Supporting Information: Insights into Topochemical versus Stress-Induced High-Pressure Reactivity of Azobenzene by Single Crystal X-ray Diffraction

Milo Agati[1,2], Sebastiano Romi[1,2,3,*], Samuele Fanetti[1,4], Krzysztof Radacki[5], Michael Hanfland[6], Holger Braunschweig[5], Todd B. Marder[5], Stewart J. Clark[7], Alexandra Friedrich[5,*], and Roberto Bini[1,2,4]

[1]LENS, European Laboratory for Non-linear Spectroscopy, Via N. Carrara 1, I-50019 Sesto Fiorentino, Firenze, Italy

[2]Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia 3, I-50019 Sesto Fiorentino, Italy

[3]INO-CNR, Istituto Nazionale di Ottica, Via N. Carrara 1, I-50019 Sesto Fiorentino, Firenze, Italy

[4]ICCOM-CNR, Istituto di Chimica dei Composti OrganoMetallici, Via Madonna del Piano 10, I-50019 Sesto Fiorentino, Firenze, Italy

[5]Julius-Maximilians-Universität Würzburg, Institut für Anorganische Chemie, Am Hubland, 97074 Würzburg, Germany

[6]European Synchrotron Radiation Facility, ESRF, 71 Avenue des Martyrs, CS40220, 38043 Cedex 9 Grenoble, France

[7]Department of Physics, University of Durham, Science Labs, South Road, Durham DH1 3LE, UK

1 Supporting Information

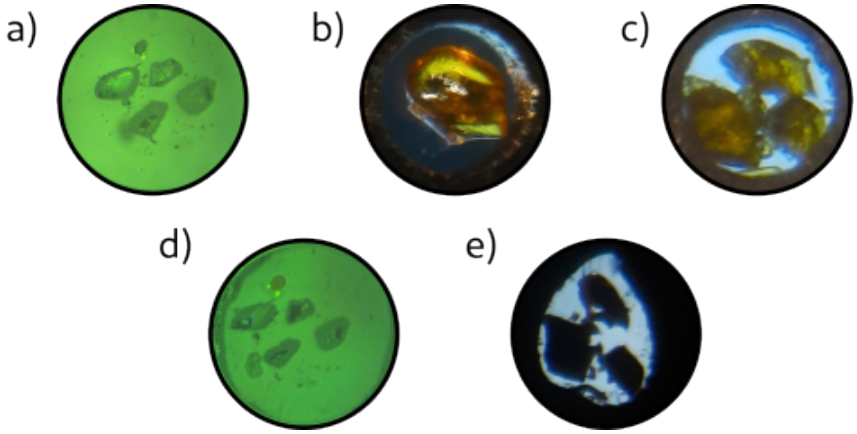

Figure S1: Photos of various samples at different experimental conditions: a) low pressure azobenzene single crystals in neon, sample employed for SC-XRD analysis; b) and c) low pressure azobenzene in argon, samples employed for FTIR analysis; d) high pressure ($\sim$ 30 GPa) azobenzene in neon; e) ambient pressure recovered product of c) after compressing the sample up to 30 GPa. As a reference, the diameter of the samples above corresponds to ca. 150 μm. The azobenzene crystals employed for the SC-XRD measurements are the bottom two crystals in samples a) and d), and were loaded together with two other single crystals of stilbene (top two crystals), ruby balls, and a small piece of gold.

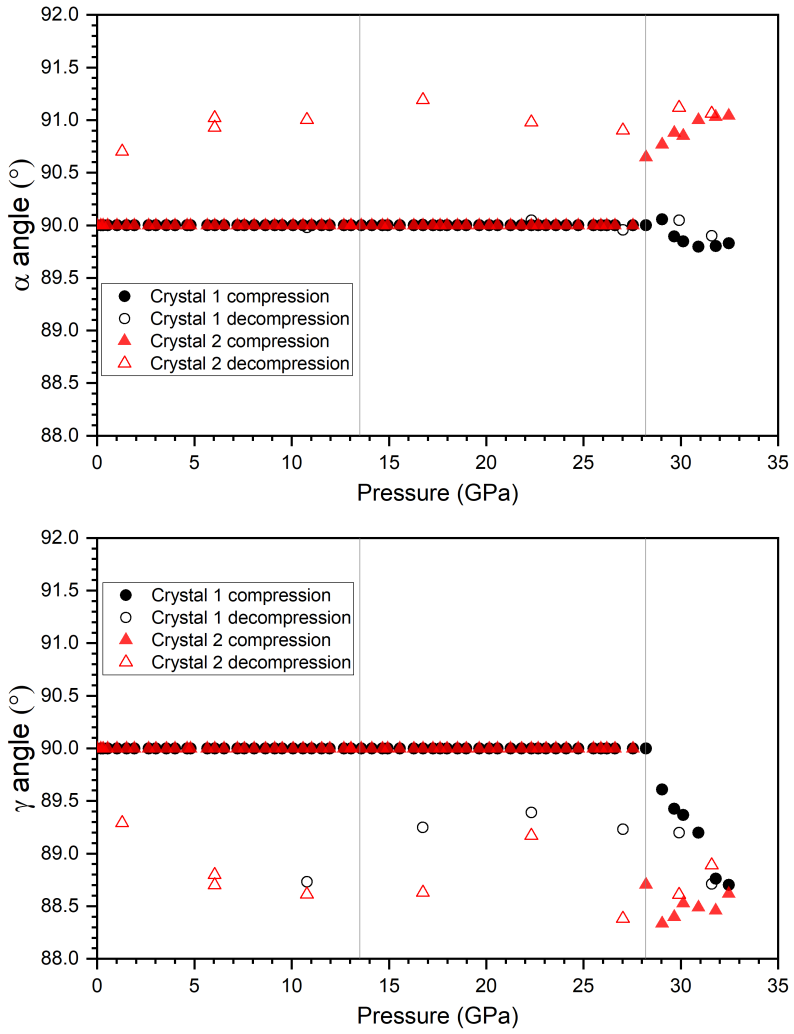

Figure S2: Pressure evolution of the α angle (top) and γ angle (bottom) of azobenzene on compression up to 32.46(6) GPa (filled symbols) and subsequent decompression (empty symbols). The two vertical lines just above 13 and 28 GPa demarcate the beginning of the high-pressure phase and polymer phase, respectively. While the angles remain 90° across the phase transition at 13 GPa, they deviate slightly from 90° in the polymer phase above 28 GPa and on decompression.

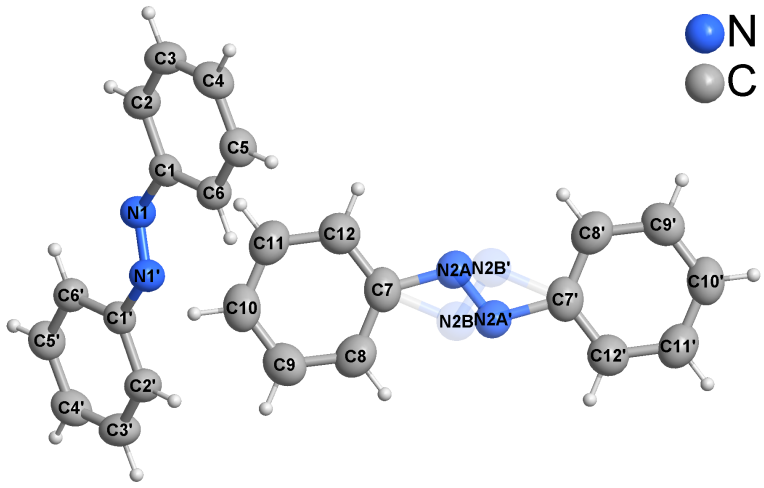

Figure S3: The solid-state molecular structure and atom labeling of the two symmetry-independent molecules A (left) and B (right) of azobenzene, determined by single-crystal X-ray diffraction at 298 K. All ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Both molecules have inversion symmetry. One of the molecules (B) shows a pedal-motion-type disorder and the site-occupation factor is expressed by the opacity of the nitrogen atom.

