Electronic Supplementary Material (ESI) for CrystEngComm.

SUPPLEMENARY MATERIAL

High-pressure polymorphism in L-threonine between ambient pressure and 22 GPa

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Table S1 High Pressure Structures in the Cambridge Structural Database (v 5.40, Nov 2018)

Compound Name	Refcode	Pressure (GPa)	3D Coords?	Molecular ?	Complex ?	R-factor (%)	Method
Carbon dioxide	SACBAA[1]	28.00	Yes	Yes	No	20.5	powder
Benzene	BENZEN09[2]	24.00	No	Yes	Yes	n/a	powder
L-threonine	n/a*	22.31	Yes	Yes	Yes	7.9	SC
benzene-1,4-diol acetonitrile clathrate	HQUACN20[3]	14.10	Yes	Yes	Yes	20.94	SC
Perdeutero-L-alanine	LALNIN51[4]	13.60	Yes	Yes	Yes	4.92	powder
dichloro-(1,4,7-oxadithionane)-palladium(ii)	NONWES30[5]	13.56	Yes	Yes	Yes	6.92	SC
4-oxo-3H,4H-benzo[1,2-d:5,4-d']bis[1,2,3]dithiazol-3-yl radical	LILRIJ06[6]	13.00	Yes	Yes	Yes	0.56	powder
pyrazinium tetrachloro-gold(iii)	BIHXIC18[7]	12.68	Yes	Yes	Yes	8.22	SC
Dibromo-(1,4,7-trithionane)-palladium(ii)	FAPBIH12[6]	11.69	Yes	Yes	Yes	7.1	SC
5-Amino-1H-tetrazole	EJIQEU02[8]	11.60	Yes	Yes	Yes	0.6	powder
bis(cyclopentadienyl)-iron	FEROCE38[9]	11.60	Yes	Yes	Yes	3.52	SC
pyrazinium tetrachloro-gold(iii)	BIJBUU[7]	10.67	Yes	Yes	Yes	6.98	SC
4,8-dioxo-4,8-dihydrobenzo[1,2-d:5,4-d']bis[1,2,3]dithiazol-6-ium-3-ide	GEHMAK05[10]	10.50	Yes	Yes	Yes	0.84	powder
α-D-mannopyranose	ADMANN25[11]	10.13	No	Yes	Yes	n/a	SC
4-Oxo-8-phenyl-3H,4H-benzo[1,2-d:5,4-d']bis[1,2,3]dithiazol-3-yl radical	EPIVEF04[12]	10.10	Yes	Yes	Yes	2.9	powder

SC=Single Crystal, *=this study.

Table S2 Crystallographic information for all structures

Pressure	0.00 GPa	1.26 GPa	2.05 GPa	3.23 GPa
Phase	I	I	I	I’
Crystal data				
Temperature (K)	298	296	296	296
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$
a, *b*, *c* (Å)	5.1481 (1), 13.6138 (2), 7.7426 (1)	5.0694 (10), 13.492 (6), 7.403 (4)	5.0359 (6), 13.462 (3), 7.2375 (16)	5.0055 (2), 13.4104 (9), 7.1162 (4)
V (Å^3)	542.64 (2)	506.4 (3)	490.67 (16)	477.68 (5)
Radiation type	Mo *Kα*	Synchrotron, λ = 0.478 Å	Synchrotron, λ = 0.478 Å	Synchrotron, λ = 0.478 Å
μ (mm-1)	0.12	0.06	0.07	0.07
Crystal size (mm)	0.20 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10
Data collection				
Diffractometer	Bruker *APEX*-II CCD	Bruker-Nonius *APEX* II	Bruker-Nonius *APEX* II'	Bruker-Nonius *APEX* II
T_{min}, T_{max}	0.676, 0.745	0.248, 0.744	0.604, 0.744	0.629, 0.744
No. of measured, independent and observed [I > 2σ(I)] reflections	5775, 1123, 1065	2231, 645, 398	2455, 627, 542	2848, 738, 684
R_{int}	0.025	0.121	0.055	0.041
(sinθ/λ)max (Å-1)	0.625	0.627	0.628	0.625
Refinement				
R[F2 > 2σ(F2)], wR(F2), S	0.026, 0.070, 0.82	0.088, 0.234, 1.00	0.064, 0.151, 1.09	0.062, 0.152, 1.05
No. of parameters	76	33	33	33
No. of restraints	0	17	17	17
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å-3)	0.18, -0.13	0.48, -0.48	0.33, -0.27	0.42, -0.31

Pressure	3.97 GPa	4.02 GPa	5.20 GPa	5.91 GPa
Phase	I’	I’	I’	I’
Crystal data				
Temperature (K)	298	296	296	298
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$
a, *b*, *c* (Å)	4.9715 (14), 13.236 (7), 7.042 (2)	4.9824 (6), 13.353 (3), 7.0029 (14)	4.9556 (9), 13.322 (4), 6.874 (2)	4.933 (2), 13.248 (9), 6.841 (3)
V (Å^3)	463.4 (3)	465.89 (15)	453.8 (2)	447.1 (4)
Radiation type	Synchrotron, λ = 0.4959 Å	Synchrotron, λ = 0.478 Å	Synchrotron, λ = 0.478 Å	Synchrotron, λ = 0.4959 Å
μ (mm-1)	0.07	0.07	0.07	0.07
Crystal size (mm)	0.06 × 0.04 × 0.02	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.06 × 0.04 × 0.02
Data collection				
Diffractometer	Perkin-Elmer a-Si Detector	Bruker-Nonius *APEX* II	Bruker-Nonius *APEX* II	Perkin-Elmer a-Si Detector
T_{min}, T_{max}	0.424, 0.744	0.615, 0.744	0.599, 0.744	0.581, 0.744
No. of measured, independent and observed [I > 2σ(I)] reflections	1670, 453, 318	2494, 618, 546	2295, 594, 503	1638, 465, 357
R_{int}	0.117	0.055	0.069	0.079
(sinθ/λ)max (Å-1)	0.624	0.625	0.627	0.625
Refinement				
R[F2 > 2σ(F2)], wR(F2), S	0.057, 0.145, 1.01	0.062, 0.172, 1.12	0.059, 0.155, 1.07	0.057, 0.156, 1.13
No. of parameters	34	33	33	34
No. of restraints	17	17	17	17
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å-3)	0.35, -0.27	0.42, -0.31	0.38, -0.25	0.40, -0.28

