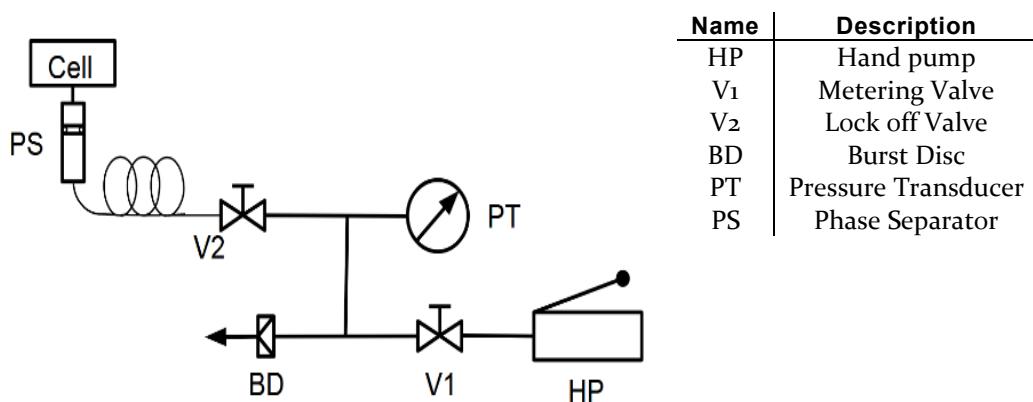
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## S1. Materials and Methods

Single crystals of hexamethylenetetramine, HMT (CAS: 100-97-0, Merck catalogue no: 398160), and its deuterated equivalent, HMTD (CAS: 23304-08-7, CND Isotopes catalogue no.: D-0817), were supplied from Sigma Aldrich/Merck and CND Isotopes, respectively, and were used without further purification.

## S2. Sapphire Capillary Cell

**Figure S1** Schematic diagram of the Sapphire Capillary Pressure Cell (SCC) connected to the pressure-pump.



**Table S1** Data collection strategy for a single crystal in a sapphire capillary pressure cell on beamline I19, Diamond Light Source

Scan	Other axis	$\kappa$ (°)	2θ (°)	Start (°)	End (°)	No. of Images	Time (s)	Detector Distance (mm)
Circle	(°)							
( $\phi/\omega$ )								
ω	-120	-45	30	-156	-30	630	0.2	85
φ	-30	-45	30	-120	0	600	0.2	85
ω	0	-45	30	-156	-30	630	0.2	85
φ	-30	-45	30	0	120	600	0.2	85
ω	120	-45	30	-156	-30	630	0.2	85

### S3. Sapphire Capillary Pressure Cell Safety Protocols

#### S.3.1 Pressure Rating for the Sapphire Capillary Cell and Pump-System

All commercial components of the pressure cell have a maximum operating pressure of 2000 bar (2 kbar) or above. As the pump does not have its own safety release valve, a burst disk was included in the high-pressure side of the set-up to prevent over-pressurisation. This disk was rated to 2500 bar as per the manufacturer's instructions, which state that the maximum operating pressure (2000 bar) should not exceed 80 % of the nominal burst pressure.

The sapphire capillary is the most likely point of failure in the entire cell. Calculating safe working pressures was challenging due to the brittle nature of the sapphire, and so each pressure cell was pressure tested on a separate rig to give a maximum working pressure of each cell. In use, the pressure during an experiment should not exceed 80% of the maximum working pressure. Therefore, a cell with a maximum working pressure of 1250 bar should not be used above 1000 bar, and so on.

#### S.3.2 Protection Against Cell Failure

The greatest hazard to the user during a data collection using the sapphire capillary cell is the catastrophic failure of the cell body. Should this occur, it would do so with no prior indication. Upon failure, the cell disintegrates into extremely small shards of sapphire and a plume of aerosolised hydrostatic medium. To eliminate the risk to the users, the cell can be pressurised remotely from the sample preparation room, outside of the experimental hutch. Local rules prohibited pressurisation of the system before interlocking the hutch.