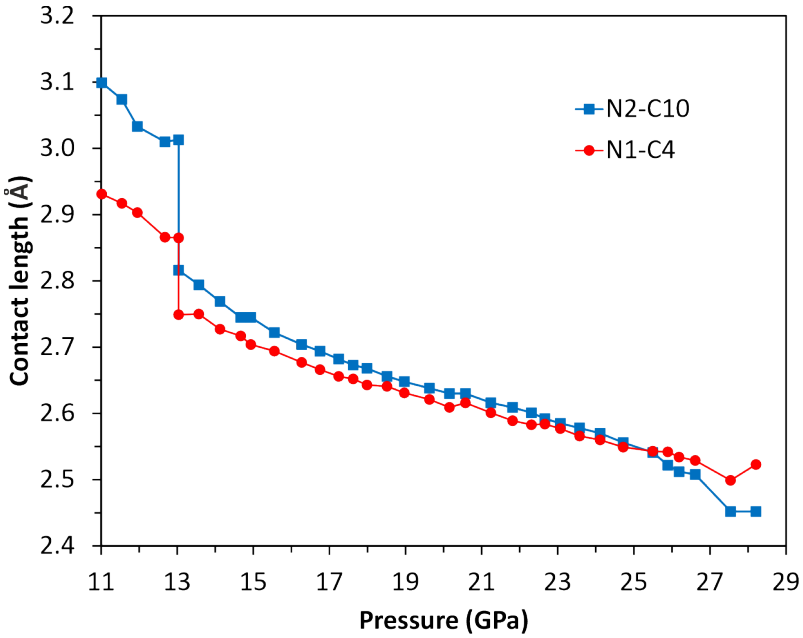

Figure S4: Short intermolecular C· · ·N contacts in the azobenzene HP phase as a function of pressure from 11 GPa up to the highest pressure (∼28 GPa) at which the structure was refined.

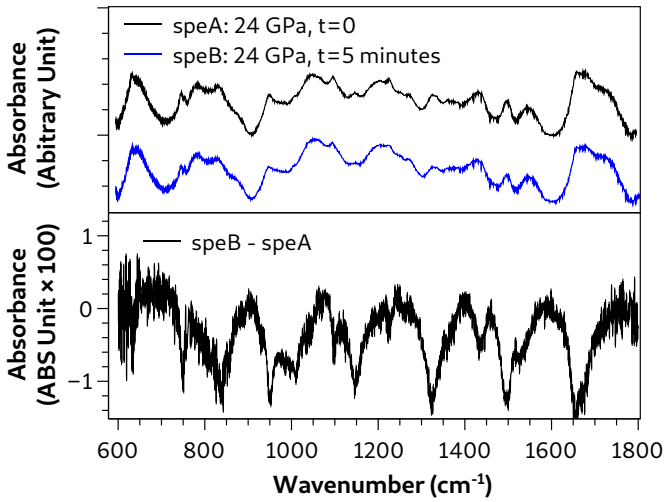

Figure S5: Upper panel: Infrared spectra of azobenzene compressed using argon as PTM in the 700-1700 cm^{-1} spectral region: the two spectra (black and blue traces) were acquired at 24 GPa separated by 5 minutes. Lower panel: difference spectrum calculated subtracting the intensities of the aforementioned spectra, the intense negative bands are due to the consumption of the reagent due to the reaction.

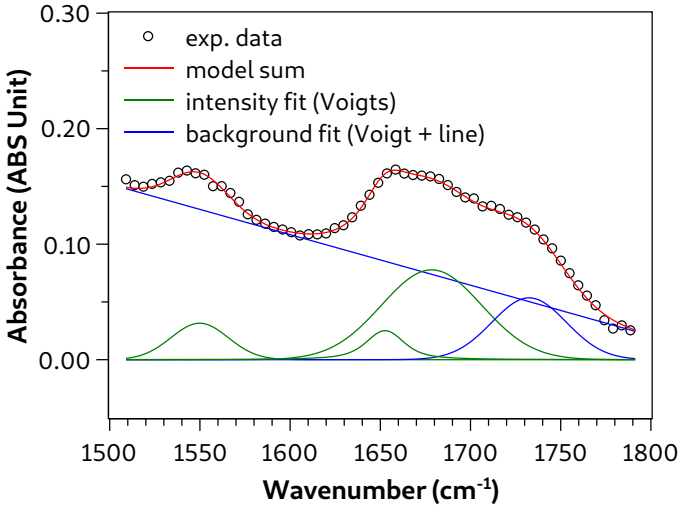

Figure S6: Example of the area determination of the vibrational bands performed to calculate the azobenzene reaction kinetics. The vibrational bands shown were chosen to measure the absorbance variation over time, as they are intense and not overlapped with other absorptions. The example provided depicts a spectral window of the azobenzene infrared spectra compressed with argon measured at 24 GPa. For the sake of clarity, only 1/20 of the experimental data have been reported as black empty dots. The fit was performed employing three Voigt functions to fit the experimental data (green curves in the figure). An additional Voigt function was employed as a background, together with a straight line (blue curves). The fit is shown as a red trace. To minimize the fit error, subsequent spectra were fitted varying only the intensity of the Voigt functions and the intercept of the straight line, maintaining fixed all the other parameters (center, shape, gwidth of the Voigts, slope of the straight line).

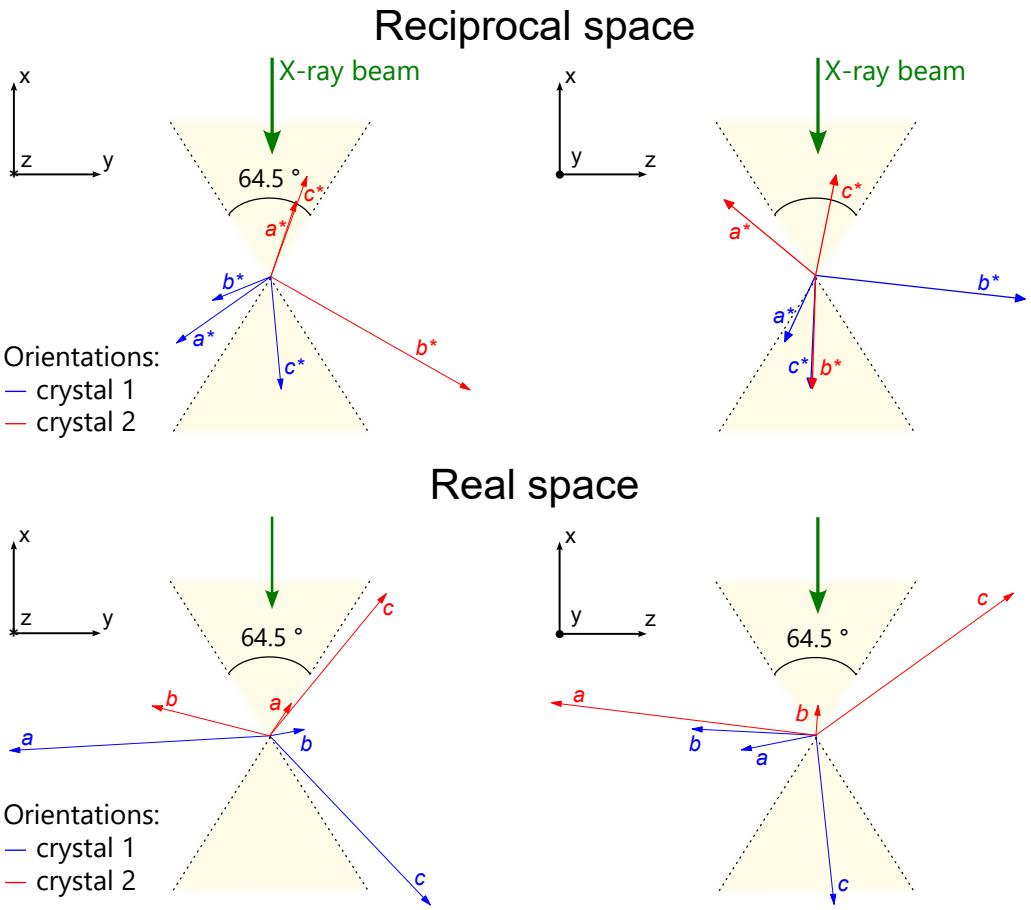

Figure S7: Unit cell axes in the reciprocal (upper images) and real space (bottom images) of the two azobenzene crystals loaded in the DAC. In the employed orthogonal system, the X-ray beam direction aligns with the x axis and the crystals inside the DAC lie on the yz plane at $\omega = 0$. The coordinates for all the vectors in the xyz frame of reference are reported in Table S14. The vectors for crystal 1 (blue) and crystal 2 (red) are reported as projections onto the xy (left) and xz planes (right). The unit cell metric of crystal 2 is rotated by 161.9° around the vector (0.74 -0.28 -0.61) in reciprocal space or [0.46 -0.88 -0.13] in direct space with respect to that of crystal 1. The 0.5° ω-scanning across the DAC's aperture (64.5°, represented by yellow shaded areas) ensures that most of the reciprocal space gets probed.