Pressure	6.12 GPa	6.67GPa
Phase	I’	I’
Crystal data		
Temperature (K)	298	296
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$
a, *b*, *c* (Å)	4.9383 (19), 13.250 (5), 6.841 (3)	4.9154 (9), 13.230 (5), 6.7665 (14)
V (Å^3)	447.6 (3)	440.04 (19)
Radiation type	Synchrotron, λ = 0.4959 Å	Synchrotron, λ = 0.478 Å
μ (mm^{-1})	0.07	0.07
Crystal size (mm)	0.06 × 0.05 × 0.04	0.10 × 0.10 × 0.10
Data collection		
Diffractometer	Perkin-Elmer a-Si Detector	Bruker-Nonius *APEX* II
T_{min}, T_{max}	0.549, 0.744	0.560, 0.744
No. of measured, independent and observed [I > 2σ(I)] reflections	1687, 486, 367	2302, 561, 431
R_{int}	0.087	0.094
(sinθ/λ)max (Å^{-1})	0.625	0.627
Refinement		
R[F2 > 2σ(F2)], wR(F2), S	0.064, 0.161, 1.04	0.067, 0.158, 1.11
No. of parameters	34	33
No. of restraints	17	17
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, -0.24	0.30, -0.28

Pressure	8.50 GPa	9.82 GPa	11.19 GPa	13.00 GPa*	13.94 GPa
Phase	I’	II	II	II	II
Crystal data					
Temperature (K)	298	298	298	298	298
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$
a, *b*, *c* (Å)	4.879 (3), 13.135 (8), 6.658 (6)	4.842 (6), 13.025 (17), 6.589 (12)	4.823 (4), 13.027 (10), 6.481 (7)	4.823 (5), 13.025 (12), 6.457 (8)	4.799 (2), 12.972 (5), 6.432 (3)
α, β, γ(°)	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90
V (Å^3)	426.7 (5)	415.5 (11)	407.2 (7)	405.7 (7)	400.4 (3)
Radiation type	Synchrotron, λ = 0.4959 Å	Synchrotron, λ = 0.478 Å	Synchrotron, λ = 0.478 Å	Synchrotron, λ = 0.478 Å	Synchrotron, λ = 0.4959 Å
μ (mm^{-1})	0.08	0.08	0.08	0.08	0.08
Crystal size (mm)	0.06 × 0.05 × 0.04	0.06 × 0.05 × 0.04	0.06 × 0.05 × 0.04	0.06 × 0.05 × 0.04	0.06 × 0.05 × 0.04
Data collection					
Diffractometer	Perkin-Elmer a-Si Detector	Perkin-Elmer a-Si Detector	Perkin-Elmer a-Si Detector	Perkin-Elmer a-Si Detector	Perkin-Elmer a-Si Detector
T_{min}, T_{max}	0.453, 0.744	0.555, 0.744	0.561, 0.744	0.486, 0.744	0.529, 0.744
No. of measured, independent and observed [I > 2σ(I)] reflections	766, 227, 192	711, 329, 194	831, 341, 279	836, 220, 199	737, 281, 249
R_{int}	0.089	0.100	0.067	0.050	0.042
θmax (°)	14.4	18.1	18.1	14.4	16.4
(sinθ/λ)max (Å^{-1})	0.500	0.625	0.628	0.500	0.568
Refinement					
R[F2 > 2σ(F2)], wR(F2), S	0.062, 0.142, 1.08	0.091, 0.245, 1.05	0.053, 0.142, 1.04	0.058, 0.156, 1.27	0.055, 0.140, 1.04
No. of parameters	34	34	34	33	33
No. of restraints	17	17	17	17	17
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, -0.23	0.36, -0.36	0.23, -0.21	0.30, -0.22	0.25, -0.23

*decompression

Pressure	15.20 GPa	15.78 GPa	17.05 GPa	18.20 GPa
Phase	II	II	II	III
Crystal data				
Temperature (K)	298	298	298	298
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1$
a, *b*, *c* (Å)	4.771 (3), 12.903 (6), 6.361 (4)	4.773 (3), 12.910 (8), 6.363 (6)	4.768 (4), 12.883 (10), 6.353 (7)	4.735 (5), 12.823 (13), 6.275 (8)
α, β, γ(°)	90, 90, 90	90, 90, 90	90, 90, 90	90, 91.14 (3), 90
V (Å^3)	391.6 (4)	392.0 (5)	390.2 (6)	380.9 (8)
Radiation type	Synchrotron, λ = 0.4959 Å	Synchrotron, λ = 0.478 Å	Synchrotron, λ = 0.478 Å	Synchrotron, λ = 0.4959 Å
μ (mm^{-1})	0.08	0.08	0.09	0.09
Crystal size (mm)	0.06 × 0.05 × 0.04	0.06 × 0.05 × 0.04	0.06 × 0.05 × 0.04	0.06 × 0.05 × 0.04
Data collection				
Diffractometer	Perkin-Elmer a-Si Detector	Perkin-Elmer a-Si Detector	Perkin-Elmer a-Si Detector	Perkin-Elmer a-Si Detector
T_{min}, T_{max}	0.283, 0.744	0.445, 0.744	0.408, 0.744	0.463, 0.744
No. of measured, independent and observed [I > 2σ(I)] reflections	1196, 370, 246	1245, 366, 253	1101, 331, 208	901, 378, 305
R_{int}	0.066	0.062	0.070	0.055
θmax (°)	18.1	18.1	18.1	16.1
(sinθ/λ)max (Å^{-1})	0.628	0.627	0.627	0.558
Refinement				
R[F2 > 2σ(F2)], wR(F2), S	0.065, 0.161, 0.95	0.067, 0.176, 1.00	0.086, 0.228, 1.11	0.078, 0.192, 1.05
No. of parameters	34	33	33	67
No. of restraints	17	17	17	51

$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, -0.31	0.36, -0.27	0.31, -0.34	0.30, -0.27

Pressure	20.62 GPa	22.31 GPa
Phase	III	III
Crystal data		
Temperature (K)	298	298
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1$
a, *b*, *c* (Å)	4.679 (6), 12.659 (13), 6.143 (9)	4.620 (9), 12.52 (2), 6.037 (14)
α, β, γ(°)	90, 91.42 (3), 90	90, 92.54 (4), 90
V (Å^3)	363.7 (8)	348.9 (12)
Radiation type	Synchrotron, λ = 0.4959 Å	Synchrotron, λ = 0.478 Å
μ (mm^{-1})	0.09	0.10
Crystal size (mm)	0.06 × 0.05 × 0.04	0.06 × 0.05 × 0.04
Data collection		
Diffractometer	Perkin-Elmer a-Si Detector	Perkin-Elmer a-Si Detector
T_{min}, T_{max}	0.253, 0.744	0.610, 0.744
No. of measured, independent and observed [I > 2σ(I)] reflections	649, 310, 205	334, 183, 156
R_{int}	0.093	0.061
θmax (°)	17.0	14.3
(sinθ/λ)max (Å^{-1})	0.589	0.499
Refinement		
R[F2 > 2σ(F2)], wR(F2), S	0.112, 0.295, 1.18	0.079, 0.196, 1.15
No. of parameters	67	66
No. of restraints	51	51
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, -0.46	0.24, -0.30

