A First Order Phase Transition in Blatter's Radical at High Pressure

Supporting information

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Supporting Figures

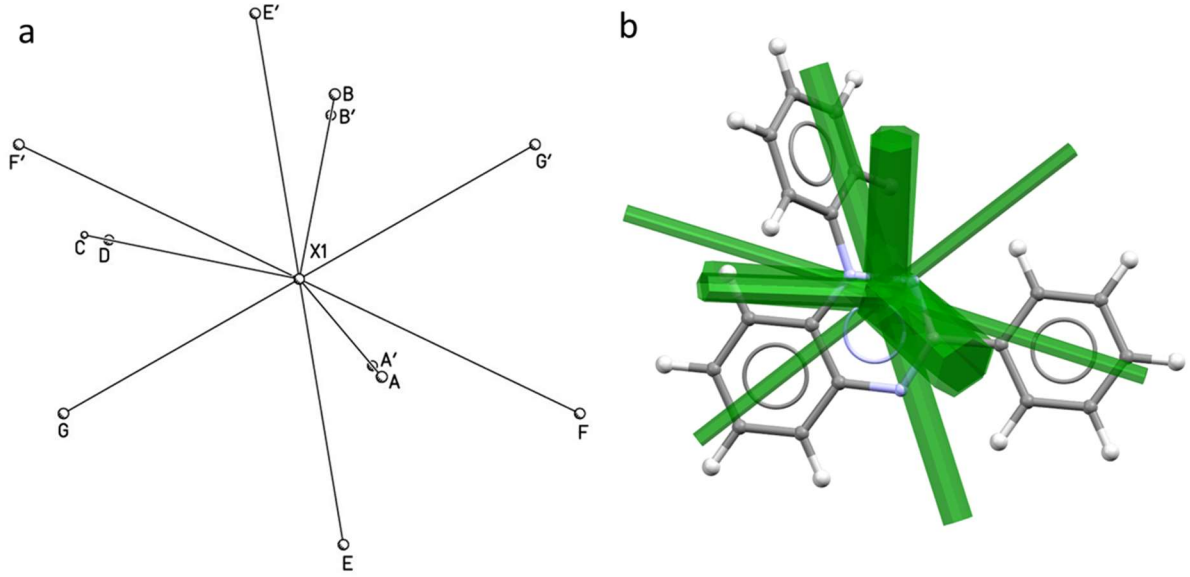

Figure S1 Diagram depicting the hcp-like stacking arrangement of the Blatter radical centroids in the first molecular coordination sphere. a) Centroids of each interacting molecules (A-F'), surrounding a central molecule (X1), labelled as in Table 2. b) Total energy of the interactions of 1 calculated via the PIXEL method in the first coordination sphere, shown as energy frameworks. Both views are along the *b* axis.

