Electronic Supplementary Material (ESI) for CrystEngComm.

SUPPLEMENTARY MATERIAL

Discerning Subtle High-Pressure Phase Transitions in Glyphosate.

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Section A: Occupied volume calculations

N randomly-generated points are placed in the unit cell (volume *V*); those within the van der Waals radius of any atom are classified as lying in the space occupied by the network of atoms and their contacts, the remainder sample the void space. If there are N_{net} points within the network, an estimate of the network volume V_{net} is given by $(N_{net}/N)V$. The void volume is then $V_{void} = V - V_{net}$. This is implemented in the CellVol code.[1] The volume estimates converge as *N* increases, and in this work a value of *N* = 1 million yielded a standard deviation of ≤0.1% of the network volume when the calculation was executed three times (Figure S1).

The uncertainties in the experimental structural parameters were propagated by repeating the above calculation using 50 structures in which the coordinates were perturbed with Gaussian random numbers taken from the distribution defined by each coordinate's standard uncertainty. The 50 calculations yield a distribution of V_{net} and V_{void} from which the standard uncertainties of each can be evaluated. Since precision is not defined for DFT-optimised structures, the standard uncertainty of V_{net} and V_{void} reflect only the reproducibility of each Monte Carlo run, typically, as indicated above, ≤0.1% of the network volume.

In an effort to identify which intermolecular interactions undergo the largest changes at the transitions, the volumes of the glyphosate molecule and each of the intermolecular dimers, A-H, were calculated by placing a box around them. The box is defined by producing a reference frame based on the three principal inertial axes of the molecules using the algorithm described by Gavezzotti.[2] The atomic coordinates of all the points within the molecules were used to construct an inertial matrix, ignoring atomic masses, and the eigenvalues of this matrix used to define the principal moments of inertia. The origin of our inertial reference frame is then taken as the centre of all atomic coordinates with the eigenvectors of the inertial matrix defining the rotation matrix between the original and inertial reference frame. By expressing the atomic coordinates within the inertial reference frame, the extreme points occupied by atoms of the molecule in each of the three inertial axes can then be located. These are used to define the box extended in all three dimensions beyond these values by a set length (2.5 Å in this work). When calculated for a single isolated molecule, the longest inertial axes is defined as the long axes of the molecule, used for discussions of the second transition within the main body of the text. The occupied volume

was then evaluated using a similar Monte Carlo procedure to that described above for unit cells.

The same procedure can be applied to dimers and clusters of molecules extracted from the crystal structure.

Section B: Supplementary Tables

High pressure crystallography: Crystal and refinement data

Table S1: Experimental parameters by high-pressure single-crystal measurements.