Table S3 PIXEL calculated lattice energies and their breakdown into component terms

Pressure (GPa)	Coulombic (kJ/mol)	Polarisation (kJ/mol)	Dispersion (kJ/mol)	Repulsion (kJ/mol)	Total Energy (kJ/mol)
0.00	-254.7	-90.6	-97.6	191.0	-252.0
1.26*	-288.9	-103.1	-114.8	249.5	-257.2
2.05*	-301.6	-108.4	-123.4	277.7	-255.7
3.23*	-311.7	-114.9	-131.5	307.1	-251.0
3.97	-323.1	-124.2	-141.0	339.6	-248.6
4.02*	-320.1	-118.5	-139.3	335.6	-242.4
5.20*	-335.8	-125.3	-148.0	373.2	-235.9
5.91	-343.3	-133.7	-154.6	399.7	-231.8
6.12	-340.1	-132.4	-154.2	394.0	-232.7
6.67*	-357.9	-138.7	-159.7	433.5	-222.8
8.50	-372.4	-150.7	-172.3	482.7	-212.7
9.82	-396.3	-166.5	-181.8	549.4	-195.1
11.19	-418.6	-176.7	-190.1	600.5	-184.8
13.94	-430.2	-186.3	-198.6	646.7	-168.4
15.20	-455.2	-199.9	-208.5	714.2	-149.4
15.78	-450.5	-197.3	-208.6	707.5	-148.8
17.05	-465.1	-204.0	-211.0	728.7	-151.4
18.20	-463.9	-205.8	-231.5	776.4	-124.9
20.62	-539.4	-252.3	-256.5	995.4	-52.9
22.31	-620.8	-300.7	-281.5	1247.7	44.6

** indicates diffraction data collected on Beamline 9.8. Other data were collected on Beamline 12.2.2 at ALS.*

Table S4 PIXEL and DFT calculated crystal lattice enthalpies

Pressure (GPa)	DFT Dispersion corrected energy (eV)	DFT U_{rel} (eV)	DFT U_{rel} (kJ mol^{-1})	PIXEL Total (kJ mol^{-1})	PIXEL U_{rel} (kJ mol^{-1})
0.00	-9493.620531	0.169778908	0	-252.0	0
3.97	-9492.941415	0.293205396	16.381	-248.6	3.4
5.91	-9492.447709	0.288365751	28.290	-231.8	20.2
6.12	-9492.467068	0.520823162	27.823	-232.7	19.3
8.50	-9491.537238	0.687574378	50.252	-212.7	39.3
9.82	-9490.870233	0.831784605	66.341	-195.1	56.9
11.19	-9490.293392	0.964681887	80.255	-184.8	67.2
13.94	-9489.761803	1.157547977	93.077	-168.4	83.6
15.20	-9488.990339	1.145929923	111.686	-149.4	102.6
15.78	-9489.036811	1.188910624	110.565	-148.8	103.2
17.05	-9488.864888	1.424269783	114.712	-151.4	100.6
18.20	-9487.923452	1.953744444	137.421	-124.9	127.1
20.62	-9485.805553	2.533769554	188.507	-52.9	199.1
22.31	-9483.485453	0.169778908	244.471	44.6	296.6

Table S5 Breakdown of contact energies at 18.2 GPa with molecule A set as the central reference molecule. All energies are in kJ mol^{-1}.

Label	Centroid Distance (Å)	Symmetry	PIXEL Coulombic	Polarization	Dispersion	Repulsion	Total	Contacts
A	4.960	x, y, z	-151.3	-59.8	-46.2	156.0	-101.3	O2···H3N1/H4(C2) = 1.98/2.41 Å C4H8···O1 = 2.02 Å C3H5···O2 = 2.32 Å
B	4.915	x, y, 1+z	-158.3	-63.7	-48.8	179.9	-90.9	O2···H3N1/H4(C2) = 2.06/2.26 Å C4H8···O1 = 1.97 Å C3H5···O2 = 2.27 Å
C D	6.562	2-x, -1/2+y, 1-z 2-x, 1/2+y, 1-z	-99.4	-44.7	-18.4	124.0	-38.6	O3H6···O1/O2= 1.77/2.70 Å C4H7···O1 = 2.63 Å
E	5.625	1+x, y, z	-104.6	-36.5	-24.0	73.1	-92.0	O1···H3(N1)/H2(N1) = 1.92/2.52 Å
F	5.478	-1+x, y, -1+z	-40.7	-27.6	76.7	76.7	-99.5	O1···H3(N1)/H2(N1) = 1.93/2.50 Å C2H5···O1 = 2.60 Å
G H	4.735	-1+x, y, z 1+x, y, z	-52.1	-63.1	-50.6	178.2	12.4	N1H1···O2/H8(C4) = 1.84/2.13 Å C4H9···H2(N1)/O3 = 2.19/2.25 Å O1···O2 = 2.68(2) Å C4H8···O3 = 2.57 Å
I J	7.625	1-x, -1/2+y, 1-z 1-x, 1/2+y, 1-z	-8.1	-4.5	-4.2	2.4	-14.5	long contact C4H9···O2 = 2.89 Å
K	4.346	2-x, 1/2+y, 1-z	-62.8	-46.7	-45.5	151.7	-3.4	C2H4···H6(O3)/H6 = 2.07/1.99 Å C4H9···O3/H4(C2) /H2(N1)= 2.47/2.27/1.85 Å N1H2···O3= 2.04 Å
L	4.311	1-x, 1/2+y, 1-z	-60.5	-57.9	-50.9	184.0	14.7	C2H4···H6(O3)/H6 = 2.08/2.01 Å C4H9···O3/H4(C2)/H2(N1)= 2.37/2.17/1.76 Å N1H2···O3/H6(O3)= 2.00/2.15 Å
M	5.635	1-x, 1/2+y, -z	-17.9	-29.4	-29.6	99.0	22.2	C4H7···H6(O3)/O3/H5(C3) = 1.94/2.45/1.83 Å C4H8···H6(O3)/H7(C4) = 2.38/2.34 Å
N	5.765	2-x, 1/2+y, -z	-19.1	-20.9	-23.9	76.9	13.0	C4H7···H6(O3)/O3/(H5)C3 = 1.98/2.39/1.91 Å C4H8···H6(O3) = 2.22Å

Table S6 Breakdown of contact energies at 18.2 GPa with molecule B set as the central reference molecule. All energies are in kJ mol^{-1}.