To mitigate the risk of damage to equipment within the hutch, particularly the detector, the stored energy in the system is minimised by using the phase separator. This ensures that the majority of the pressurised liquid in the cell is a highly incompressible hydraulic fluid, significantly limiting the stored potential energy. A precautionary Kapton<sup>©</sup> polyimide film (75 µm in thickness) is also affixed to the face of the detector.

### S4. The Effect of Pressure on HMT and HMTD

All crystallographic data have been deposited with the CCDC (CCDC 2008808-2008842) and can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.CB21EZ, UK (fax +441223336033; email deposit@ccdc.cam.ac.uk).

#### S4.1 Ambient Pressure Single Crystal X-Ray Diffraction

Ambient temperature single crystal X-ray diffraction for HMT are previously reported.<sup>s</sup>(Stevens & Hope, 1975) Ambient temperature and pressure single-crystal data were collected for HMTD on a three-circle Bruker SMART APEXII diffractometer with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data were collected at 297 K, under a stream of nitrogen.<sup>s</sup>(Cosier & Glazer, 1986) A refined strategy was used to obtain a complete and highly redundant data set (redundancy = 26.4 out to 0.8  $\text{\AA}$ ). Cell indexing and data processing were carried out using the Bruker APEX3 software.(Bruker, 2016) Integration was performed using the program SAINT and the absorption corrections were carried out using the program SADABS.<sup>s</sup>(Bruker, 2016, Bruker & Saint, 2002) Structure refinements were carried out in CRYSTALS.<sup>s</sup>(Paul *et al.*, 2003) The structure was refined anisotropically against F<sup>2</sup> with an I/ $\sigma$  cut-off set to -3.00 and a [Sin  $\theta/\lambda$ ]2 of 0.01. The deuterium atoms was placed geometrically and constrained to ride the carbon atom.

**Table S2** Single crystal X-ray crystallographic data for HMTD under ambient conditions collected on a Bruker SMART APEXII diffractometer,  $T = 297 \text{ K}$ ,  $\lambda = 0.71073 \text{ \AA}$ .

HMTD	
<b>Crystal data</b>	
Chemical formula	C <sub>6</sub> D <sub>12</sub> N <sub>4</sub>
$M_r$	140.19
Crystal system, space group	Cubic, $I\bar{4}3m$
Temperature (K)	293
$a$ ( $\text{\AA}$ )	7.0194 (2)
$V$ ( $\text{\AA}^3$ )	345.86 (3)
$Z$	2
Radiation type	Mo K $\alpha$
$\mu$ ( $\text{mm}^{-1}$ )	0.09
Crystal size (mm)	0.20 $\times$ 0.20 $\times$ 0.10
<b>Data collection</b>	
Diffractometer	Bruker SMART APEXII
Absorption correction	–
No. of measured, independent and observed [ $I > 2.0\sigma(I)$ ] reflections	1305, 82, 72
$R_{\text{int}}$	0.074
$(\sin \theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.747
<b>Refinement</b>	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.042, 0.108, 0.96
No. of reflections	82
No. of parameters	10
No. of restraints	3
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e $\text{\AA}^{-3}$ )	0.10, -0.14

#### S4.1.1. S4.1 Single Crystal X-Ray Diffraction in the Sapphire Capillary Cell

A single crystal of each HMTH and HMTD were mounted into separate sapphire capillary cells, following their characterisation under ambient conditions. A hydrostatic medium of a hydraulic oil, ENERPAC HF-Series, was used to directly compress the crystals. Diffraction data using the sapphire capillary pressure cell were collected on station I19 at Diamond Light Source, Rutherford Appleton Laboratory on station EH2. All diffraction data were collected at ambient temperature. Measurements were taken at ambient pressure and then at 100 bar intervals, up to 1000 bar. Decompression data were then recorded at 200 bar intervals, returning to ambient pressure. Data were collected using a DECTRIS PILATUS 300K hybrid-pixel detector using synchrotron radiation ( $\lambda = 0.4859 \text{ \AA}$ ). Crystallographic data are summarised in *Tables S3 and S4*.