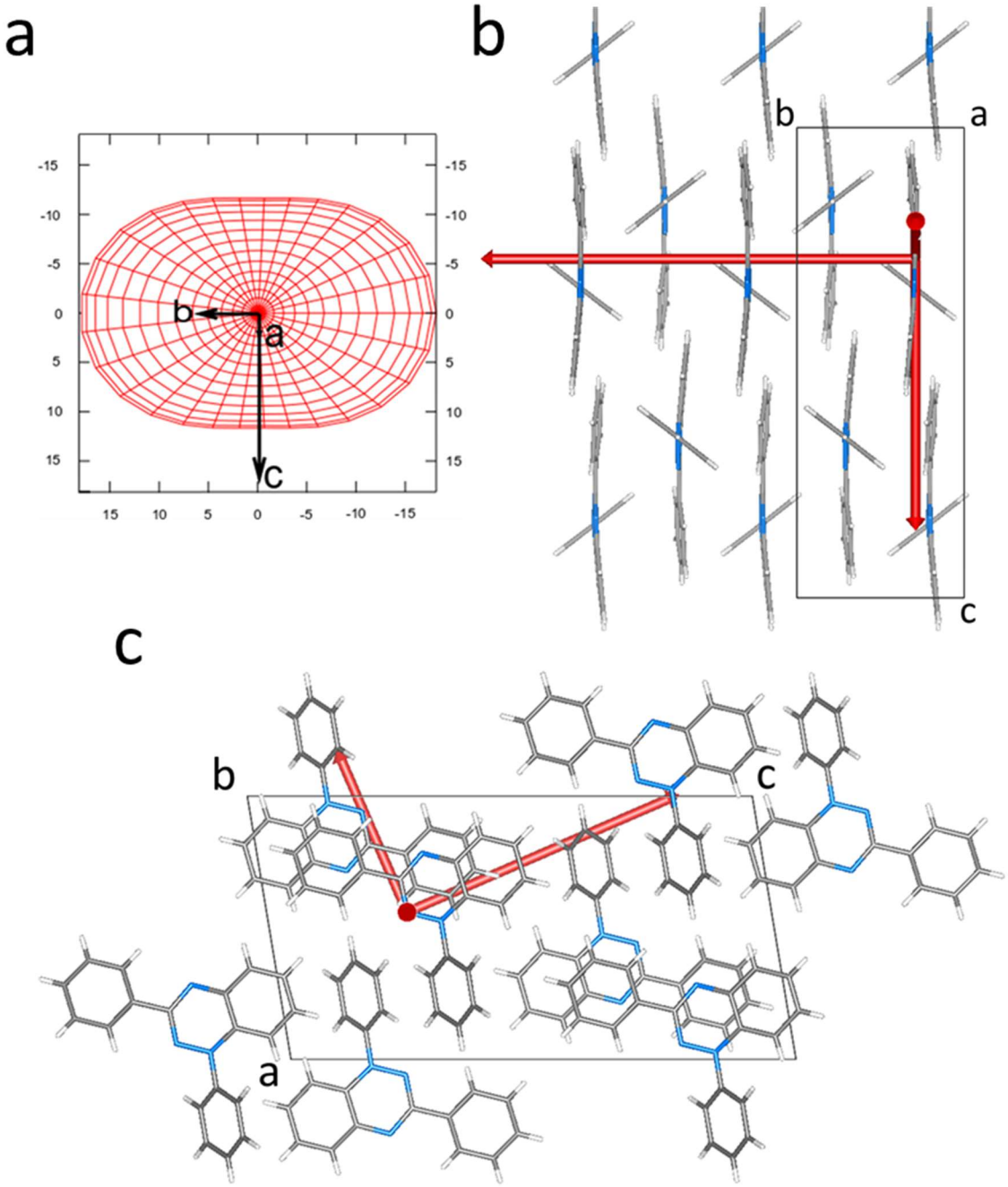

Figure S2 a) The compressibility indicatrix for the crystal structure of radical 1. b) Vectors corresponding to X_1, X_2 and X_3 in Table 3 of the main text calculated using PASCaL added to the crystal structure (red arrows), viewed along the *a* direction and c) *b* axes.

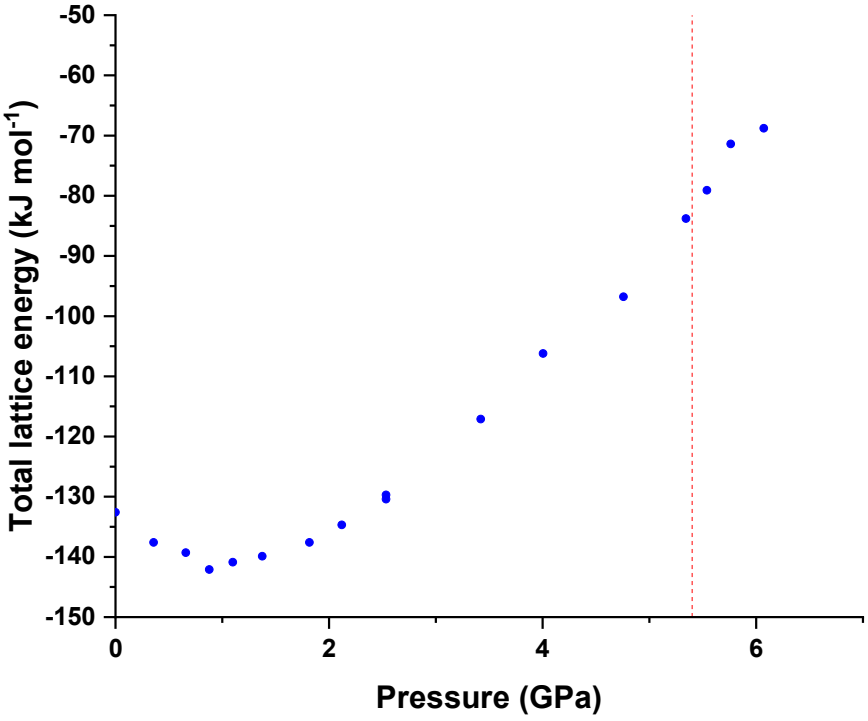

Figure S3 Pressure dependence of the lattice energy of radical 1.