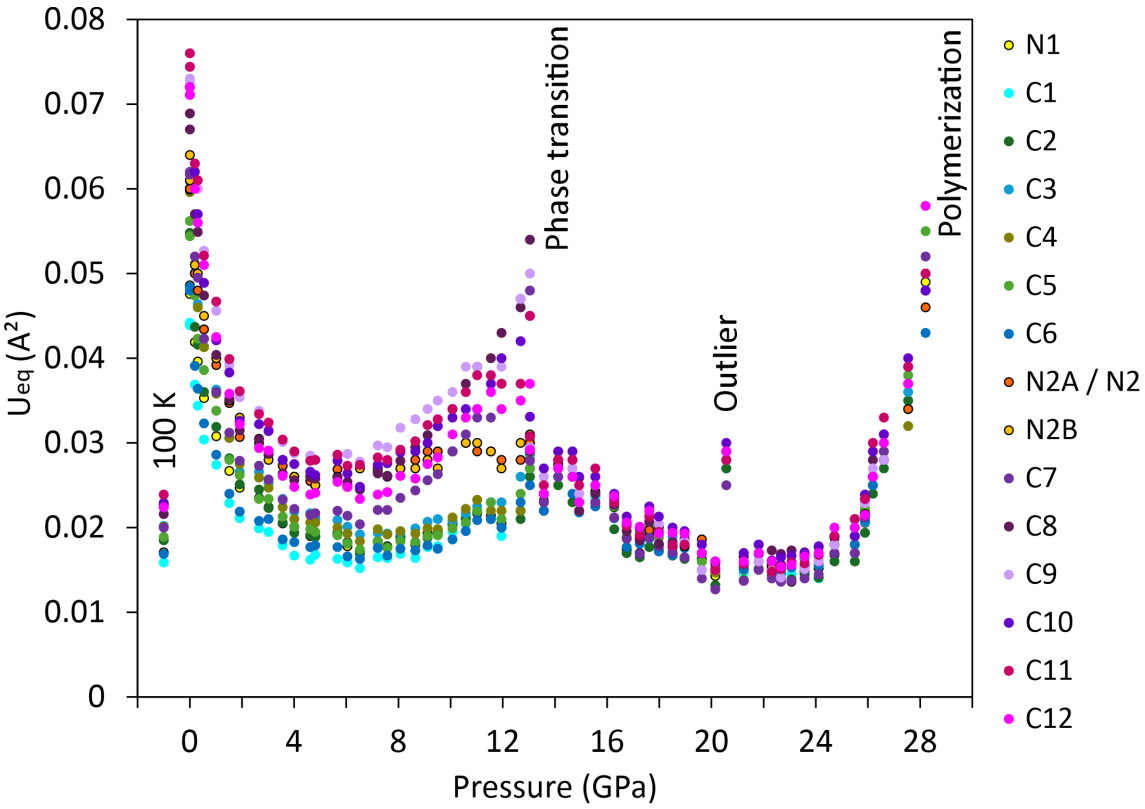

Figure S8: Plot of the equivalent isotropic displacement parameters of all the atoms as a function of pressure. At ambient pressure, data from the synchrotron experiment in the DAC and from in-house measurements on a free crystal are included in the plot and they produce very similar values. The U_{eq} at 100 K at ambient pressure are also plotted for comparison. A decrease of all the U_{eq} with increasing pressure is expected due to the density increase of the crystal. Before the phase transition, molecule B (atoms N2A/N2B, C7–C12) has larger values of U_{eq} than molecule A and its behavior closely resembles the pedal motion disorder (Figure 4 of the main text). Just before the phase transition at 13 GPa, the isotropic displacement parameters first increase and then continue to decrease, with the U_{eq} of the molecule B that have an abrupt drop in value. Just before the polymerization threshold at 28 GPa, another rapid increase is observed which is indicative of a reactive state.

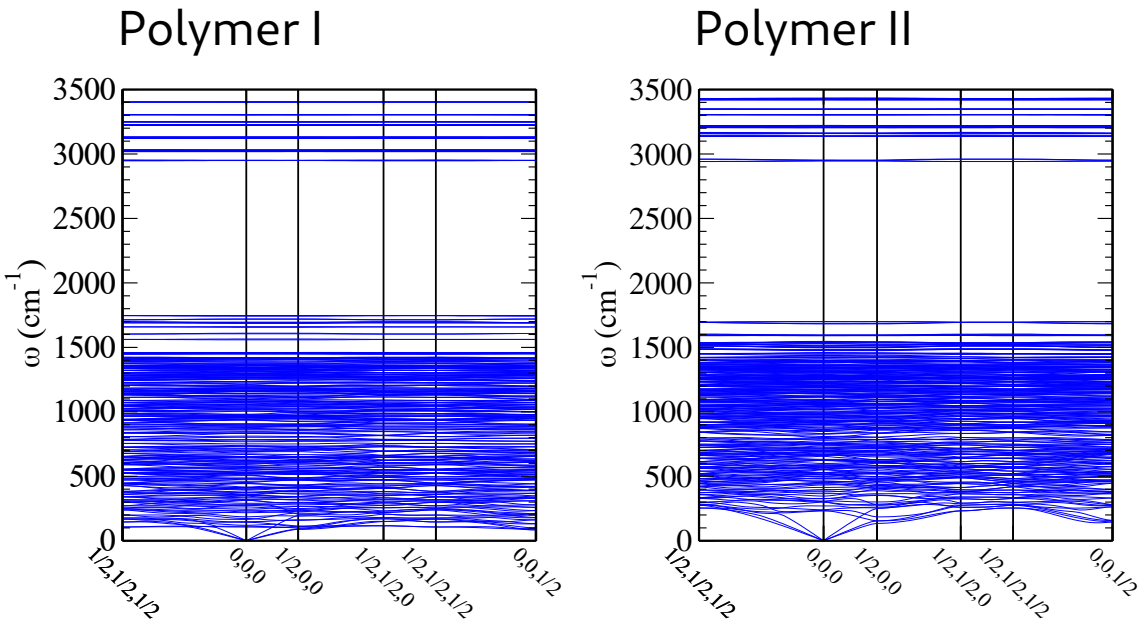

Figure S9: Calculated phonon dispersion curves at 30 GPa for polyazobenzene "polymer I" and "polymer II", respectively. Both structures have no imaginary vibrational modes, ensuring that the calculated geometries are in a local or global energy minimum.

Table S1. Single-crystal X-ray diffraction data and structure refinements of **azobenzene** at 100 K and 298 K and ambient pressure.

CCDC	2336566	2336607
Empirical formula	$C_{12}H_{10}N_2$	$C_{12}H_{10}N_2$
M_r / g·mol^{-1}	182.22	182.22
T / K	100(2)	298(2)
Radiation, λ / Å	Cu-K$_\alpha$, 1.54184	Cu-K$_\alpha$, 1.54184
Crystal size/mm^3	0.04×0.13×0.21	0.27×0.17×0.08
Crystal color, habit	orange plate	orange plate
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / Å	14.9840(4)	15.2269(4)
b / Å	5.69830(10)	5.78897(13)
c / Å	12.0341(3)	12.1743(3)
α / °	90	90
β / °	112.452(3)	112.455(3)
γ / °	90	90
Volume / Å^3	949.63(4)	991.78(5)
Z	4	4
ρ_{calc} / g·cm^{-3}	1.275	1.220
μ / mm^{-1}	0.603	0.577
F(000)	384	384
θ range / °	3.191 – 74.476	3.140 – 74.423
Reflections collected	10160	10691
Unique reflections	1920	1997
Parameters / restraints	168 / 0	138 / 36
GooF on F^2	1.060	1.056
R_1 [$I \geq 2\sigma$ (I)]	0.0335	0.0366
wR_2 [all data]	0.0856	0.1014
Max. / min. residual electron density/ e·Å^{-3}	0.244 / –0.164	0.125 / –0.112
Disorder / %	0 (< 3)	17(2)

Table S2: Single-crystal X-ray diffraction data and structure refinements of monoclinic **azobenzene**, $C_{12}H_{10}N_2$ (space group $P2_1/c$, $Z = 4$, Formula weight: 182.22 g·mol^{-1}, $F(000) = 384$, $T = 298(2)$ K). Combined refinement of the data sets of two crystals if not otherwise stated.