**Table S3** Single crystal X-ray crystallographic data for HMT in a sapphire capillary cell using a PTM of ENERPAC HF Series oil. Data are collected on beamline I19 at Diamond Light Source,  $T = 297\text{ K}$ ,  $\lambda = 0.4859\text{ \AA}$ . Table continued below...

	0 bar	100 bar	200 bar	300 bar	400 bar
<b>Crystal data</b>					
Chemical formula	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>				
$M_f$	140.19	140.19	140.19	140.19	140.19
Crystal system, space group	cubic, $\bar{I}\bar{4}3m$				
$a\text{ (\AA)}$	7.0266 (4)	7.0232 (4)	7.0212 (4)	7.0192 (4)	7.0159 (5)
$V\text{ (\AA}^3)$	346.93 (6)	346.42 (6)	346.13 (6)	345.83 (6)	345.34 (5)
$Z$	2	2	2	2	2
$\mu\text{ (mm}^{-1})$	0.09	0.09	0.09	0.09	0.09
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
<b>Data collection</b>					
Diffractometer	Pilatus 300K Multi-scan <i>DENZO/SCALEPACK</i> (Otwinowski & Minor, 1997)				
Absorption correction	(Otwinowski & Minor, 1997)				
No. of measured, independent and observed (?) reflections	1600, 72, 62	1472, 72, 60	1712, 72, 58	1726, 72, 61	1688, 72, 61
$R_{\text{int}}$	0.064	0.122	0.092	0.083	0.089
$(\sin \theta/\lambda)_{\text{max}}\text{ (\AA}^{-1})$	0.712	0.712	0.712	0.712	0.712
<b>Refinement</b>					
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.044, 0.114, 1.12	0.051, 0.126, 1.13	0.048, 0.112, 0.88	0.048, 0.120, 1.05	0.045, 0.101, 1.17
No. of reflections	72	72	72	72	72

No. of parameters	10	10	10	10	10
No. of restraints	3	4	3	3	3
H-atom treatment	Parameters constrained				
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.09, -0.20	0.12, -0.27	0.14, -0.25	0.10, -0.24	0.12, -0.35

**Table S3 continued...** Single crystal X-ray crystallographic data for HMT in a sapphire capillary cell using a PTM of ENERPAC HF Series oil. Data are collected on beamline I19 at Diamond Light Source,  $T = 297$  K,  $\lambda = 0.4859$  Å. Decreasing pressure points are marked by an asterisk (\*). Table continued below...

	1000 bar	800 bar *	600 bar *	400 bar *	200 bar *
<b>Crystal data</b>					
Chemical formula	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>
$M_r$	140.19	140.19	140.19	140.19	140.19
Crystal system, space group	cubic, $I\bar{4}3m$	cubic, $I\bar{4}3m$	cubic, $I\bar{4}3m$	cubic, $I\bar{4}3m$	cubic, $I\bar{4}3m$
$a$ (Å)	7.0142 (4)	7.0118 (3)	7.0100 (3)	7.0072 (3)	7.0033 (2)
$V$ (Å <sup>3</sup> )	345.10 (5)	344.74 (5)	344.48 (5)	344.08 (4)	343.48 (2)
$Z$	2	2	2	2	2
$\mu$ (mm <sup>-1</sup> )	0.09	0.09	0.09	0.09	0.09
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
<b>Data collection</b>					
Diffractometer	Pilatus 300K Multi-scan	Pilatus 300K Multi-scan	Pilatus 300K Multi-scan	Pilatus 300K Multi-scan	Pilatus 300K Multi-scan
Absorption correction	DENZO/SCALEPACK (Otwinowski & Minor, 1997)	DENZO/SCALEPACK & (Otwinowski & Minor, 1997)	DENZO/SCALEPACK & (Otwinowski & Minor, 1997)	DENZO/SCALEPACK (Otwinowski & Minor, 1997)	DENZO/SCALEPACK (Otwinowski & Minor, 1997)