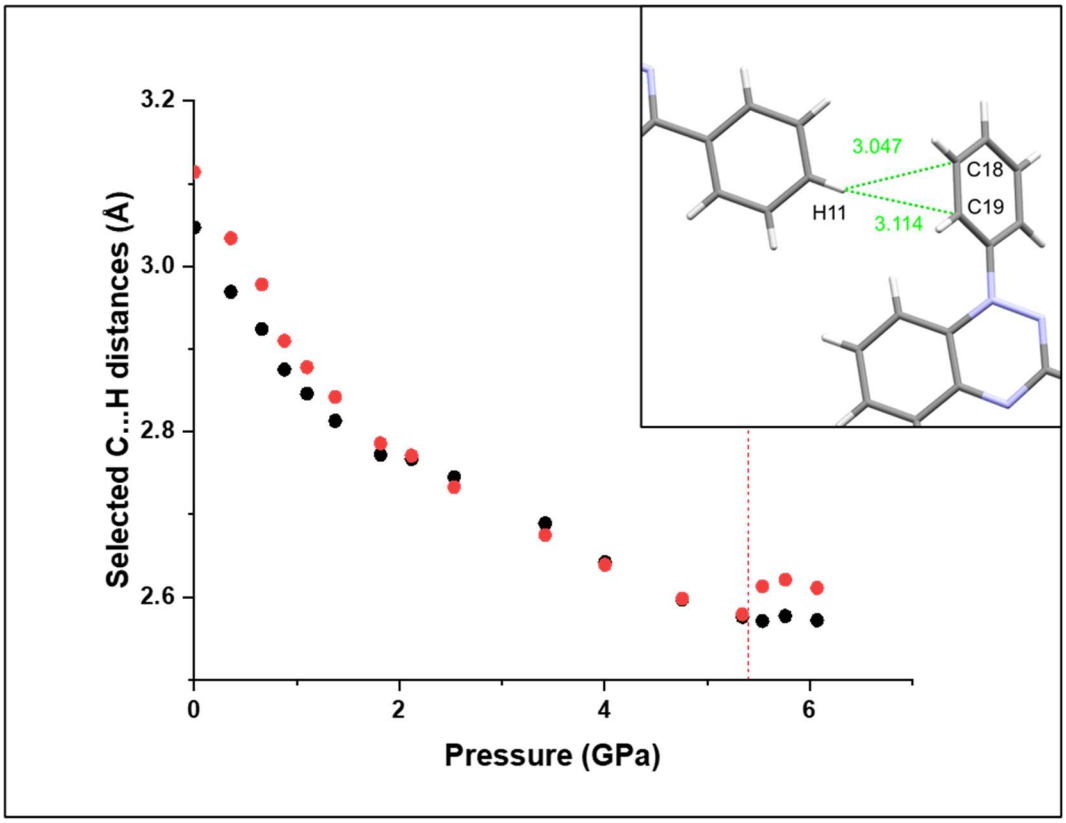

Figure S4 Variation of C···H distances with increasing pressure. Red = C19···H11 and black = C18···H11. Insert: C···H contacts in interaction F.

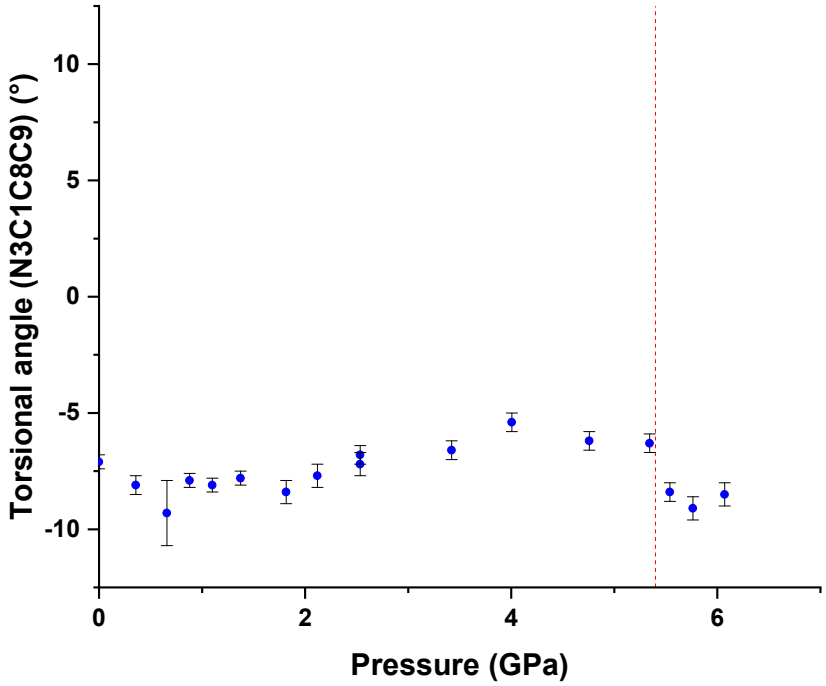

Figure S5 C-Ph torsional angle with increasing pressure. Red dashed line marks a phase transition.