Pressure / GPa	0.0001	0.19(2)	0.31(2)	0.54(2)	1.02(2)
CCDC number	2336562	2336563	2336564	2336565	2336588
λ / Å, radiation type			0.4100, synchrotron		
a / Å	15.223(14)	15.088(13)	14.998(11)	14.890(10)	14.710(10)
b / Å	5.7851(5)	5.7289(4)	5.6940(3)	5.6496(3)	5.5772(3)
c / Å	12.174(4)	12.059(4)	11.992(3)	11.905(3)	11.759(3)
α / °	90	90	90	90	90
β / °	112.45(7)	112.42(7)	112.43(6)	112.44(5)	112.39(5)
γ / °	90	90	90	90	90
Volume / Å^3	990.9(11)	963.6(10)	946.6(9)	925.6(7)	892.0(7)
ρ_{calc} / g·cm^{-3}	1.221	1.256	1.279	1.308	1.357
μ / mm^{-1}	0.033	0.034	0.035	0.036	0.037
θ range / °	1.930 – 21.468	1.949 – 21.261	1.960 – 21.393	1.974 – 21.427	1.999 – 20.999
Unique reflections	4002	4279	4294	4254	4288
Unique or all reflections [I>2σ(I)]	2663	2992	3112	3205	3223
Parameters / restraints	139 / 96	138 / 96	138 / 96	138 / 96	138 / 96
GooF on F^2	1.045	1.051	1.078	1.058	1.077
R_1, wR_2 [I>2σ(I)]	$R_1 = 0.0609$, $wR_2 = 0.1434$	$R_1 = 0.0620$, $wR_2 = 0.1587$	$R_1 = 0.0591$, $wR_2 = 0.1652$	$R_1 = 0.0579$, $wR_2 = 0.1579$	$R_1 = 0.0554$, $wR_2 = 0.1580$
R_1, wR_2 (all data)	$R_1 = 0.0935$, $wR_2 = 0.1625$	$R_1 = 0.0862$, $wR_2 = 0.1783$	$R_1 = 0.0795$, $wR_2 = 0.1784$	$R_1 = 0.0746$, $wR_2 = 0.1700$	$R_1 = 0.0718$, $wR_2 = 0.1688$
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.178 / –0.151	0.201 / –0.185	0.184 / –0.162	0.224 / –0.181	0.265 / –0.185
Disorder / %	15(2)	14(2)	12(2)	10(2)	8(1)

Table S2 (continued).

Pressure / GPa	1.51(2)	1.91(2)	2.65(2)	3.02(2)	3.56(4)
CCDC number	2336589	2336590	2336608	2336609	2336610
λ / Å, radiation type			0.4100, synchrotron		
a / Å	14.547(13)	14.455(9)	14.296(10)	14.222(8)	14.122(8)
b / Å	5.5258(3)	5.4916(2)	5.4336(3)	5.4119(2)	5.37914(19)
c / Å	11.659(4)	11.591(3)	11.476(3)	11.430(2)	11.365(2)
α / °	90	90	90	90	90
β / °	112.40(7)	112.41(5)	112.42(6)	112.42(5)	112.44(4)
γ / °	90	90	90	90	90
Volume / Å^3	866.5(9)	850.6(6)	824.1(7)	813.2(6)	797.9(5)
ρ_{calc} / g·cm^{-3}	1.397	1.423	1.469	1.488	1.517
μ / mm^{-1}	0.038	0.039	0.040	0.040	0.041
θ range / °	2.016 – 21.065	2.313 – 21.167	2.048 – 21.310	2.056 – 21.400	2.068 – 21.34
Unique reflections	4050	3995	3847	3772	3757
Unique or all reflections [I>2σ(I)]	3314	3372	3201	3202	3261
Parameters / restraints	138 / 96	138 / 96	138 / 6	138 / 6	138 / 6
GooF on F^2	1.071	1.059	1.056	1.064	1.066
R_1, wR_2 [I>2σ(I)]	$R_1 = 0.0586$, $wR_2 = 0.1621$	$R_1 = 0.0559$, $wR_2 = 0.1582$	$R_1 = 0.0593$, $wR_2 = 0.1644$	$R_1 = 0.0635$, $wR_2 = 0.1818$	$R_1 = 0.0533$, $wR_2 = 0.1465$
R_1, wR_2 (all data)	$R_1 = 0.0687$, $wR_2 = 0.1708$	$R_1 = 0.0644$, $wR_2 = 0.1660$	$R_1 = 0.0685$, $wR_2 = 0.1724$	$R_1 = 0.0706$, $wR_2 = 0.1891$	$R_1 = 0.0598$, $wR_2 = 0.1522$
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.257 / –0.199	0.384 / –0.235	0.318 / –0.225	0.470 / –0.260	0.354 / –0.213
Disorder / %	7(1)	5(1)	4.5(8)	4.7(8)	4.4(8)

Table S2 (continued).

Pressure / GPa	4.00(2)	4.62(5)	4.80(2)	5.66(4)	6.04(4)
CCDC number	2336611	2336612	2336613	2336614	2336615
λ / Å, radiation type			0.4100, synchrotron		
a / Å	14.037(7)	13.935(7)	13.912(7)	13.808(7)	13.767(7)
b / Å	5.35545(18)	5.32579(17)	5.32080(18)	5.29256(18)	5.27967(16)
c / Å	11.315(2)	11.253(2)	11.243(2)	11.185(2)	11.158(2)
α / °	90	90	90	90	90
β / °	112.49(4)	112.51(4)	112.55(4)	112.58(4)	112.60(4)
γ / °	90	90	90	90	90
Volume / Å^3	785.9(5)	771.5(5)	768.6(5)	754.7(5)	748.8(4)
ρ_{calc} / g·cm^{-3}	1.540	1.569	1.575	1.604	1.616
μ / mm^{-1}	0.042	0.043	0.043	0.044	0.044
θ range / °	2.077 – 21.401	2.089 – 21.527	2.090 – 21.549	2.101 – 21.670	2.106 – 21.435
Unique reflections	3710	3676	3651	3600	3591
Unique or all reflections [I>2σ(I)]	3235	3207	3206	3151	3134
Parameters / restraints	138 / 6	138 / 6	138 / 6	138 / 6	138 / 6
GooF on F^2	1.064	1.089	1.084	1.068	1.077
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0516, wR_2 = 0.1460	R_1 = 0.0502, wR_2 = 0.1428	R_1 = 0.0505, wR_2 = 0.1402	R_1 = 0.0509, wR_2 = 0.1433	R_1 = 0.0502, wR_2 = 0.1399
R_1, wR_2 (all data)	R_1 = 0.0573, wR_2 = 0.1510	R_1 = 0.0558, wR_2 = 0.1474	R_1 = 0.0557, wR_2 = 0.1445	R_1 = 0.0564, wR_2 = 0.1479	R_1 = 0.0559, wR_2 = 0.1442
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.388 / –0.208	0.410 / –0.194	0.385 / –0.185	0.317 / –0.245	0.398 / –0.180
Disorder / %	4.1(9)	4.7(9)	4.9(9)	5.2(9)	6(1)

Table S2 (continued).