No. of measured, independent and observed (?) reflections	1620, 72, 61	1604, 72, 62	1524, 72, 61	1472, 72, 62	1593, 72, 63
$R_{\text{int}}$	0.087	0.088	0.080	0.069	0.085
$(\sin \theta/\lambda)_{\text{max}} (\text{\AA}^{-1})$	0.713	0.713	0.713	0.714	0.714

<b>Refinement</b>					
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.046, 0.111, 1.05	0.042, 0.116, 1.11	0.043, 1.03, 1.11	0.042, 0.088, 1.58	0.046, 0.108, 1.20
No. of reflections	72	72	72	72	72
No. of parameters	10	10	10	10	10
No. of restraints	3	3	3	3	3
H-atom treatment	Parameters constrained				
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} (\text{e \AA}^{-3})$	0.13, -0.27	0.07, -0.19	0.10 -0.18	0.14, -0.19	0.15, -0.036

**Table S3 continued...** Single crystal X-ray crystallographic data for HMT in a sapphire capillary cell using a PTM of ENERPAC HF Series oil. Data are collected on beamline I19 at Diamond Light Source,  $T = 297 \text{ K}$ ,  $\lambda = 0.4859 \text{ \AA}$ . Decreasing pressure points are marked by an asterisk (\*).

	<b>100 bar *</b>	<b>0 bar *</b>
Chemical formula	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>
$M_r$	140.19	140.19
Crystal system, space group	cubic, $I\bar{4}3m$	cubic, $I\bar{4}3m$
$a (\text{\AA})$	7.00066 (2)	7.0166 (3)
$V (\text{\AA}^3)$	343.97(3)	345.45 (4)
$Z$	2	2
$\mu (\text{mm}^{-1})$	0.09	0.09
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10

**Data collection**

Diffractometer	Pilatus 300K Multi-scan <i>DENZO/SCALEPACK</i>	Pilatus 300K Multi-scan <i>DENZO/SCALEPACK</i>
Absorption correction	(Otwinowski & Minor, (Otwinowski & Minor, 1997)	1997)
No. of measured, independent and observed (?) reflections	Pilatus 300K	Pilatus 300K
$R_{\text{int}}$	0.085	0.081
$(\sin \theta / \lambda)_{\text{max}} (\text{\AA}^{-1})$	0.714	0.713

**Refinement**

$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.045, 0.188, 1.14	0.040, 0.120, 1.09
No. of reflections	72	72
No. of parameters	10	10
No. of restraints	3	3
H-atom treatment	Parameters constrained	Parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} (\text{e \AA}^{-3})$	0.11, -0.36	0.13, -0.15

**Table S4** Single crystal X-ray crystallographic data for HMTD in a sapphire capillary cell using a PTM of ENERPAC HF Series oil. Data are collected on beamline I19 at Diamond Light Source,  $T = 297$  K,  $\lambda = 0.4859$  Å. Table continued below...

0 bar	100 bar	200 bar	300 bar	<b>400 bar</b>
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**Crystal data**

Chemical formula	C <sub>6</sub> D <sub>12</sub> N <sub>4</sub>				
<i>M<sub>r</sub></i>	152.26	152.26	152.26	152.26	152.26
Crystal system, space group	cubic, <i>I</i> 43 <i>m</i>				
<i>a</i> , Å	7.0190 (3)	7.0154 (2)	7.0132 (2)	7.0097 (2)	7.0078 (2)
<i>V</i> (Å <sup>3</sup> )	345.80 (4)	345.28 (3)	344.95 (3)	344.43 (3)	344.15(3)
<i>Z</i>	2	2	2	2	2
$\mu$ (mm <sup>-1</sup> )	0.09	0.09	0.09	0.09	0.09
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10