Label	Centroid Distance (Å)	Symmetry	PIXEL Coulombic	Polarization	Dispersion	Repulsion	Total	Contacts
A	4.915	x, y, -1+z	-158.3	-63.7	-48.8	179.9	-90.9	O2···H3N1/H4(C2) = 2.06/2.26 Å C4H8···O1 = 1.97 Å C3H5···O2 = 2.27 Å
B	4.960	x, y, z	-151.3	-59.8	-46.2	156.0	-101.3	O2···H3N1/H4(C2) = 1.98/2.41 Å C4H8···O1 = 2.02 Å C3H5···O2 = 2.32 Å
C D	6.519	1-x, 1/2+y, -z 1-x, -1/2+y, -z	-67.2	-27.7	-18.4	83.8	-29.6	O3H6···O1/O2= 1.97/2.62 Å C4H7···O1 = 2.57 Å
E	5.478	-1+x, y, -1+z	-108.0	-40.7	-27.6	76.7	-99.5	O1···H3(N1)/H2(N1) = 1.93/2.50 Å C2H5···O1 = 2.60 Å
F	5.625	-1+x, y, z	-104.6	-36.5	-24.0	73.1	-92.0	O1···H3(N1)/H2(N1) = 1.92/2.52 Å
G H	4.735	1+x, y, z -1+x, y, z	-57.1	-61.8	-48.6	165.6	-1.8	N1H1···O2/H8(C4) = 1.82/2.27 Å C4H9···H2(N1)/O3/H6 = 2.29/2.24/2.23 Å O1···O2 = 2.74(2) Å C4H8···O3 = 2.67 Å
I J	7.706	2-x, 1/2+y, -z 2-x, -1/2+y, -z	-3.5	-3.9	-3.5	1.3	-9.5	long contact C4H9···O2 = 3.07 Å
K	4.311	1-x, -1/2+y, 1-z	-60.5	-57.9	-50.9	184.0	14.7	C2H4···H6(O3)/H6 = 2.08/2.01 Å C4H9···O3/H4(C2)/H2(N1)= 2.37/2.17/1.76 Å N1H2···O3/H6(O3)= 2.00/2.15 Å
L	4.346	2-x, -1/2+y, 1-z	-62.8	-46.7	-45.5	151.7	-3.4	C2H4···H6(O3)/H6 = 2.07/1.99 Å C4H9···O3/H4(C2) /H2(N1)= 2.47/2.27/1.85 Å N1H2···O3= 2.04 Å
M	5.765	2-x, -1/2+y, -z	-19.1	-20.9	-23.9	76.9	13.0	C4H7···H6(O3)/O3/(H5)C3 = 1.98/2.39/1.91 Å C4H8···H6(O3) = 2.22Å
N	5.635	1-x, -1/2+y, -z	-17.9	-29.4	-29.6	99.1	22.2	C4H7···H6(O3)/O3/H5(C3) = 1.94/2.45/1.83 Å C4H8···H6(O3)/H7(C4) = 2.38/2.34 Å

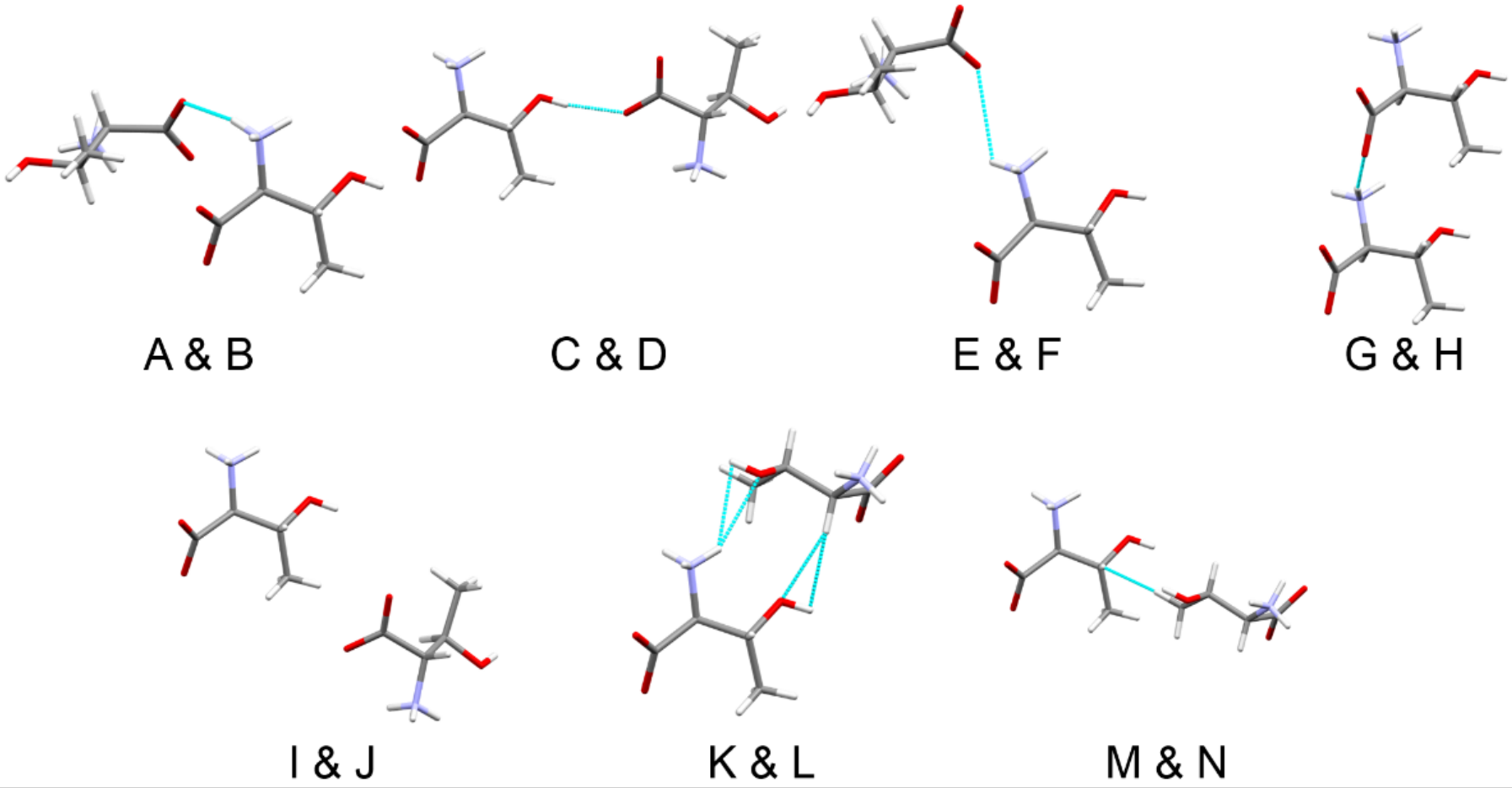

Figure S1 The most energetically significant contacts in phase I at ambient pressure.