Pressure / GPa	6.52(5)	7.21(2)	7.57(3)	8.07(6)	8.65(7)
CCDC number	2336616	2336617	2336618	2336619	2336620
λ / Å, radiation type			0.4100, synchrotron		
a / Å	13.693(8)	13.618(6)	13.573(7)	13.529(8)	13.462(8)
b / Å	5.26420(19)	5.24215(16)	5.23258(19)	5.2210(2)	5.20920(19)
c / Å	11.124(2)	11.0763(19)	11.057(2)	11.031(2)	11.001(2)
α / °	90	90	90	90	90
β / °	112.65(5)	112.67(4)	112.71(4)	112.74(4)	112.81(5)
γ / °	90	90	90	90	90
Volume / Å^3	740.0(5)	729.6(4)	724.4(4)	718.6(5)	711.1(5)
ρ_{calc} / g·cm^{-3}	1.636	1.659	1.671	1.684	1.702
μ / mm^{-1}	0.044	0.045	0.045	0.046	0.046
θ range / °	2.113 – 21.335	2.122 – 21.430	2.126 – 21.471	2.310 – 21.522	2.136 – 21.576
Unique reflections	3440	3392	3384	3401	3383
Unique or all reflections [I>2σ(I)]	3013	2961	2959	2937	2934
Parameters / restraints	138 / 6	138 / 6	138 / 6	138 / 6	138 / 96
GooF on F^2	1.057	1.069	1.076	1.091	1.076
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0510, wR_2 = 0.1403	R_1 = 0.0517, wR_2 = 0.1414	R_1 = 0.0535, wR_2 = 0.1511	R_1 = 0.0559, wR_2 = 0.1561	R_1 = 0.0624, wR_2 = 0.1724
R_1, wR_2 (all data)	R_1 = 0.0562, wR_2 = 0.1442	R_1 = 0.0575, wR_2 = 0.1456	R_1 = 0.0585, wR_2 = 0.1549	R_1 = 0.0623, wR_2 = 0.1612	R_1 = 0.0687, wR_2 = 0.1783
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.424 / –0.233	0.405 / –0.220	0.487 / –0.244	0.482 / –0.251	0.488 / –0.293
Disorder / %	8(1)	9(1)	9(1)	10(1)	12(2)

Table S2 (continued).

Pressure / GPa	9.12(5)	9.51(4)	10.07(8)	10.58(8)	11.02(2)
CCDC number	2336621	2336622	2336567	2336568	2336569
λ / Å, radiation type			0.4100, synchrotron		
a / Å	13.420(8)	13.377(7)	13.319(9)	13.261(8)	13.220(8)
b / Å	5.2012(2)	5.19477(16)	5.1800(2)	5.1782(2)	5.1750(2)
c / Å	10.982(2)	10.966(2)	10.928(3)	10.915(2)	10.904(3)
α / °	90	90	90	90	90
β / °	112.85(5)	112.89(4)	112.91(5)	113.01(5)	113.08(5)
γ / °	90	90	90	90	90
Volume / Å^3	706.4(5)	702.0(4)	694.4(6)	689.9(5)	686.3(5)
ρ_{calc} / g·cm^{-3}	1.713	1.724	1.743	1.754	1.764
μ / mm^{-1}	0.047	0.047	0.047	0.048	0.048
θ range / °	2.140 – 21.613	2.143 – 21.643	2.151 – 21.711	2.153 – 21.642	2.342 – 21.659
Unique reflections	3336	3333	3233	3215	3125
Unique or all reflections [I>2σ(I)]	2920	2920	2778	2740	2534
Parameters / restraints	138 / 96	138 / 6	138 / 6	138 / 6	138 / 12
GooF on F^2	1.070	1.052	1.066	1.068	1.070
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0584, wR_2 = 0.1585	R_1 = 0.0601, wR_2 = 0.1617	R_1 = 0.0644, wR_2 = 0.1757	R_1 = 0.0684, wR_2 = 0.1874	R_1 = 0.0706, wR_2 = 0.1966
R_1, wR_2 (all data)	R_1 = 0.0647, wR_2 = 0.1637	R_1 = 0.0664, wR_2 = 0.1670	R_1 = 0.0721, wR_2 = 0.1822	R_1 = 0.0763, wR_2 = 0.1941	R_1 = 0.0816, wR_2 = 0.2064
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.510 / –0.306	0.521 / –0.340	0.568 / –0.366	0.530 / –0.411	0.495 / –0.396
Disorder / %	14(2)	16(2)	20(2)	23(2)	26(2)

Table S2 (continued).

Pressure / GPa	11.54(4)	11.95(7)	12.68(5) [a]	13.04(6) [a]	13.04(6) [a,b]
CCDC number	2336570	2336571	2336572	2336573	2336574
λ / Å, radiation type			0.4100, synchrotron		
a / Å	13.162(11)	13.111(17)	13.08(2)	13.08(3)	12.452(8)
b / Å	5.1734(3)	5.1676(4)	5.1502(8)	5.1368(12)	5.4749(6)
c / Å	10.885(3)	10.860(5)	10.814(7)	10.777(9)	10.723(4)
α / °	90	90	90	90	90
β / °	113.15(7)	113.15(10)	113.12(14)	112.98(19)	114.90(7)
γ / °	90	90	90	90	90
Volume / Å^3	681.5(7)	676.5(10)	670.0(14)	666.4(19)	663.0(6)
ρ_{calc} / g·cm^{-3}	1.776	1.789	1.806	1.816	1.825
μ / mm^{-1}	0.048	0.049	0.049	0.049	0.050
θ range / °	2.159 – 21.675	2.164 – 21.708	2.173 – 21.790	2.181 – 20.401	2.385 – 20.722
Unique reflections	2908	2814	777	783	1019
Unique or all reflections [I>2σ(I)]	2206	2017	559	513	638
Parameters / restraints	138 / 12	138 / 102	137 / 102	137 / 102	127 / 84
GooF on F^2	1.103	1.142	1.344	1.180	0.954
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0731, wR_2 = 0.2059	R_1 = 0.0765, wR_2 = 0.2242	R_1 = 0.0902, wR_2 = 0.2457	R_1 = 0.1062, wR_2 = 0.2887	R_1 = 0.0684, wR_2 = 0.1727
R_1, wR_2 (all data)	R_1 = 0.0888, wR_2 = 0.2192	R_1 = 0.0966, wR_2 = 0.2379	R_1 = 0.1132, wR_2 = 0.2604	R_1 = 0.1379, wR_2 = 0.3108	R_1 = 0.0987, wR_2 = 0.1857
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.420 / –0.367	0.451 / –0.372	0.289 / –0.220	0.282 / –0.281	0.232 / –0.240
Disorder / %	30(2)	33(2)	33(2)	33(2)	0

[a] Refinement of a single data set of 1 crystal only. [b] Structure refinement of the high-pressure phase.

Table S2 (continued).

Pressure / GPa	13.57(4)	14.12(10)	14.67(2)	14.93(3)	15.55(7)
CCDC number	2336575	2336576	2336577	2336578	2336579
λ / Å, radiation type			0.4100, synchrotron		
a / Å	12.38(2)	12.32(2)	12.24(2)	12.230(15)	12.162(16)
b / Å	5.4468(7)	5.4498(7)	5.4747(6)	5.4789(4)	5.4949(4)
c / Å	10.725(6)	10.697(8)	10.639(7)	10.620(6)	10.602(6)
α / °	90	90	90	90	90
β / °	114.53(13)	114.60(15)	114.84(14)	114.88(11)	115.15(11)
γ / °	90	90	90	90	90
Volume / Å^3	657.7(13)	653.0(14)	647.1(13)	645.5(10)	641.4(10)
ρ_{calc} / g·cm^{-3}	1.840	1.853	1.870	1.875	1.887
μ / mm^{-1}	0.050	0.050	0.051	0.051	0.051
θ range / °	2.191 – 21.372	2.397 – 21.395	2.209 – 21.408	2.213 – 21.420	2.216 – 21.412
Unique reflections	2814	2541	2408	2764	2608
Unique or all reflections [I>2σ(I)]	2063	1843	1818	2213	2079
Parameters / restraints	128 / 84	128 / 84	128 / 84	128 / 84	128 / 84
GooF on F^2	1.096	1.025	1.116	1.116	1.138
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0819, wR_2 = 0.2257	R_1 = 0.0810, wR_2 = 0.2295	R_1 = 0.0907, wR_2 = 0.2564	R_1 = 0.0847, wR_2 = 0.2452	R_1 = 0.0817, wR_2 = 0.2356
R_1, wR_2 (all data)	R_1 = 0.1049, wR_2 = 0.2412	R_1 = 0.0994, wR_2 = 0.2453	R_1 = 0.1057, wR_2 = 0.2777	R_1 = 0.0946, wR_2 = 0.2566	R_1 = 0.0925, wR_2 = 0.2476
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.397 / –0.275	0.421 / –0.304	0.421 / –0.297	0.497 / –0.280	0.388 / –0.282
Disorder / %	0	0	0	0	0

Table S2 (continued).