**Data collection**

Diffractometer	Pilatus 300K	Pilatus 300K	Pilatus 300K	Pilatus 300K	Pilatus 300K
Absorption correction	Multi-scan <i>DENZO/SCALEPACK</i> (Otwinowski & Minor, 1997)	Multi-scan <i>DENZO/SCALEPACK</i> (Otwinowski & Minor, 1997)			
No. of measured, independent and observed (?) reflections	1671, 83, 76	1773, 83, 77	1770, 83, 75	1805, 83, 76	1608, 83, 76
<i>R</i> <sub>int</sub>	0.053	0.059	0.054	0.053	0.049
(sin $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.747	0.747	0.748	0.748	0.748

**Refinement**

<i>R</i> [ $F^2 > 2\sigma(F^2)$ ], <i>wR</i> ( $F^2$ ), <i>S</i>	0.038, 0.103, 1.04	0.037, 0.112, 1.06	0.041, 0.119, 1.11	0.037, 0.093, 1.13	0.041, 0.106, 1.15
No. of reflections	83	82	82	82	783
No. of parameters	8	10	10	10	10
No. of restraints	3	3	3	3	3
H-atom treatment	Parameters constrained				
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.11, -0.20	0.09, -0.09	0.14, -0.11	0.13, -0.11	0.09, -0.20

**Table S4 continued...** Single crystal X-ray crystallographic data for HMTD in a sapphire capillary cell using a PTM of ENERPAC HF Series oil. Data are collected on beamline I19 at Diamond Light Source,  $T = 297$  K,  $\lambda = 0.4859$  Å. Table continued below...

	500 bar	600 bar	700 bar	800 bar	900 bar
<b>Crystal data</b>					
Chemical formula	C <sub>6</sub> D <sub>12</sub> N <sub>4</sub>	C <sub>6</sub> D <sub>12</sub> N <sub>4</sub>			
<i>M</i> <sub>r</sub>	152.26	152.26	152.26	152.26	152.26
Crystal system, space group	cubic, <i>I</i> 43 <i>m</i>	cubic, <i>I</i> 43 <i>m</i>			
<i>a</i> , Å	7.0045 (4)	7.0019 (2)	6.9993 (2)	6.9964 (2)	6.9939 (2)
<i>V</i> (Å <sup>3</sup> )	343.67 (3)	343.27 (3)	342.90 (3)	342.47 (3)	342.11 (3)
<i>Z</i>	2	2	2	2	2
$\mu$ (mm <sup>-1</sup> )	0.09	0.09	0.09	0.09	0.09
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
<b>Data collection</b>					
Diffractometer	Pilatus 300K	Pilatus 300K	Pilatus 300K	Pilatus 300K	Pilatus 300K
Absorption correction	Multi-scan <i>DENZO/SCALEPACK</i> (Otwinowski & Minor, 1997)	Multi-scan <i>DENZO/SCALEPACK</i> (Otwinowski & Minor, 1997)			
No. of measured, independent and observed (?) reflections	1781, 83, 77	1781, 83, 79	1795, 83, 77	1775, 83, 75	1795, 83, 76
<i>R</i> <sub>int</sub>	0.049	0.055	0.055	0.060	0.050
(sin $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.749	0.749	0.749	0.750	0.750
<b>Refinement</b>					
$R[F^2 > 2\sigma(F^2)]$ , <i>wR</i> ( $F^2$ ), <i>S</i>	0.041, 0.109, 1.21	0.035, 0.086, 1.18	0.036, 0.089, 1.16	0.036, 0.088, 1.13	0.036, 0.089, 1.09
No. of reflections	83	83	83	83	83
No. of parameters	8	10	10	10	10
No. of restraints	3	3	3	3	3
H-atom treatment	Parameters constrained	Parameters constrained	Parameters constrained	Parameters constrained	Parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.07, -0.23	0.09, -0.16	0.08, -0.21	0.12, -0.19	0.11, -0.14

**Table S4 continued...** Single crystal X-ray crystallographic data for HMTD in a sapphire capillary cell using a PTM of ENERPAC HF Series oil. Data are collected on beamline I19 at Diamond Light Source,  $T = 297$  K,  $\lambda = 0.4859$  Å. Decreasing pressure points are marked by an asterisk (\*). Table continued below...