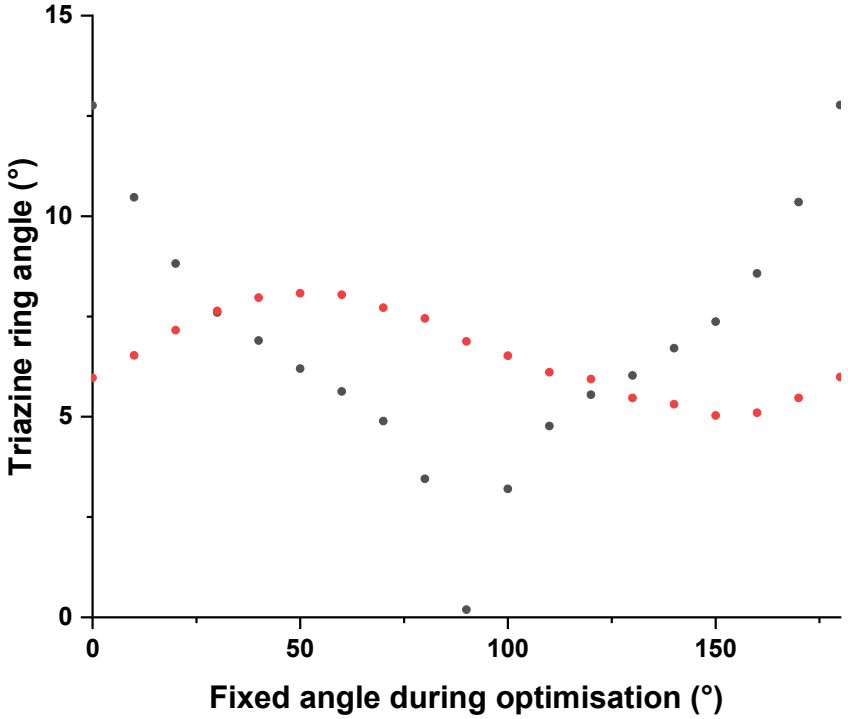

Figure S6 Calculated (DFT) angle between the N1-C3-C2-N3 and N1-N2-C1-N3 mean planes of the triazinyl moiety during rotation of the N-Ph (black) and C-Ph (red) substituents.

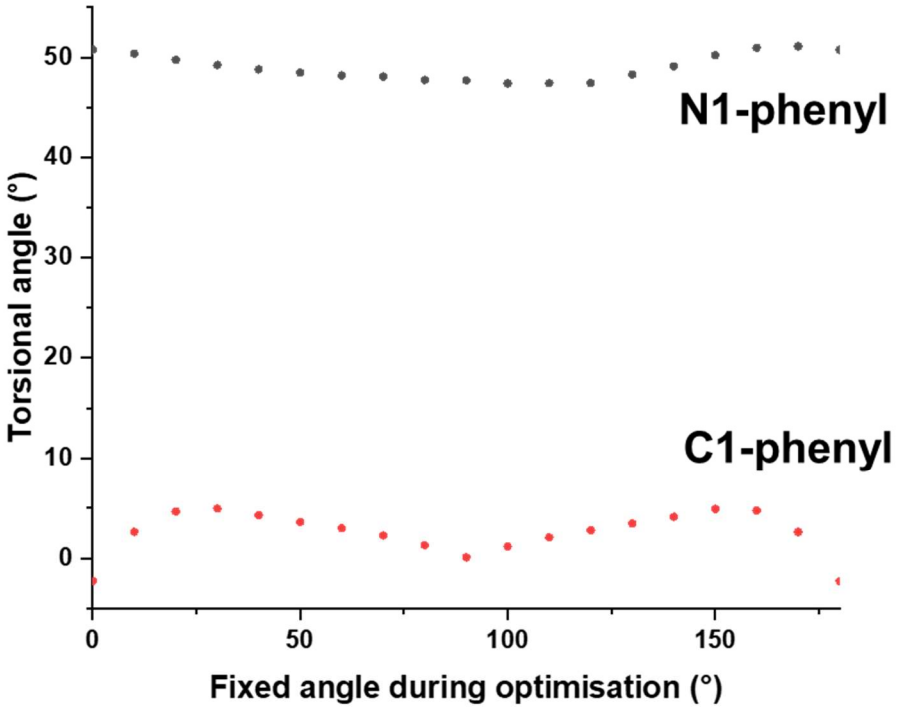

Figure S7 Measured torsional angles of the phenyl groups that were not fixed during the geometry optimisation. Black dots = N-Ph. Red dots = C-Ph.