Pressure / GPa	16.27(8)	16.75(10)	17.25(8)	17.62(7)	17.98(4)
CCDC number	2336580	2336581	2336582	2336583	2336584
λ / Å, radiation type			0.4100, synchrotron		
a / Å	12.096(15)	12.064(14)	12.013(14)	11.979(13)	11.945(14)
b / Å	5.5053(4)	5.5054(4)	5.5124(4)	5.5148(4)	5.5180(4)
c / Å	10.570(5)	10.545(5)	10.539(5)	10.530(5)	10.526(5)
α / °	90	90	90	90	90
β / °	115.42(11)	115.46(10)	115.68(10)	115.74(10)	115.90(11)
γ / °	90	90	90	90	90
Volume / Å^3	635.8(10)	632.3(9)	629.0(9)	626.6(9)	624.1(9)
ρ_{calc} / g·cm^{-3}	1.904	1.914	1.924	1.932	1.939
μ / mm^{-1}	0.052	0.052	0.052	0.053	0.053
θ range / °	2.223 – 21.432	2.228 – 21.460	2.230 – 21.457	2.231 – 21.463	2.232 – 21.465
Unique reflections	2557	2591	2693	2667	2636
Unique or all reflections [I>2σ(I)]	2049	2118	2205	2173	2159
Parameters / restraints	128 / 84	128 / 84	128 / 84	128 / 84	128 / 84
GooF on F^2	1.123	1.140	1.105	1.102	1.132
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0687, wR_2 = 0.2026	R_1 = 0.0642, wR_2 = 0.1906	R_1 = 0.0603, wR_2 = 0.1745	R_1 = 0.0624, wR_2 = 0.1788	R_1 = 0.0628, wR_2 = 0.1857
R_1, wR_2 (all data)	R_1 = 0.0778, wR_2 = 0.2122	R_1 = 0.0723, wR_2 = 0.1988	R_1 = 0.0679, wR_2 = 0.1817	R_1 = 0.0719, wR_2 = 0.1867	R_1 = 0.0711, wR_2 = 0.1949
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.341 / –0.253	0.326 / –0.260	0.350 / –0.258	0.288 / –0.240	0.335 / –0.254
Disorder / %	0	0	0	0	0

Table S2 (continued).

Pressure / GPa	18.51(7)	18.97(4)	19.63(9)	20.15(4)	20.57(5)
CCDC number	2336585	2336586	2336587	2336591	2336592
λ / Å, radiation type			0.4100, synchrotron		
a / Å	11.918(13)	11.882(11)	11.834(10)	11.814(10)	11.789(11)
b / Å	5.5121(3)	5.5101(3)	5.5100(3)	5.5065(2)	5.5068(3)
c / Å	10.502(5)	10.490(4)	10.478(4)	10.466(4)	10.461(5)
α / °	90	90	90	90	90
β / °	115.90(9)	116.01(9)	116.14(7)	116.17(8)	116.23(9)
γ / °	90	90	90	90	90
Volume / Å^3	620.6(8)	617.3(8)	613.4(7)	611.1(7)	609.2(8)
ρ_{calc} / g·cm^{-3}	1.950	1.961	1.973	1.981	1.987
μ / mm^{-1}	0.053	0.053	0.054	0.054	0.054
θ range / °	2.237 – 21.502	2.240 – 21.522	2.242 – 21.539	2.245 – 21.560	2.246 – 21.566
Unique reflections	2903	2831	2815	2829	2583
Unique or all reflections [I>2σ(I)]	2484	2423	2376	2393	1922
Parameters / restraints	128 / 84	128 / 84	128 / 84	128 / 84	128 / 84
GooF on F^2	1.119	1.097	1.115	1.103	1.530
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0606, wR_2 = 0.1731	R_1 = 0.0628, wR_2 = 0.1789	R_1 = 0.0722, wR_2 = 0.2069	R_1 = 0.0662, wR_2 = 0.1912	R_1 = 0.1256, wR_2 = 0.3305
R_1, wR_2 (all data)	R_1 = 0.0666, wR_2 = 0.1788	R_1 = 0.0686, wR_2 = 0.1848	R_1 = 0.0783, wR_2 = 0.2130	R_1 = 0.0728, wR_2 = 0.1983	R_1 = 0.1457, wR_2 = 0.3640
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.369 / –0.241	0.333 / –0.338	0.347 / –0.440	0.389 / –0.329	0.431 / –0.457
Disorder / %	0	0	0	0	0

Table S2 (continued).

Pressure / GPa	21.24(6)	21.81(6)	22.31(4)	22.66(5)	23.07(3)
CCDC number	2336593	2336594	2336595	2336596	2336597
λ / Å, radiation type			0.4100, synchrotron		
a / Å	11.750(9)	11.719(9)	11.694(10)	11.671(10)	11.660(10)
b / Å	5.5030(2)	5.5018(2)	5.4975(2)	5.4939(2)	5.4890(2)
c / Å	10.447(4)	10.440(4)	10.427(4)	10.418(4)	10.407(4)
α / °	90	90	90	90	90
β / °	116.33(7)	116.41(7)	116.44(8)	116.47(8)	116.47(8)
γ / °	90	90	90	90	90
Volume / Å^3	605.4(6)	602.9(6)	600.2(7)	598.0(7)	596.2(7)
ρ_{calc} / g·cm^{-3}	1.999	2.008	2.016	2.024	2.030
μ / mm^{-1}	0.054	0.055	0.055	0.055	0.055
θ range / °	2.249 – 21.591	2.251 – 21.604	2.254 – 21.627	2.255 – 21.644	2.258 – 21.668
Unique reflections	2730	2695	2649	2848	2805
Unique or all reflections [I>2σ(I)]	2256	2195	2132	2381	2309
Parameters / restraints	128 / 84	128 / 84	128 / 84	128 / 84	128 / 84
GooF on F^2	1.122	1.162	1.113	1.117	1.117
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0757, wR_2 = 0.2277	R_1 = 0.0769, wR_2 = 0.2354	R_1 = 0.0693, wR_2 = 0.2042	R_1 = 0.0658, wR_2 = 0.2016	R_1 = 0.0687, wR_2 = 0.2058
R_1, wR_2 (all data)	R_1 = 0.0824, wR_2 = 0.2360	R_1 = 0.0852, wR_2 = 0.2470	R_1 = 0.0791, wR_2 = 0.2151	R_1 = 0.0732, wR_2 = 0.2116	R_1 = 0.0764, wR_2 = 0.2143
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.560 / –0.483	0.566 / –0.432	0.437 / –0.369	0.460 / –0.445	0.519 / –0.319
Disorder / %	0	0	0	0	0

Table S2 (continued).

Pressure / GPa	23.57(4)	24.11(4)	24.72(7)	25.50(7)	25.89(3)
CCDC number	2336598	2336599	2336600	2336601	2336602
λ / Å, radiation type			0.4100, synchrotron		
a / Å	11.626(10)	11.592(9)	11.550(11)	11.513(11)	11.47(2)
b / Å	5.4869(2)	5.4837(2)	5.4830(3)	5.4804(3)	5.4795(5)
c / Å	10.397(4)	10.385(4)	10.377(4)	10.357(4)	10.352(8)
α / °	90	90	90	90	90
β / °	116.56(8)	116.64(7)	116.73(8)	116.78(9)	116.77(17)
γ / °	90	90	90	90	90
Volume / Å^3	593.2(7)	590.1(6)	586.9(7)	583.4(7)	580.7(14)
ρ_{calc} / g·cm^{-3}	2.040	2.051	2.062	2.075	2.084
μ / mm^{-1}	0.055	0.056	0.056	0.056	0.057
θ range / °	2.260 – 21.685	2.263 – 21.707	2.264 – 21.719	2.269 – 21.747	2.270 – 21.752
Unique reflections	2737	2705	2286	2373	2488
Unique or all reflections [I>2σ(I)]	2268	2201	1894	1959	2015
Parameters / restraints	128 / 84	129 / 84	128 / 84	128 / 84	128 / 84
GooF on F^2	1.092	1.113	1.251	1.335	1.170
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0693, wR_2 = 0.2057	R_1 = 0.0675, wR_2 = 0.2059	R_1 = 0.0866, wR_2 = 0.2686	R_1 = 0.0923, wR_2 = 0.2859	R_1 = 0.0754, wR_2 = 0.2348
R_1, wR_2 (all data)	R_1 = 0.0767, wR_2 = 0.2140	R_1 = 0.0762, wR_2 = 0.2147	R_1 = 0.0935, wR_2 = 0.2812	R_1 = 0.0996, wR_2 = 0.3003	R_1 = 0.0837, wR_2 = 0.2448
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.542 / –0.371	0.422 / –0.405	0.667 / –0.536	0.725 / –0.449	0.690 / –0.380
Disorder / %	0	0	0	0	0

Table S2 (continued).