	1000 bar	800 bar *	600 bar *	400 bar *	200 bar *
<b>Crystal data</b>					
Chemical formula	C <sub>6</sub> D <sub>12</sub> N <sub>4</sub>	C <sub>6</sub> D <sub>12</sub> N <sub>4</sub>			
$M_r$	152.26	152.26	152.26	152.26	152.26
Crystal system, space group	cubic, $I\bar{4}3m$	cubic, $I\bar{4}3m$	cubic, $I\bar{4}3m$	cubic, $I\bar{4}3m$	cubic, $I\bar{4}3m$
$a$ , Å	6.9914 (3)	6.9972 (2)	7.0014 (2)	7.0075 (2)	7.0135 (2)
$V$ , Å <sup>3</sup>	342.74 (4)	342.59 (3)	343.21 (3)	344.10 (3)	344.98 (3)
$Z$	2	2	2	2	2
$\mu$ (mm <sup>-1</sup> )	0.09	0.09	0.09	0.09	0.09
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
<b>Data collection</b>					
Diffractometer	Pilatus 300K	Pilatus 300K	Pilatus 300K	Pilatus 300K	Pilatus 300K
Absorption correction	Multi-scan <i>DENZO/SCALEPACK</i> (Otwinowski & Minor, 1997)	Multi-scan <i>DENZO/SCALEPACK</i> (Otwinowski & Minor, 1997)			
No. of measured, independent and observed (?) reflections	1794, 83, 75	1775, 83, 75	1783, 83, 75	1778, 82, 72	1885, 83, 75
$R_{int}$	0.054	0.061	0.087	0.064	0.061
$(\sin \theta / \lambda)_{max}$ (Å <sup>-1</sup> )	0.750	0.749	0.749	0.748	0.748
<b>Refinement</b>					
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.037, 0.096, 1.17	0.034, 0.099, 1.30	0.033, 0.090, 1.10	0.034, 0.096, 1.14	0.035, 0.092, 1.21
No. of reflections	83	83	83	83	83
No. of parameters	8	10	10	10	10

No. of restraints	3	3	3	3	3
H-atom treatment	Parameters constrained				
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.07, -0.17	0.11, -0.16	0.14, -0.08	0.13, -0.12	0.14, -0.13

**Table S4 continued...** Single crystal X-ray crystallographic data for HMTD in a sapphire capillary cell using a PTM of ENERPAC HF Series oil. Data are collected on beamline I19 at Diamond Light Source,  $T = 297$  K,  $\lambda = 0.4859$  Å. Decreasing pressure points are marked by an asterisk (\*).

<b>0 bar *</b>	
<b>Crystal data</b>	
Chemical formula	C <sub>6</sub> D <sub>12</sub> N <sub>4</sub>
$M_r$	152.26
Crystal system, space group	cubic, $I\bar{4}3m$
$a$ (Å)	7.0187 (3)
$V$ (Å <sup>3</sup> )	345.75 (4)
$Z$	2
$\mu$ (mm <sup>-1</sup> )	0.09
Crystal size (mm)	0.20 × 0.20 × 0.10
<b>Data collection</b>	
Diffractometer	Pilatus 300K
	Multi-scan
Absorption correction	DENZO/SCALEPACK (Otwinowski & Minor, 1997)
No. of measured, independent and observed (?) reflections	1773, 83, 75
$R_{\text{int}}$	0.050
$(\sin \theta/\lambda)_{\max}$ (Å <sup>-1</sup> )	0.747

**Refinement**

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$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.034, 0.098, 1.18
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No. of reflections	83
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No. of parameters	10
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No. of restraints	3
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H-atom treatment	Parameters constrained
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$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.15, -0.08
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## S5 Birch-Murnaghan Equation of State Calculations