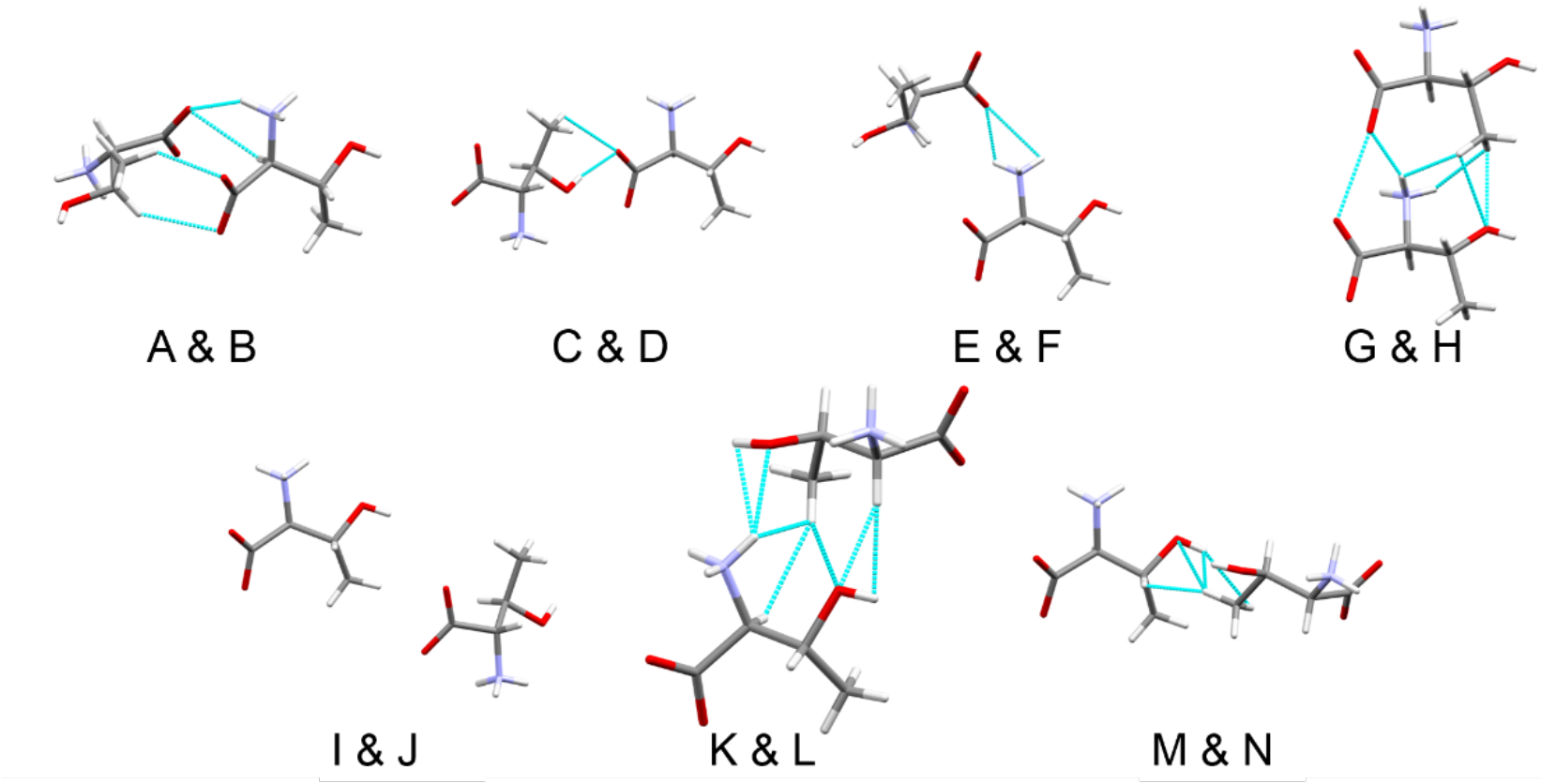

Figure S2 The most energetically significant contacts in phase II just below the phase transition at 17.1 GPa

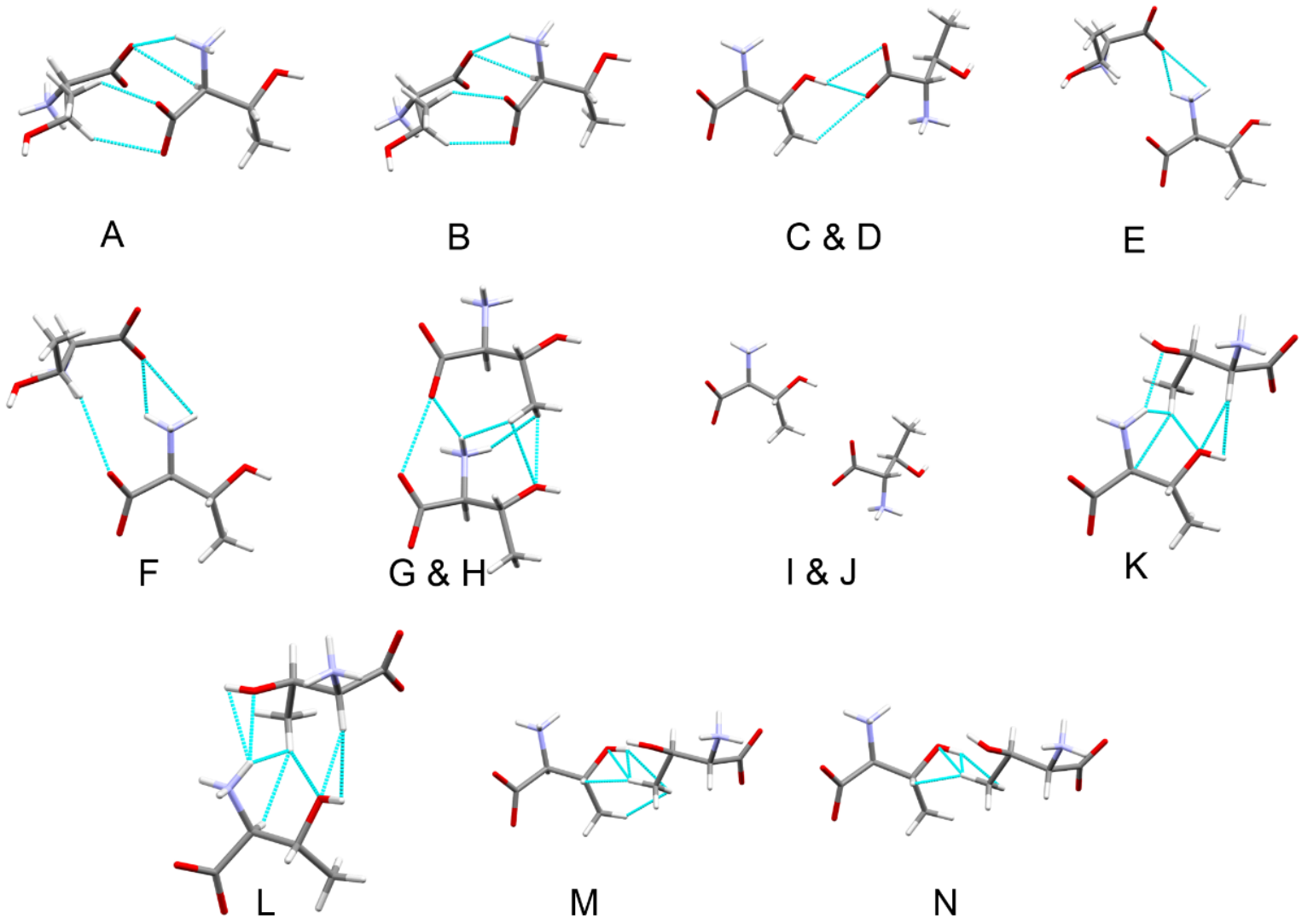

Figure S3 The most energetically significant contacts in phase III (central reference molecule 1) just above the phase transition at 18.2 GPa.