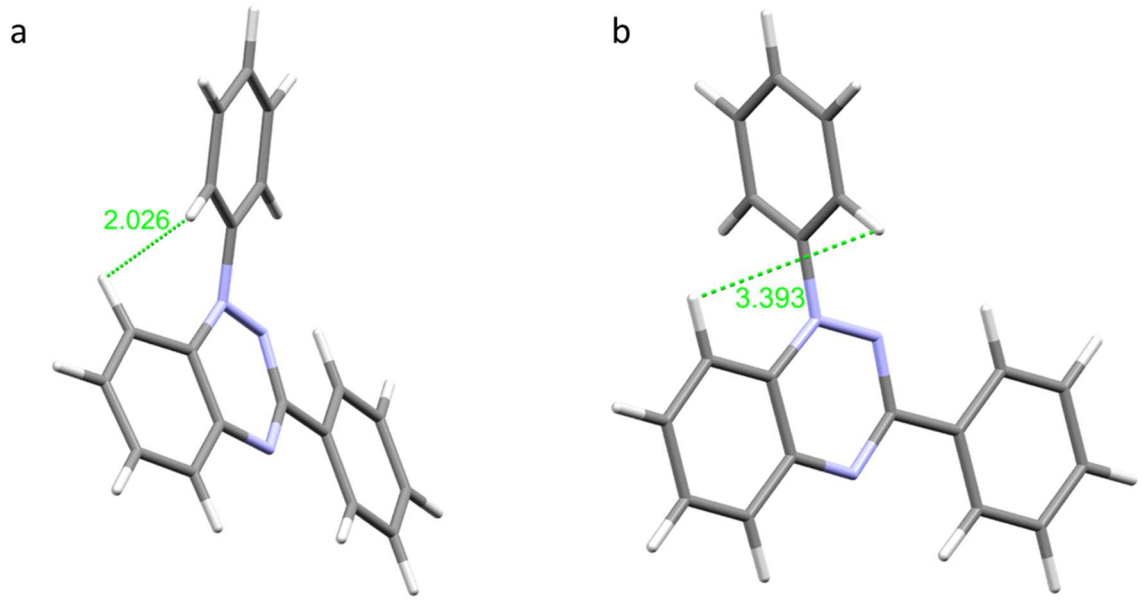

Figure S8 Blatter's radical 1 with the C3-N1-C14-C19 torsional angle at a) 0° and b) 90°. The H19…H4 distance is shown in Å.

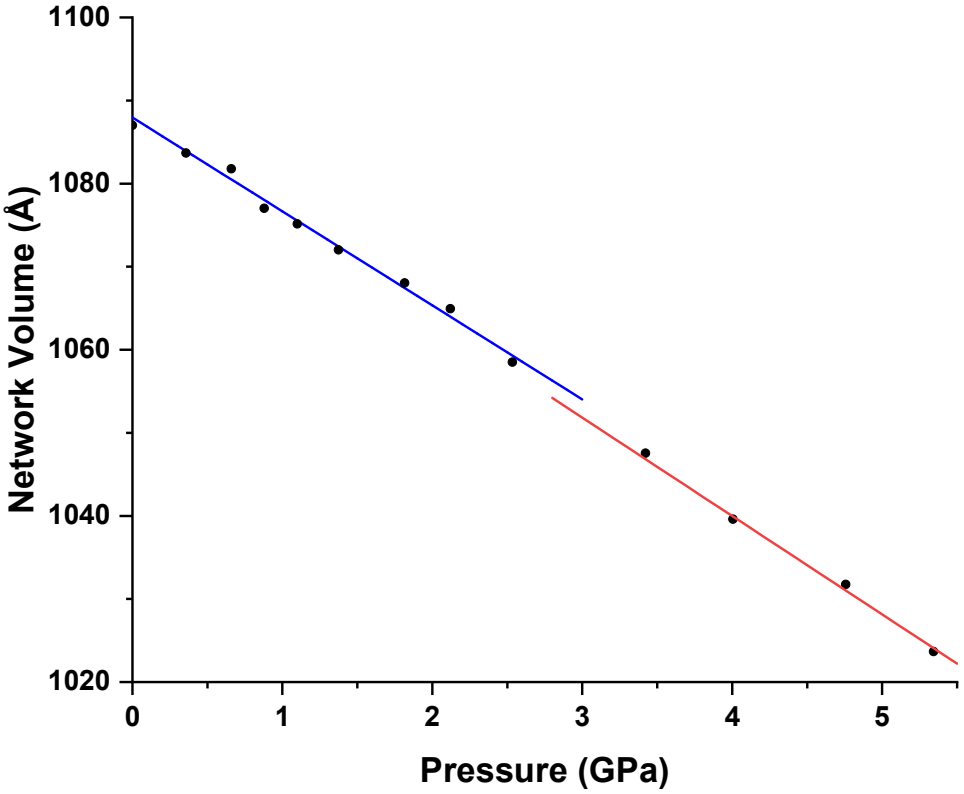

Figure S9 Comparison of network volumes across the pressure series. Blue line = linear fit to the pressure points up to 2.53 GPa. Red line = linear fit to the points above 2.54 GPa. Error bars lie within the symbols.

Supporting Tables

Table S1 Experimental data collection and refinement information for each pressure point of the series.For all structures: $C_{19}H_{14}N_3$, M_r = 284.33, monoclinic, $P2_1/n$, Z = 4. Experiments were carried out with Mo $K\alpha$ radiation using a Bruker SMART APEX2 area detector. H−atom parameters were constrained. T = 298 K. The precision of the pressure measurements is typically 0.05 GPa.