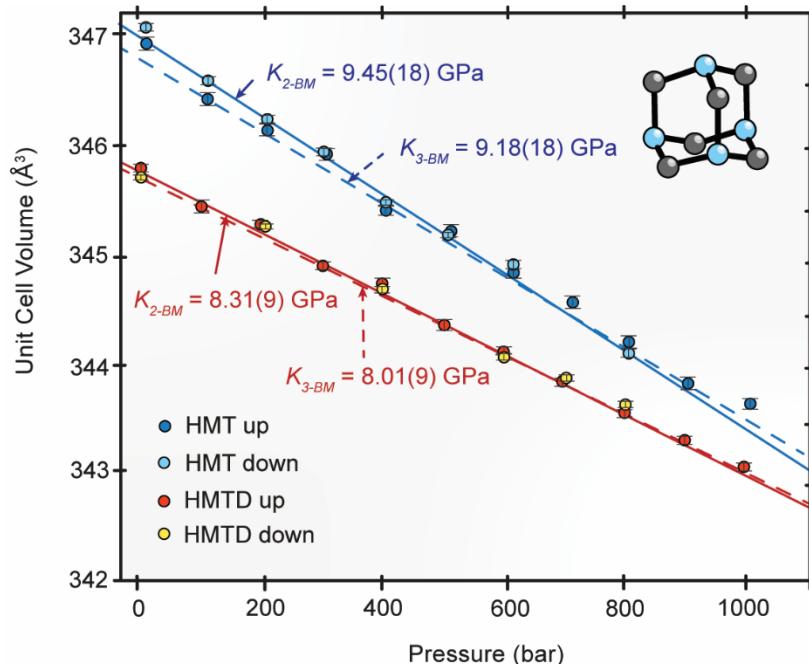
Bulk moduli for HMT and HMTD were calculated using a second-order Birch-Murnaghan equation of state. For a second-order Birch-Murnaghan, pressure,  $P$ , is given by equation 1, where  $K_0$  is the isothermal bulk modulus,  $V$  is the measured volume and  $V_0$  is the volume at ambient pressure.

$$P = \frac{3K_0}{2} \left[ \left( \frac{V}{V_0} \right)^{\frac{7}{3}} - \left( \frac{V}{V_0} \right)^{\frac{5}{3}} \right] \quad (1)$$

The bulk modulus of a material is a measure of its resistance to compression: the higher the bulk modulus, the harder the solid is to compress. Some representative values for scale: 6.6 GPa for Ru<sub>3</sub>(CO)<sub>12</sub>, 13.1 GPa L-alanine, 25 GPa NaCl, 37 GPa for quartz and 440 GPa for diamond.<sup>S6,S7</sup> The bulk modulus of HMTD was calculated to be significantly lower than that for HMTH ( $>3\sigma$  difference) and is, therefore, a softer material.

The unit cell compression was also fitted to a third-order Birch-Murnaghan equation of state, given by equation 2, where  $K'_{T_0}$  is the pressure derivative of the isothermal bulk modulus at standard temperature. The volume at ambient pressure,  $V_0$ , for each HMT and HMTD were refined in the calculation. However, the EoS fit for HMT deviated from the measured unit cell parameter (Figure S2, dashed blue line). A smaller deviation was measured for the second-order Birch-Murnaghan fit for HMT (Figure S2, solid blue line), indicating that the compression is better represent by a quadratic EoS in this moderate pressure range (<1000 bar).

$$P = \frac{3K_0}{2} \left[ \left( \frac{V}{V_0} \right)^{\frac{7}{3}} - \left( \frac{V}{V_0} \right)^{\frac{5}{3}} \right] + \left[ 1 + \frac{1}{3}(K'_{T_0} - 4) \left\{ \left( \frac{V}{V_0} \right)^{\frac{2}{3}} - 1 \right\} \right] \quad (2)$$



**Figure S2** Figure S2 Contraction and expansion of the unit cell volume in HMT (blue) and HMTD (red) during compression and decompression (up and down), respectively, in a sapphire

capillary cell in a PTM of hydraulic oil (ENERPAC H Series). Vertical error bars are shown in grey. Third-order and second-order Birch-Murnaghan EoS<sup>23</sup> fits are shown as dashed and solid lines, respectively. Bulk moduli for HMT and HTMD calculated by third-order and second-order Birch-Murnaghan EoS are overlaid.

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