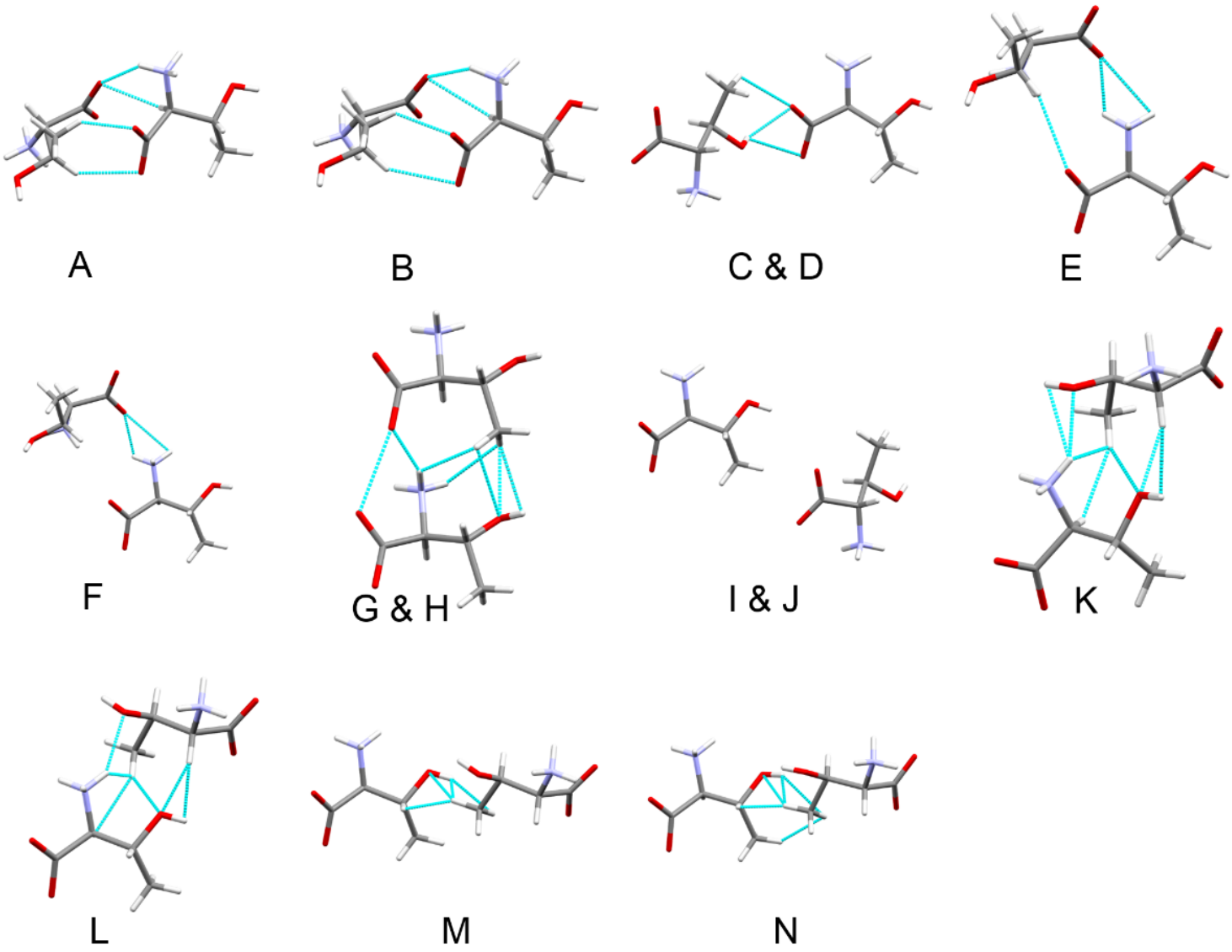

Figure S4 The most energetically significant contacts in phase III (central reference molecule 2) just above the phase transition at 18.2 GPa.