Pressure / GPa	26.19(2)	26.61(6)	27.54(6)	28.21(11) [a]
CCDC number	2336603	2336604	2336605	2336606
λ / Å, radiation type			0.4100, synchrotron	
a / Å	11.44(3)	11.43(3)	11.37(4)	11.26(5)
b / Å	5.4806(6)	5.4777(7)	5.4748(8)	5.4851(12)
c / Å	10.344(11)	10.328(10)	10.291(15)	10.25(2)
α / °	90	90	90	90
β / °	116.8(2)	116.8(2)	116.8(3)	116.6(4)
γ / °	90	90	90	90
Volume / Å^3	579.3(18)	577.1(18)	572(3)	566(4)
ρ_{calc} / g·cm^{-3}	2.089	2.097	2.116	2.139
μ / mm^{-1}	0.057	0.057	0.058	0.058
θ range / °	2.272 – 21.758	2.275 – 21.782	2.283 – 20.916	2.293 – 20.731
Unique reflections	2459	2350	2135	581
Unique or all reflections [I>2σ(I)]	1822	1629	1198	278
Parameters / restraints	128 / 84	128 / 84	128 / 84	127 / 84
GooF on F^2	1.165	1.158	1.609	1.362
R_1, wR_2 [I>2σ(I)]	R_1 = 0.0871, wR_2 = 0.2703	R_1 = 0.0896, wR_2 = 0.2717	R_1 = 0.1378, wR_2 = 0.4255	R_1 = 0.1517, wR_2 = 0.3713
R_1, wR_2 (all data)	R_1 = 0.1014, wR_2 = 0.2850	R_1 = 0.1112, wR_2 = 0.2923	R_1 = 0.1903, wR_2 = 0.4577	R_1 = 0.2243, wR_2 = 0.4140
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ / e·Å^{-3}	0.809 / –0.391	0.718 / –0.477	0.798 / –0.651	0.258 / –0.290
Disorder / %	0	0	0	0

[a] Refinement of a single data sets of 1 crystal only.

Table S3: Pressure evolution of the unit cell parameters (distances in Å, angles in °, and volume in Å³) of crystal 1 of **azobenzene**, $C_{12}H_{10}N_2$.

Pressure (GPa)	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	*V* (Å³)
0.0001 [a]	14.9840(4)	5.69830(10)	12.0341(3)	90	112.452(3)	90	949.63(4)
0.0001 [b]	15.2269(4)	5.78897(13)	12.1743(3)	90	112.455(3)	90	991.78(5)
0.0001	15.223(14)	5.7851(5)	12.174(4)	90	112.45(7)	90	990.9(11)
0.19(2)	15.088(13)	5.7289(4)	12.059(4)	90	112.42(7)	90	963.6(10)
0.31(2)	14.998(11)	5.6940(3)	11.992(3)	90	112.43(6)	90	946.6(9)
0.54(2)	14.890(10)	5.6496(3)	11.905(3)	90	112.44(5)	90	925.6(7)
1.02(2)	14.710(10)	5.5772(3)	11.759(3)	90	112.39(5)	90	892.0(7)
1.51(2)	14.547(13)	5.5258(3)	11.659(4)	90	112.40(7)	90	866.5(9)
1.91(2)	14.455(9)	5.4916(2)	11.591(3)	90	112.41(5)	90	850.6(6)
2.65(2)	14.296(10)	5.4336(3)	11.476(3)	90	112.42(6)	90	824.1(7)
3.02(2)	14.222(8)	5.4119(2)	11.430(2)	90	112.42(5)	90	813.2(6)
3.56(4)	14.122(8)	5.37914(19)	11.365(2)	90	112.44(4)	90	797.9(5)
4.00(2)	14.037(7)	5.35545(18)	11.315(2)	90	112.49(4)	90	785.9(5)
4.62(5)	13.935(7)	5.32579(17)	11.253(2)	90	112.51(4)	90	771.5(5)
4.80(2)	13.912(7)	5.32080(18)	11.243(2)	90	112.55(4)	90	768.6(5)
5.66(4)	13.808(7)	5.29256(18)	11.185(2)	90	112.58(4)	90	754.7(5)
6.04(4)	13.767(7)	5.27967(16)	11.158(2)	90	112.60(4)	90	748.8(4)
6.52(5)	13.693(8)	5.26420(19)	11.124(2)	90	112.65(5)	90	740.0(5)
7.21(2)	13.618(6)	5.24215(16)	11.0763(19)	90	112.67(4)	90	729.6(4)
7.57(3)	13.573(7)	5.23258(19)	11.057(2)	90	112.71(4)	90	724.4(4)
8.07(6)	13.529(8)	5.2210(2)	11.031(2)	90	112.74(4)	90	718.6(5)
8.65(7)	13.462(8)	5.20920(19)	11.001(2)	90	112.81(5)	90	711.1(5)
9.12(5)	13.420(8)	5.2012(2)	10.982(2)	90	112.85(5)	90	706.4(5)
9.51(4)	13.377(7)	5.19477(16)	10.966(2)	90	112.89(4)	90	702.0(4)
10.07(8)	13.319(9)	5.1800(2)	10.928(3)	90	112.91(5)	90	694.4(6)
10.58(8)	13.261(8)	5.1782(2)	10.915(2)	90	113.01(5)	90	689.9(5)
11.02(2)	13.220(8)	5.1750(2)	10.904(3)	90	113.08(5)	90	686.3(5)
11.54(4)	13.162(11)	5.1734(3)	10.885(3)	90	113.15(7)	90	681.5(7)
11.95(7)	13.111(17)	5.1676(4)	10.860(5)	90	113.15(10)	90	676.5(10)
12.68(5)	13.08(2)	5.1502(8)	10.814(7)	90	113.12(14)	90	670.0(14)
13.04(6)	13.08(3)	5.1368(12)	10.777(9)	90	112.98(19)	90	666.4(19)
High-pressure structure							
13.57(4)	12.38(2)	5.4468(7)	10.725(6)	90	114.53(13)	90	657.7(13)
14.12(10)	12.32(2)	5.4498(7)	10.697(8)	90	114.60(15)	90	653.0(14)
14.67(2)	12.24(2)	5.4747(6)	10.639(7)	90	114.84(14)	90	647.1(13)
14.93(3)	12.230(15)	5.4789(4)	10.620(6)	90	114.88(11)	90	645.5(10)
15.55(7)	12.162(16)	5.4949(4)	10.602(6)	90	115.15(11)	90	641.4(10)
16.27(8)	12.096(15)	5.5053(4)	10.570(5)	90	115.42(11)	90	635.8(10)
16.75(10)	12.064(14)	5.5054(4)	10.545(5)	90	115.46(10)	90	632.3(9)
17.25(8)	12.013(14)	5.5124(4)	10.539(5)	90	115.68(10)	90	629.0(9)
17.62(7)	11.979(13)	5.5148(4)	10.530(5)	90	115.74(10)	90	626.6(9)
17.98(4)	11.945(14)	5.5180(4)	10.526(5)	90	115.90(11)	90	624.1(9)
18.51(7)	11.918(13)	5.5121(3)	10.502(5)	90	115.90(9)	90	620.6(8)
18.97(4)	11.882(11)	5.5101(3)	10.490(4)	90	116.01(9)	90	617.3(8)
19.63(9)	11.834(10)	5.5100(3)	10.478(4)	90	116.14(7)	90	613.4(7)
20.15(4)	11.814(10)	5.5065(2)	10.466(4)	90	116.17(8)	90	611.1(7)
20.57(5)	11.789(11)	5.5068(3)	10.461(5)	90	116.23(9)	90	609.2(8)
21.24(6)	11.750(9)	5.5030(2)	10.447(4)	90	116.33(7)	90	605.4(6)
21.81(6)	11.719(9)	5.5018(2)	10.440(4)	90	116.41(7)	90	602.9(6)
22.31(4)	11.694(10)	5.4975(2)	10.427(4)	90	116.44(8)	90	600.2(7)
22.66(5)	11.671(10)	5.4939(2)	10.418(4)	90	116.47(8)	90	598.0(7)
23.07(3)	11.660(10)	5.4890(2)	10.407(4)	90	116.47(8)	90	596.2(7)
23.57(4)	11.626(10)	5.4869(2)	10.397(4)	90	116.56(8)	90	593.2(7)

[a] Data collected at 100 K on a free crystal.