Pressure /GPa	0, DAC	0.206	0.302	0.645	0.934	1.210	1.609	1.940
				Crystal data				
Temperature (K)	293	293	293	293	293	293	293	293
Spacegroup	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, b, c (Å)	8.6693(13) 7.9704(6) 9.8968(7)	8.6720(6) 7.9508(3) 9.8213(3)	8.6626(10) 7.9208(4) 9.7820(5)	8.6567(16) 7.8828(7) 9.7114(9)	8.6512(13) 7.8496(6) 9.6513(8)	8.6419(10) 7.8197(4) 9.6036(6)	8.6334(14) 7.7827(7) 9.5468(9)	8.6285(9) 7.7531(4) 9.4944(5)
β (°)	105.644(9)	106.235(4)	106.599(7)	107.244(11)	107.785(9)	108.174(7)	108.729(10)	109.104(5)
V (Å^3)	658.51(12)	650.17(6)	643.22(9)	632.91(15)	624.08(12)	616.61(9)	607.49(13)	600.17(8)
Z	4	4	4	4	4	4	4	4
μ (mm^{-1})	0.203	0.206	0.208	0.211	0.214	0.217	0.220	0.223
Crystal size (mm)	0.15 × 0.135 × 0.05	0.19 × 0.17 × 0.05	0.15 × 0.135 × 0.05	0.15 × 0.135 × 0.05	0.15 × 0.135 × 0.05	0.15 × 0.135 × 0.05	0.15 × 0.135 × 0.05	0.19 × 0.17 × 0.05
				Data Collection				
Wavelength (Å)	0.56086	0.56086	0.56086	0.56086	0.56086	0.56086	0.56086	0.56086
Absorption correction (wR^2_{bef}, wR^2_{aft}, max : min transmission)	0.0895, 0.0623, 0.6587	0.0581, 0.0477, 0.8968	0.0856, 0.0589, 0.6493	0.0912, 0.0666, 0.7006	0.0833, 0.0627, 0.7371	0.0884, 0.0645, 0.6571	0.0855, 0.0635, 0.7825	0.0589, 0.0464, 0.8885
T_{min}, T_{max}	0.4904, 0.7445	0.6677, 0.7445	0.4834, 0.7445	0.5216, 0.7445	0.5488, 0.7445	0.4892, 0.7445	0.5826, 0.7445	0.6615, 0.7445
Measured, independent and observed reflections	3682, 517, 365	5852, 511, 435	5682, 517, 376	5611, 506, 375	5430, 490, 383	5409, 494, 382	5243, 471, 373	5320, 468, 416
R_{int}	0.0762	0.0422	0.0703	0.0783	0.0738	0.0724	0.0762	0.0363
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625	0.627	0.625	0.625	0.625	0.627	0.625	0.626
				Refinement				
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0413, 0.1108, 1.069	0.0253, 0.0642, 1.071	0.0369, 0.1008, 1.052	0.0352, 0.0937, 1.097	0.0375, 0.0820, 1.052	0.0365, 0.0946, 1.042	0.0298, 0.0720, 1.067	0.0236, 0.0622, 1.103
Data completeness	0.394	0.391	0.404	0.400	0.395	0.399	0.391	0.393
No. of reflections	517	511	517	506	490	494	471	468
No. of parameters	93	93	93	93	94	93	93	93
No. of restraints	82	82	82	82	82	82	82	82
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.216, -0.242	0.103, -0.144	0.208, -0.283	0.214, -0.238	0.165, -0.168	0.189, -0.212	0.134, -0.132	0.120, -0.138

Pressure /GPa	2.244	2.410	3.117	3.630	3.783	4.228	4.813	5.176
				Crystal data				
Temperature (K)	293	293	293	293	293	293	293	293
Spacegroup	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
	8.6185(7)	8.616(5)	8.5889(9)	8.5740(13)	8.562(2)	8.5435(9)	8.526(2)	8.496(5)
a, b, c (Å)	7.7238(3)	7.706(2)	7.6517(4)	7.6158(5)	7.6058(9)	7.5706(4)	7.5312(9)	7.510(2)
	9.4573(4)	9.438(3)	9.3709(5)	9.3347(7)	9.3306(12)	9.2993(5)	9.2654(12)	9.249(3)
β (˚)	109.454(4)	109.78(3)	110.256(5)	110.657(7)	110.868(13)	111.200(6)	111.625(13)	111.96(3)
V (Å^3)	593.61(6)	589.6(4)	577.77(8)	570.35(11)	567.79(18)	560.77(8)	553.06(17)	547.3(4)
Z	4	4	4	4	4	4	4	4
μ (mm^{-1})	0.225	0.227	0.231	0.234	0.235	0.238	0.242	0.244
Crystal size (mm)	0.19 ×	0.15 ×	0.19 ×	0.19 ×	0.15 ×	0.15 ×	0.15 ×	0.15 ×
	0.17 ×	0.135 ×	0.17 ×	0.17 ×	0.135 ×	0.135 ×	0.135 ×	0.135 ×
	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
				Data Collection				
Wavelength (Å)	0.56086	0.56086	0.56086	0.56086	0.56086	0.56086	0.56086	0.56086
Absorption correction (wR^2_{bef}, wR^2_{aft}, max : min transmission)	0.0580, 0.0473, 0.8547	0.0823, 0.0662, 0.7907	0.0562, 0.0466, 0.8880	0.0759, 0.0600, 0.7511	0.0830, 0.0617, 0.8156	0.0732, 0.0614, 0.8109	0.0679, 0.0568, 0.8423	0.0697, 0.0560, 0.8176
T_{min}, T_{max}	0.6363, 0.7445	0.5887, 0.7445	0.6611, 0.7445	0.5592, 0.7445	0.6072, 0.7445	0.6037, 0.7445	0.6271, 0.7445	0.6087, 0.7445
Measured, independent and observed reflections	5389, 468, 411	4649, 479, 376	5234, 466, 418	5032, 446, 399	4804, 532, 408	4847, 527, 412	4936, 526, 420	4692, 551, 426
R_{int}	0.0378	0.0740	0.0371	0.0502	0.0726	0.0701	0.0619	0.0587
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.627	0.625	0.627	0.626	0.630	0.625	0.625	0.625
				Refinement				
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0242, 0.0658, 1.097	0.0348, 0.0760, 1.038	0.0236, 0.0624, 1.093	0.0262, 0.0659, 1.141	0.0397, 0.0920, 1.045	0.0366, 0.0883, 1.092	0.0333, 0.0797, 1.106	0.0377, 0.0985, 1.139
Data completeness	0.390	0.402	0.397	0.388	0.464	0.467	0.471	0.497
No. of reflections	468	479	466	446	532	527	526	551
No. of parameters	93	93	93	93	93	93	93	93
No. of restraints	82	82	82	82	82	82	82	82
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.111, -0.144	0.188, -0.188	0.127, -0.137	0.117, -0.139	0.208, -0.250	0.202, -0.234	0.206, -0.274	0.222, -0.279