Pressure	0.00 GPa	0.36 GPa	0.66 GPa	0.88 GPa	1.10 GPa	1.37 GPa	1.82 GPa	2.12 GPa
Crystal #/Phase	1/I	2/I	2/I	1/I	2/I	2/I	1/I	2/I
Crystal data								
a, *b*, *c* (Å)	10.4887 (4), 6.9632 (2), 19.8755 (7)	10.4160 (6), 6.8137 (4), 19.690 (2)	10.3807 (7), 6.7430 (5), 19.605 (3)	10.3374 (18), 6.629 (3), 19.466 (4)	10.3045 (6), 6.5805 (4), 19.408 (2)	10.2760 (5), 6.5173 (3), 19.3323 (19)	10.2411 (11), 6.4507 (6), 19.247 (4)	10.2225 (8), 6.4019 (5), 19.203 (3)
β (°)	99.441 (2)	99.691 (6)	99.757 (8)	99.780 (8)	99.823 (6)	99.826 (5)	99.913 (13)	99.864 (8)
V (Å^3)	1431.94 (9)	1377.5 (2)	1352.5 (2)	1314.5 (6)	1296.7 (2)	1275.73 (15)	1252.5 (3)	1238.2 (2)
μ (mm^{-1})	0.08	0.08	0.09	0.09	0.09	0.09	0.09	0.09
Crystal size (mm)	0.6 × 0.4 × 0.2	0.18 × 0.14 × 0.09	0.18 × 0.14 × 0.09	0.16 × 0.14 × 0.09	0.18 × 0.14 × 0.09	0.18 × 0.14 × 0.09	0.16 × 0.14 × 0.09	0.18 × 0.14 × 0.09
Data Collection								

Absorption correction ($wR2_{bef}$, $wR2_{aft}$, max : min transmission)	0.1139, 0.0475, 0.8684	0.0501, 0.0399, 0.9005	0.0633, 0.0418, 0.9156	0.1200, 0.0476, 0.8464	0.0580, 0.0448, 0.8904	0.0528, 0.0392, 0.9029	0.0770, 0.0513, 0.8345	0.1040, 0.0459, 0.8593
T_{min}, T_{max}	0.648, 0.746	0.671, 0.745	0.683, 0.745	0.631, 0.745	0.664, 0.745	0.673, 0.745	0.622, 0.745	0.641, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8006, 2511, 1422	8076, 968, 641	6476, 918, 604	4283, 846, 479	7436, 888, 613	7309, 878, 623	7133, 900, 537	6022, 851, 558
R_{int}	0.044	0.041	0.037	0.072	0.038	0.033	0.060	0.042
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595	0.625	0.625	0.622	0.625	0.624	0.625	0.623
Refinement								
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.188, 1.06	0.037, 0.100, 1.04	0.034, 0.092, 1.03	0.049, 0.109, 1.05	0.032, 0.085, 1.03	0.033, 0.089, 1.08	0.046, 0.123, 1.06	0.039, 0.102, 1.04
Data Completeness	0.991	0.343	0.331	0.319	0.335	0.338	0.353	0.340
No. of reflections	2511	968	918	846	888	878	900	851
No. of parameters	200	199	199	194	199	199	199	194
No. of restraints	0	231	231	249	231	231	231	201
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.17	0.09, −0.08	0.07, −0.11	0.14, −0.14	0.08, −0.07	0.07, −0.08	0.13, −0.14	0.13, −0.15

Pressure	2.53 GPa	2.53 GPa	3.42 GPa	4.01 GPa	4.76 GPa	5.34 GPa	5.54 GPa	5.76 GPa	6.07 GPa
Crystal #/Phase	1/I	2/I	1/I	1/I	1/I	1/I	1/II	1/II	1/II
Crystal data									
a, *b*, *c* (Å)	10.1831 (9), 6.3399 (5), 19.111 (4)	10.1864 (8), 6.3323 (5), 19.118 (3)	10.1302 (4), 6.2215 (3), 18.9550 (18)	10.0953 (4), 6.1527 (3), 18.8502 (18)	10.0607 (6), 6.0918 (4), 18.733 (3)	10.0326 (6), 6.0553 (4), 18.571 (3)	10.0002 (5), 6.0842 (3), 18.352 (2)	9.9832 (7), 6.0752 (4), 18.290 (3)	9.9663 (7), 6.0642 (4), 18.252 (3)
β (°)	99.868 (11)	99.822 (9)	99.899 (5)	99.934 (5)	99.951 (7)	100.029 (7)	100.026 (6)	100.005 (9)	100.025 (9)
V (Å^3)	1215.6 (3)	1215.1 (3)	1176.85 (13)	1153.29 (13)	1130.84 (19)	1110.93 (19)	1099.55 (15)	1092.4 (2)	1086.3 (2)
μ (mm^{-1})	0.09	0.09	0.10	0.10	0.10	0.10	0.10	0.11	0.11
Crystal size (mm)	0.16 × 0.14 × 0.09	0.18 × 0.14 × 0.09	0.16 × 0.14 × 0.09	0.16 × 0.14 × 0.09	0.16 × 0.14 × 0.09	0.16 × 0.14 × 0.09	0.16 × 0.14 × 0.09	0.16 × 0.14 × 0.09	0.16 × 0.14 × 0.09
Data Collection									
Absorption correction (*wR2*$_{bef}$, *wR2*$_{aft}$, max : min transmission)	0.1003, 0.0528, 0.8006	0.1563, 0.0780, 0.8154	0.0569, 0.0430, 0.8822	0.0612, 0.0433, 0.9141	0.0643, 0.0459, 0.8964	0.0995, 0.0536, 0.8569	0.0585, 0.0406, 0.8887	0.1389, 0.0678, 0.9054	0.1695, 0.0802, 0.7794
T_{min}, T_{max}	0.597, 0.745	0.608, 0.745	0.658, 0.745	0.681, 0.745	0.668, 0.745	0.639, 0.745	0.662, 0.745	0.675, 0.745	0.581, 0.745