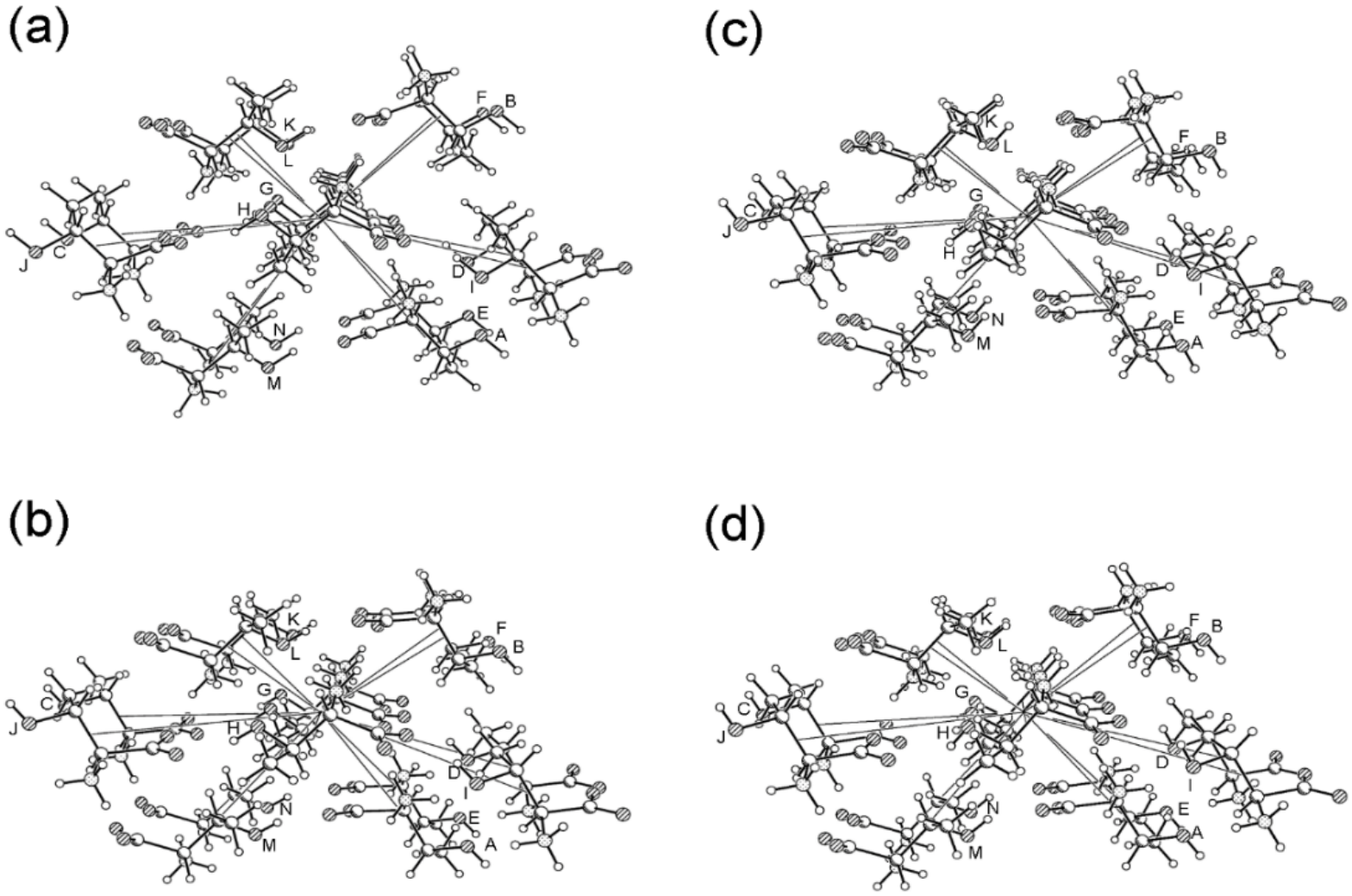

Figure S5 The first coordination spheres of at (a) 0.0 GPa, (b) 17.1 GPa; and (c) 18.2 GPa, with molecule 1 as the central reference molecule and (d) at 18.2 GPa with molecule 2 as the central reference molecule.

Table S7 Structural differences in the DFT geometry optimised structures

Bond Distances (Å)

Bond	0 GPa	Molecule 1 22.3 GPa	Molecule 2 22.3 GPa	Difference (Å)	
C1-O1	1.2592	1.2609	1.261	0.002	0.002
C1-O2	1.2689	1.248	1.2516	-0.021	-0.017
C1-C2	1.5396	1.4683	1.4757	-0.071	-0.064
C2-N1	1.4923	1.4375	1.4362	-0.055	-0.056
C2-C3	1.540	1.4964	1.4935	-0.044	-0.047
C3-C4	1.5215	1.4785	1.4753	-0.043	-0.046
C3-O3	1.4317	1.4034	1.4074	-0.028	-0.028

Valence Angles (°)

Bond	0 GPa	Molecule 1 22.3 GPa	Molecule 2 22.3 GPa	Difference (°)	
O1-C1-O2	127.12	124.10	123.40	-3.020	-3.720
N1-C2-C1	110.47	107.28	107.02	-3.190	-3.450
O3-C3-C2	104.18	103.56	106.08	-0.620	1.900
O1-C1-C2	116.63	114.56	114.87	-2.070	-1.760
N1-C2-C3	109.35	111.44	110.77	2.090	1.420
O3-C3-C4	111.03	107.63	107.92	-3.400	-3.110
O2-C1-C2	116.25	121.33	121.68	5.080	5.430
C1-C2-C3	113.94	114.23	112.82	0.290	-1.120
C2-C3-C4	113.76	106.68	108.38	-7.080	-5.380

Dihedral Angles (°)

Bond	0 GPa	Molecule 1 22.3 GPa	Molecule 2 22.3 GPa	Difference (°)	
O1-C1-C2-N1	-24.55	-10.05	-5.88	14.50	18.67
O2-C1-C2-C3	-80.19	-64.92	-61.36	15.27	18.83
C1-C2-C3-O3	-178.47	-162.69	-163.55	15.78	14.92
O1-C1-C2-C3	99.00	113.99	116.20	14.99	17.20
N1-C2-C3-O3	-54.32	-40.90	-43.60	13.42	10.72
C1-C2-C3-C4	60.48	83.88	80.78	23.40	20.30
O2-C1-C2-N1	156.26	171.04	176.55	14.78	20.29
N1-C2-C3-C4	-175.36	-154.33	-159.27	21.03	16.09

Table S8 Similarity statistics of the DFT optimised ambient pressure and 22.3 GPa molecules

	Molecule 1 22.3 GPa RMSD (Å)		Molecule 2 22.3 GPa RMSD (Å)
N1A	0.145	N1B	0.126
C2A	0.097	C2B	0.064
C1A	0.052	C1B	0.053
O1A	0.339	O1B	0.349
O2A	0.368	O2B	0.412
C3A	0.118	C3B	0.107
O3A	0.31	O3B	0.29
C4A	0.458	C4B	0.435
Total	**0.275**	**Total**	**0.274**

Table S9 Similarity statistics of the experimental and DFT geometry optimised structures at 0.0 GPa

Atom 1	Atom 2	Distance (Å)
O3	O3	0.026
N1	N1	0.018
O1	O1	0.055
C4	C4	0.022
O2	O2	0.027
C3	C3	0.02
C2	C2	0.025
C1	C1	0.011
	RMSD	0.0284

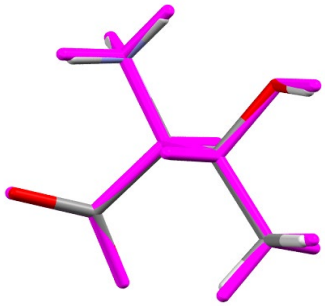

Figure S6 Structure overlay of the experimental (coloured by element) and DFT geometry optimised (pink) structure at 0.0 GPa.