Pressure /GPa	0, fibre
Crystal data	
Temperature (K)	270
Spacegroup	$P2_1/c$
a, b, c (Å)	8.6764(5) 7.9722(5) 9.8883(6)
β (˚)	105.691(2)
V (Å^3)	658.48(7)
Z	4
μ (mm^{-1})	0.384
Crystal size (mm)	0.15 × 0.135 × 0.05
Data Collection	
Wavelength (Å)	0.71073
Absorption correction (wR^2_{bef}, wR^2_{aft}, max : min transmission)	0.0923, 0.0443, 0.9144
T_{min}, T_{max}	0.6822, 0.7461
Measured, independent and observed reflections	12666, 1981, 1747
R_{int}	0.0318
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.715
Refinement	
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0285, 0.0805, 1.112
Data completeness	0.982
No. of reflections	1981
No. of parameters	93
No. of restraints	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.419, - 0.324

Strain Tensor Results

The Strain tensor was calculated as described in ref.[3] Eigenvalues and vectors were calculated using JACOBI from ref.[4] Results at each pressure are represented below in Table S2. Table S3 features these results scaled by GPa which are plotted in Figure S4. Glyphosate shows remarkably 2D compression with strain axes 1 barely varying from zero. After a minor increase, this strain axes decreases indicating minor negative linear compressibility.

Table S2: Calculated strain axes in glyphosate.

Pressure /GPa	1	2	3	a	b	c	α	β	γ
0	0	0	0	8.669	7.97	9.897	90	105.644	90
0.206	0.001613	-0.00246	-0.01187	8.672	7.951	9.821	90	106.235	90
0.302	0.001687	-0.00622	-0.01886	8.663	7.921	9.782	90	106.599	90
0.645	0.002734	-0.01099	-0.03112	8.657	7.883	9.711	90	107.244	90
0.934	0.003467	-0.01516	-0.0415	8.651	7.85	9.651	90	107.785	90
1.21	0.003363	-0.01891	-0.04944	8.642	7.82	9.604	90	108.174	90
1.609	0.003856	-0.02355	-0.05981	8.633	7.783	9.547	90	108.729	90
1.94	0.003874	-0.02726	-0.06788	8.628	7.753	9.494	90	109.104	90
2.244	0.003668	-0.03094	-0.07463	8.618	7.724	9.457	90	109.454	90
2.41	0.004416	-0.03319	-0.07967	8.616	7.706	9.438	90	109.782	90
3.117	0.002475	-0.03999	-0.0904	8.589	7.652	9.371	90	110.256	90
3.63	0.00201	-0.04449	-0.09778	8.574	7.616	9.335	90	110.657	90
3.783	0.001865	-0.04574	-0.10068	8.562	7.606	9.331	90	110.868	90
4.228	0.000852	-0.05016	-0.10708	8.543	7.571	9.299	90	111.2	90
4.813	0.000292	-0.0551	-0.11468	8.526	7.531	9.265	90	111.625	90
5.176	-0.00119	-0.05781	-0.12043	8.496	7.51	9.249	90	111.961	90

Table S3: Calculated strain axes scaled by GPa.