No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5150, 798, 504	6204, 865, 558	5411, 805, 558	6509, 772, 518	6290, 758, 553	6150, 748, 537	4978, 734, 545	5042, 736, 535	5236, 727, 481
R_{int}	0.055	0.050	0.035	0.043	0.037	0.043	0.032	0.037	0.057
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.613	0.623	0.622	0.624	0.625	0.623	0.624	0.624	0.625
				Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.150, 1.04	0.043, 0.112, 1.05	0.036, 0.097, 1.03	0.036, 0.096, 1.07	0.038, 0.107, 1.11	0.037, 0.102, 1.09	0.033, 0.086, 1.08	0.040, 0.116, 1.09	0.050, 0.140, 1.00
Data completeness	0.341	0.352	0.339	0.327	0.327	0.330	0.327	0.331	0.327
No. of reflections	798	865	805	772	758	748	734	736	727
No. of parameters	199	199	199	199	199	199	199	199	199
No. of restraints	231	231	231	231	231	231	231	231	231
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.16	0.14, −0.12	0.10, −0.11	0.11, −0.11	0.12, −0.15	0.12, −0.15	0.10, −0.11	0.13, −0.15	0.16, −0.14

Computer programs: *SAINT* V8.40A (Bruker, 2019), *SHELXT* 2014/5 (Sheldrick, 2014), XL (Sheldrick, 2008), Olex2 1.3 (Dolomanov *et al.*, 2009).

Table S2 Breakdown of the lattice energy of Blatter's radical 1 across the pressure series. Calculated via the PIXEL method. All energies in kJ mol^{-1}.

Collection code	Pressure (GPa)	Coulombic	Polarisation	Dispersion	Repulsion	Total
SP20030	0.00	−33.2	−19.0	−177.1	96.7	−132.6
SP20038	0.36	−42.5	−24.5	−198.7	128.2	−137.6
SP20040	0.66	−48.4	−28.0	−210.8	147.8	−139.3
SP20034	0.88	−59.1	−33.7	−230.1	180.9	−142.1
SP20041	1.10	−65.0	−36.8	−239.4	200.3	−140.9
SP20043	1.37	−72.6	−41.0	−251.5	225.3	−139.9
SP20035	1.82	−82.5	−46.7	−266.4	258.0	−137.6
SP20049	2.12	−89.3	−50.5	−275.3	280.4	−134.7
SP20037	2.53	−100.3	−56.9	−289.9	316.8	−130.4
SP20051	2.53	−101.2	−58.1	−291.0	320.7	−129.7
SP20039	3.42	−122.8	−70.4	−317.5	393.7	−117.1
SP20042	4.01	−140.0	−81.5	−337.1	452.5	−106.2
SP20044	4.76	−156.9	−94.6	−356.0	510.7	−96.8
SP20048	5.34	−172.0	−107.3	−372.1	567.5	−83.8
SP20050	5.54	−173.4	−110.3	−382.8	587.4	−79.1
SP20052	5.76	−177.8	−112.8	−388.5	607.8	−71.4
SP20053	6.07	−182.1	−115.6	−394.8	623.7	−68.8

Table S3 Total energy of the interactions in the first coordination sphere with increasing pressure. All energies are in kJ mol^{-1}.