Table S10 Similarity statistics of the experimental and DFT geometry optimised structures at 22.3 GPa

Atom 1	Atom 2	Distance (Å)
O3B	O3B	0.221
N1B	N1B	0.209
O1B	O1B	0.075
C4B	C4B	0.179
O2B	O2B	0.145
C3B	C3B	0.048
C2B	C2B	0.115
C1B	C1B	0.134
O2A	O2A	0.037
O1A	O1A	0.18
C1A	C1A	0.082
C2A	C2A	0.133
N1A	N1A	0.078
C3A	C3A	0.072
C4A	C4A	0.119
O3A	O3A	0.088
	RMSD	0.131

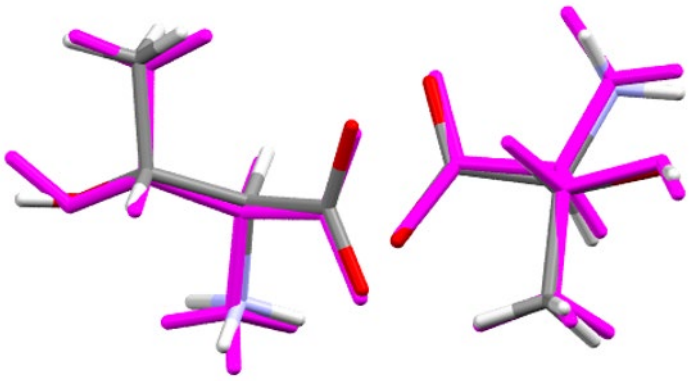

Figure S7 Structure overlay of the experimental (coloured by element) and DFT geometry optimised (pink) structures at 22.3 GPa.

Table S11 Similarity statistics of the structures at 22.3 GPa obtained using geometry optimised distance restraints, and that of the structure obtained by traditional SHELX treatment (calculated H positions and ambient pressure distance restraints).

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
C1A	C1A	0.103	C1B	C1B	0.114
C2A	C2A	0.155	C2B	C2B	0.066
C3A	C3A	0.081	C3B	C3B	0.039
C4A	C4A	0.093	C4B	C4B	0.097
H1A	H1A	0.328	H1B	H1B	0.264
H2A	H2A	0.377	H2B	H2B	0.301
H3A	H3A	0.252	H3B	H3B	0.167
H4A	H4A	0.151	H4B	H4B	0.139
H5A	H5A	0.13	H5B	H5B	0.048
H6A	H6A	0.183	H6B	H6B	0.448
H7A	H7A	0.189	H7B	H7B	0.110
H8A	H8A	0.150	H8B	H8B	0.244
H9A	H9A	0.208	H9B	H9B	0.144
N1A	N1A	0.122	N1B	N1B	0.089
O1A	O1A	0.119	O1B	O1B	0.037
O2A	O2A	0.066	O2B	O2B	0.052
O3A	O3A	0.103	O3B	O3B	0.165
		RMS Total	**0.185 Å**		

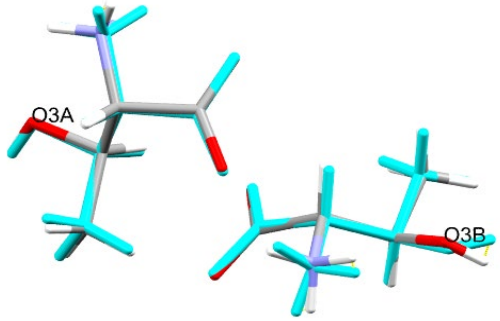

Figure S8 Overlay of the geometry optimisation restrained model (blue) and SHELXL derived experimental model (coloured by element) at 22.3 GPa

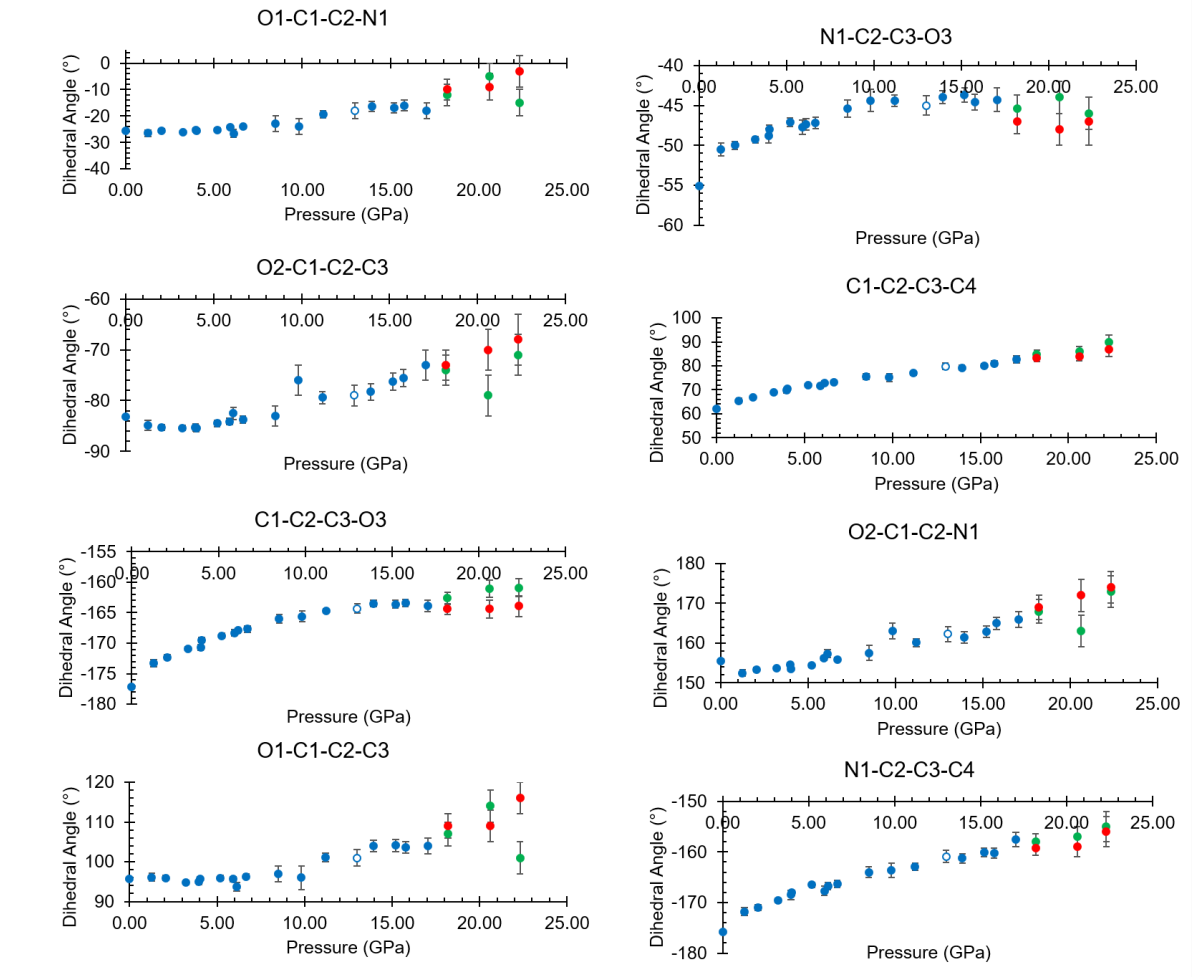

Figure S9 Torsion angles as a function of pressure from 0.0 to 22.3 GPa. Blue markers represent the $P2_12_12_1$ phases. Green and red markers represent molecules A and B, respectively, in the $P2_1$ phase. The open blue marker represents the decompression measurement.

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