Pressure /GPa	1	2	3	a	b	c	α	β	γ
0	0	0	0	8.669	7.97	9.897	90	105.644	90
0.206	0.007829	-0.01194	-0.05763	8.672	7.951	9.821	90	106.235	90
0.302	0.005587	-0.02061	-0.06246	8.663	7.921	9.782	90	106.599	90
0.645	0.004239	-0.01704	-0.04825	8.657	7.883	9.711	90	107.244	90
0.934	0.003712	-0.01623	-0.04443	8.651	7.85	9.651	90	107.785	90
1.21	0.002779	-0.01563	-0.04086	8.642	7.82	9.604	90	108.174	90
1.609	0.002396	-0.01464	-0.03717	8.633	7.783	9.547	90	108.729	90
1.94	0.001997	-0.01405	-0.03499	8.628	7.753	9.494	90	109.104	90
2.244	0.001635	-0.01379	-0.03326	8.618	7.724	9.457	90	109.454	90
2.41	0.001832	-0.01377	-0.03306	8.616	7.706	9.438	90	109.782	90
3.117	0.000794	-0.01283	-0.029	8.589	7.652	9.371	90	110.256	90
3.63	0.000554	-0.01226	-0.02694	8.574	7.616	9.335	90	110.657	90
3.783	0.000493	-0.01209	-0.02661	8.562	7.606	9.331	90	110.868	90
4.228	0.000201	-0.01186	-0.02533	8.543	7.571	9.299	90	111.2	90
4.813	0.000061	-0.01145	-0.02383	8.526	7.531	9.265	90	111.625	90
5.176	-0.00023	-0.01117	-0.02327	8.496	7.51	9.249	90	111.961	90