	Interaction								
Pressure (GPa)	A&A'	B&B'	C	D	E&E'	F&F'	G&G'	H	I
0.00	−39.6	−26.3	−24.8	−16.8	−17.3	−10.2	−8.8	−7.3	−1.9
0.36	−39.2	−28.1	−25.9	−17.9	−17.8	−10.7	−8.9	−8.0	−2.3
0.66	−38.5	−28.7	−26.0	−18.5	−18.0	−10.8	−9.1	−8.6	−2.6
0.88	−37.9	−29.6	−25.8	−19.3	−17.7	−10.9	−9.5	−9.3	−2.9
1.10	−36.2	−29.9	−25.3	−19.5	−17.5	−10.7	−9.5	−9.6	−3.0
1.37	−34.7	−30.0	−24.1	−19.8	−17.3	−10.8	−9.7	−9.9	−3.2
1.82	−32.0	−29.8	−23.9	−20.1	−17.1	−10.9	−9.6	−10.2	−3.5
2.12	−29.5	−29.5	−23.0	−20.3	−16.7	−11.1	−9.4	−10.2	−3.7
2.53	−26.3	−28.9	−23.6	−20.0	−15.9	−10.9	−9.0	−10.5	−4.0
3.42	−17.9	−28.3	−21.1	−19.6	−14.2	−8.9	−8.3	−10.2	−4.3
4.01	−11.4	−26.9	−16.8	−18.6	−13.1	−8.4	−8.1	−11.0	−4.9
4.76	−4.1	−27.1	−16.0	−17.8	−12.0	−7.5	−7.7	−10.5	−4.9
5.34	2.8	−21.6	−13.7	−14.3	−13.3	−7.7	−8.0	−9.5	−4.9
5.54	6.5	−22.2	−10.9	−12.2	−15.1	−5.0	−8.6	−9.2	−5.1
5.76	9.5	−20.1	−7.8	−11.7	−15.7	−4.1	−8.3	−8.7	−5.0
6.07	11.0	−19.5	−7.3	−11.2	−16.6	−3.2	−8.2	−8.7	−5.2

Table S4 Total energy difference between the interactions in the first coordination sphere at selected pressure points. All energies are in kJ mol^{-1}.

Range (GPa)	A&A'	B&B'	C	D	E&E'	F&F'	G&G'	H	I
0.00 − 1.10	+3.4	−3.6	−0.5	−2.7	−0.2	−0.5	−0.7	−2.3	−1.1
1.10 − 5.34	+39.0	+8.3	+11.6	+5.2	+4.2	+3.0	+1.5	+0.1	−1.9
5.34 − 6.07	+8.2	+2.1	+6.4	+3.1	−3.3	+4.5	−0.2	+0.8	−0.3
0.00 − 6.07	+50.6	+6.8	+17.5	+5.6	+0.7	+7.0	0.6	−1.4	−3.3

Table S5 List of the 55 entries found in Cambridge Structural Database with the value of the hinge angle (N1-N2-C1-N3 ∠ N1-C3-C2-N3 or equivalent) on the triazinyl moiety (in degrees) given.

Refcode	Hinge Angle (°)	Refcode	Hinge Angle (°)	Refcode	Hinge Angle (°)
JUQFEI	11.179	TARXIU	3.899	OFOFIZ	2.160
DABZEN	10.811	TICMOH01	3.819	KEPWUA	2.137
BOZNAI	9.306	SIPRIS	3.752	ZUQKON	2.120
HIVRAI	8.001	HIVRAI	3.717	VUGHIR	2.083
MUPWAY	7.647	TICMOH	3.608	ZUMYUE	2.004
XIXVOS	7.267	UNEBUL	3.599	FEKVUO	1.822
LENYAH	6.534	BOPVOU	3.544	ZILYIF	1.710
OVIZAW	6.167	QIZCUZ	3.177	PENHOH	1.708
ZAGRIL	6.086	PUGJEJ	3.171	PENHOH01	1.708
KEPXAH	5.970	QIZCOT	3.109	XIXVUY	1.556
UNEBUL	5.935	OFOFIZ	2.817	UPUDIV	1.556
BIKZIH	5.906	ZUMYUE	2.765	PUWXOX	1.374
XIKPOY	5.442	VUGHIR	2.758	UNEBOF	1.069
UNEBUL	5.133	ZUQKUT	2.711	SAZXUP	0.999
XAXWAW	5.091	REFQEY	2.682	SIPRIS	0.962
ZIKBOM	5.071	NIYKUD	2.538	KEPXOV	0.923
CADSEI	4.976	DOQYOA	2.530	ZUQKIH	0.828
QABHAF	4.896	DAKPEN	2.446	QABHAF	0.807
LENYAH	4.821	XIKPUE	2.381	NECDAC	0.806
MUPWEC	4.602	BOPVOU	2.288	KEPXEL	0.785
ZUQKIH	4.403	DOQYOA	2.282	FEKWAV	0.645
QABHAF	4.180	UPUDOB	2.270	DAKPIR	0.433
KEPXIP	4.165	TARXIU	2.237	KEPXOV	0.362
LENXUA	4.068	QABHAF	2.218	CADSEI	0.156