Section C: Supplementary figures

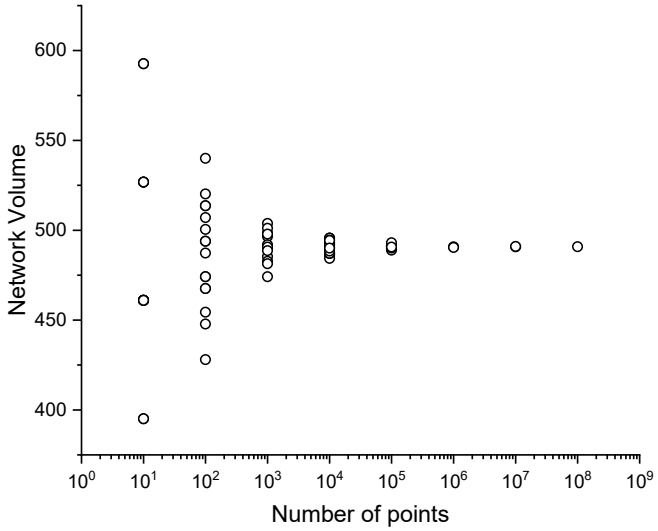


Figure S1: Convergence of points per CellVol calculation

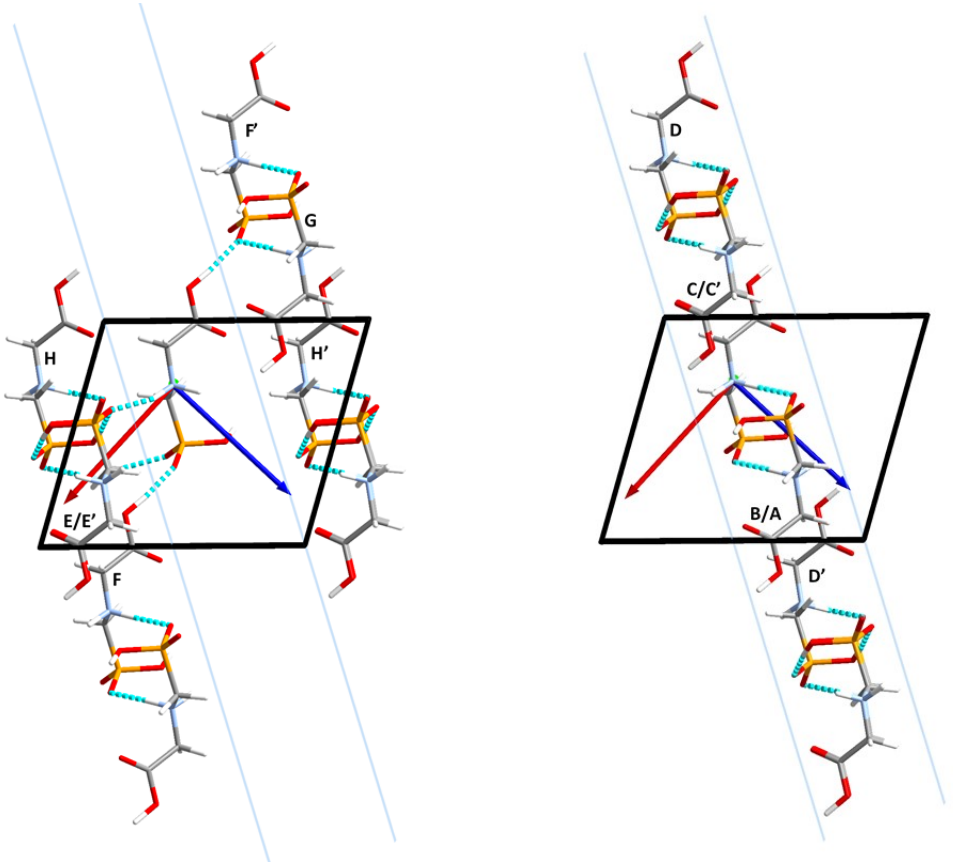
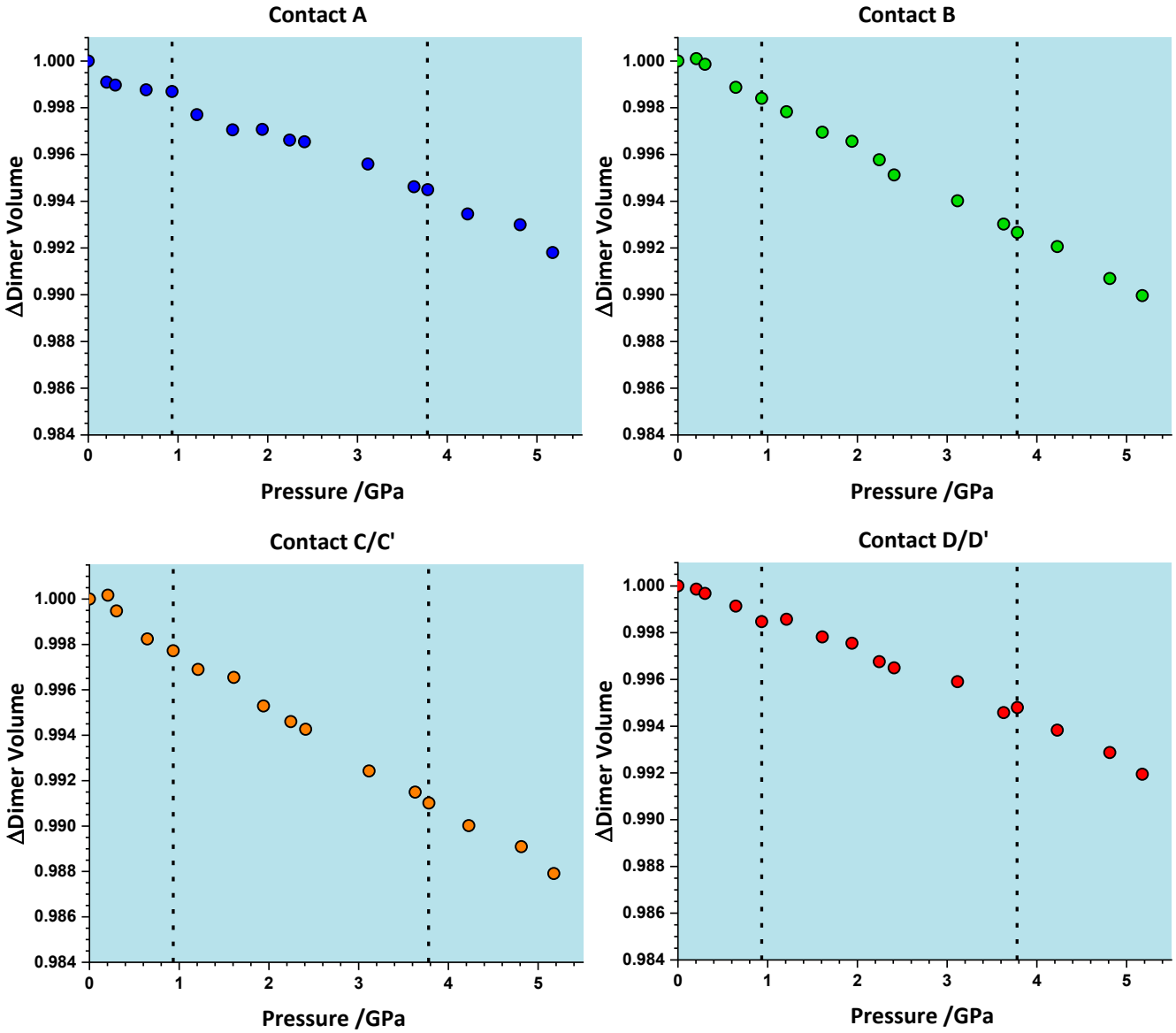


Figure S2: Contacts which make up the inter (left) and intra (right) volumes presented in the main body of the paper. Note that labels refer to molecule - molecule interactions, as listed in Table 1 of the main text, rather than individual contacts such as H-bonds.


Contact A
Contact B
Contact C/C'
Contact D/D'
ΔDimer Volume
Pressure /GPa
1.000
0.998
0.996
0.994
0.992
0.990
0.988
0.986
0.984
0
1
2
3
4
5

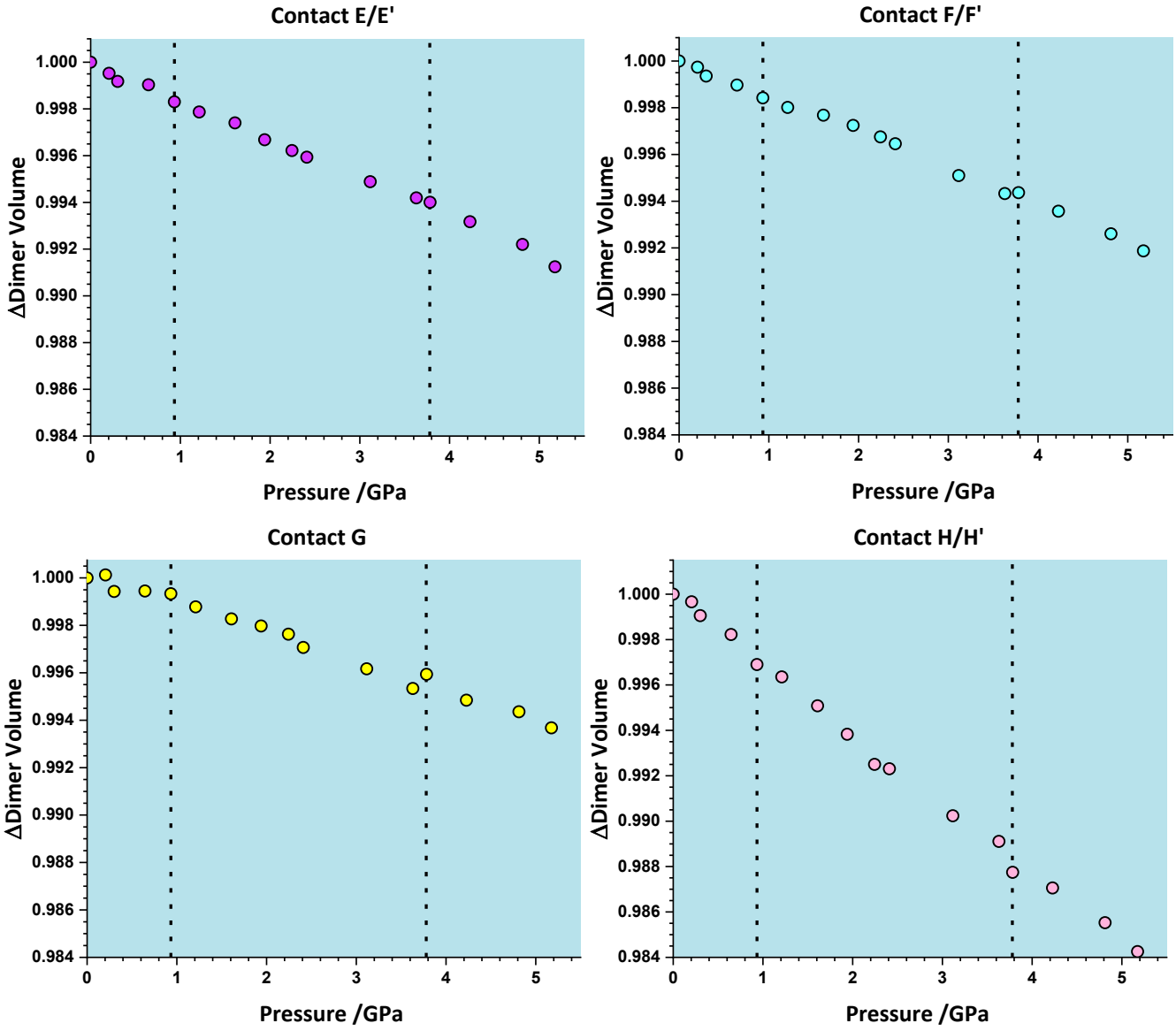


Figure S3: Molecular volume in each contact listed in Table 1 of the main text. A consistent set of vertical axes is used across all contacts to aid comparison.

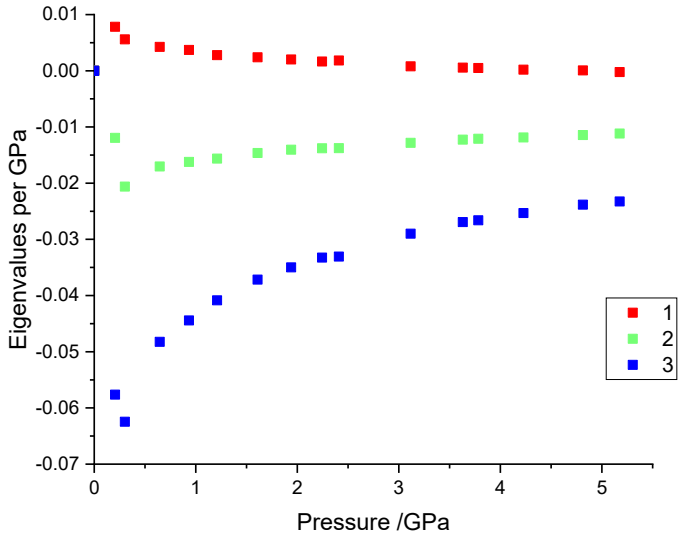


Figure S4: Eigenvalues of the strain tensor per GPa as a function of pressure.

1. C. J. G. Wilson, T. Cervenka, P. A. Wood and S. Parsons, *Cryst. Growth Des.*, 2022, **22**, 2328-2341.
2. A. Gavezzotti, *Molecular Aggregation*, Oxford University Press: Oxford , UK, 2007.
3. R. M. Hazen, Finger, L. W. , *Comparative Crystal Chemistry*, John Wiley & Sons, 1982.
4. W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling, *Numerical recipes in fortran: The art of scientific computing*, Cambridge University Press, Cambridge, UK, 2 edn., 1992.