[b] Data collected at 298 K on a free crystal.

Table S3 (continued).

Pressure (GPa)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
High-pressure structure (continued)							
24.11(4)	11.592(9)	5.4837(2)	10.385(4)	90	116.64(7)	90	590.1(6)
24.72(7)	11.550(11)	5.4830(3)	10.377(4)	90	116.73(8)	90	586.9(7)
25.50(7)	11.513(11)	5.4804(3)	10.357(4)	90	116.78(9)	90	583.4(7)
25.89(3)	11.47(2)	5.4795(5)	10.352(8)	90	116.77(17)	90	580.7(14)
26.19(2)	11.44(3)	5.4806(6)	10.344(11)	90	116.8(2)	90	579.3(18)
26.61(6)	11.43(3)	5.4777(7)	10.328(10)	90	116.8(2)	90	577.1(18)
27.54(6)	11.37(4)	5.4748(8)	10.291(15)	90	116.8(3)	90	572(3)
28.21(11)	11.26(5)	5.4851(12)	10.25(2)	90	116.6(4)	90	566(4)
Polymer structure							
29.04(12)	10.826(20)	5.526(3)	10.088(18)	90.05(7)	115.55(19)	89.60(8)	544(1)
29.66(5)	10.798(13)	5.536(2)	9.892(9)	89.89(5)	115.51(10)	89.42(5)	533.7(8)
30.12(3)	10.745(14)	5.533(2)	9.831(9)	89.84(5)	115.47(11)	89.36(6)	527.6(9)
30.91(14)	10.658(14)	5.526(3)	9.751(10)	89.79(7)	115.52(12)	89.19(8)	518.2(9)
31.79(16)	10.55(2)	5.516(4)	9.728(15)	89.80(10)	115.43(18)	88.76(12)	511(1)
32.46(6)	10.514(18)	5.522(5)	9.708(10)	89.82(8)	115.64(13)	88.70(11)	508(1)
31.58(5)	10.554(18)	5.525(4)	9.692(13)	89.89(9)	115.40(15)	88.71(10)	510(1)
29.91(10)	10.623(13)	5.551(3)	9.719(8)	90.04(6)	115.28(10)	89.19(8)	518.2(8)
27.0(2)	10.72(3)	5.573(3)	9.787(10)	89.95(7)	115.23(16)	89.23(10)	529(1)
22.3(2)	10.86(2)	5.617(4)	9.865(11)	90.04(7)	115.13(14)	89.39(10)	545(1)
16.74(14)	11.10(2)	5.680(3)	9.925(10)	90.00(6)	115.18(14)	89.24(9)	566(1)
10.78(18)	11.08(3)	5.772(5)	10.015(14)	89.97(8)	114.81(18)	88.73(12)	581(2)

Table S4: Pressure evolution of the unit cell parameters (distances in Å, angles in °, and volume in Å³) of crystal 2 of **azobenzene**, $C_{12}H_{10}N_2$.

Pressure (GPa)	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*V* (Å³)
0.0001	15.211(5)	5.7882(4)	12.180(2)	90	112.45(3)	90	991.1(4)
0.19(2)	15.075(3)	5.7301(3)	12.0638(15)	90	112.43(2)	90	963.2(3)
0.31(2)	15.002(3)	5.6999(2)	12.0055(12)	90	112.410(17)	90	949.1(2)
0.54(2)	14.885(3)	5.6550(3)	11.9177(13)	90	112.438(18)	90	927.2(2)
1.02(2)	14.691(2)	5.5786(2)	11.7656(10)	90	112.403(14)	90	891.47(18)
1.51(2)	14.5468(19)	5.52668(18)	11.6630(9)	90	112.416(12)	90	866.80(15)
1.91(2)	14.4494(19)	5.49181(18)	11.5946(9)	90	112.412(12)	90	850.58(15)
2.65(2)	14.285(2)	5.43565(19)	11.4830(9)	90	112.407(13)	90	824.34(15)
3.02(2)	14.2102(19)	5.41278(17)	11.4364(9)	90	112.427(12)	90	813.12(14)
3.56(4)	14.108(2)	5.38006(18)	11.3693(9)	90	112.449(14)	90	797.57(15)
4.00(2)	14.0259(17)	5.35781(16)	11.3215(8)	90	112.481(12)	90	786.13(13)
4.62(5)	13.9288(19)	5.32813(17)	11.2618(9)	90	112.504(13)	90	772.15(14)
4.80(2)	13.905(2)	5.3223(2)	11.2481(10)	90	112.526(15)	90	768.95(16)
5.66(4)	13.800(2)	5.29508(20)	11.1842(10)	90	112.591(15)	90	754.58(16)
6.04(4)	13.753(2)	5.28177(18)	11.1540(10)	90	112.591(14)	90	748.08(15)
6.52(5)	13.683(2)	5.2664(2)	11.1168(12)	90	112.659(17)	90	739.24(18)
7.21(2)	13.6073(19)	5.24975(17)	11.0762(9)	90	112.727(13)	90	729.79(14)
7.57(3)	13.569(2)	5.24276(19)	11.0584(11)	90	112.753(15)	90	725.45(16)
8.07(6)	13.511(2)	5.23092(19)	11.0297(11)	90	112.799(16)	90	718.61(16)
8.65(7)	13.448(2)	5.2200(2)	11.0030(12)	90	112.851(17)	90	711.76(17)
9.12(5)	13.401(2)	5.2116(2)	10.9887(12)	90	112.969(16)	90	706.60(16)
9.51(4)	13.357(3)	5.2046(2)	10.9697(12)	90	113.036(18)	90	701.77(18)
10.07(8)	13.285(3)	5.1976(3)	10.9473(15)	90	113.09(2)	90	695.4(2)
10.58(8)	13.245(3)	5.1945(3)	10.9341(16)	90	113.15(2)	90	691.7(2)
11.02(2)	13.203(4)	5.1900(4)	10.923(2)	90	113.13(3)	90	688.3(3)
11.54(4)	13.162(5)	5.1887(5)	10.910(3)	90	113.04(4)	90	685.6(4)
11.95(7)	13.128(7)	5.1793(6)	10.894(4)	90	112.83(5)	90	682.6(5)
12.68(5)	13.106(16)	5.1477(15)	10.792(8)	90	112.76(12)	90	671.4(11)
13.04(6)	13.14(2)	5.1504(18)	10.747(13)	90	112.89(17)	90	669.8(16)
High-pressure structure							
13.04(6)	12.452(8)	5.4749(6)	10.723(4)	90	114.90(7)	90	663.0(6)
13.57(4)	12.428(6)	5.4648(5)	10.666(4)	90	114.81(5)	90	657.5(5)
14.12(10)	12.366(7)	5.4796(5)	10.637(4)	90	114.90(6)	90	653.7(5)
14.67(2)	12.259(5)	5.5251(4)	10.661(3)	90	115.31(4)	90	652.8(4)
14.93(3)	12.215(6)	5.5184(5)	10.640(3)	90	115.40(5)	90	647.9(4)
15.55(7)	12.135(4)	5.5310(3)	10.639(2)	90	115.63(3)	90	643.8(3)
16.27(8)	12.049(4)	5.5387(3)	10.628(2)	90	115.87(3)	90	638.2(3)
16.75(10)	11.995(4)	5.5379(4)	10.620(2)	90	115.95(4)	90	634.3(3)
17.25(8)	11.949(5)	5.5329(4)	10.603(3)	90	115.99(4)	90	630.2(4)
17.62(7)	11.916(5)	5.5338(4)	10.599(3)	90	116.03(5)	90	628.0(4)
17.98(4)	11.881(5)	5.5332(4)	10.595(3)	90	116.10(5)	90	625.5(4)
18.51(7)	11.837(6)	5.5280(4)	10.570(3)	90	116.16(5)	90	620.8(4)
18.97(4)	11.799(6)	5.5261(4)	10.554(3)	90	116.22(5)	90	617.3(4)
19.63(9)	11.740(7)	5.5232(5)	10.541(4)	90	116.33(6)	90	612.6(5)
20.15(4)	11.708(7)	5.5183(5)	10.525(4)	90	116.36(6)	90	609.3(5)
20.57(5)	11.680(8)	5.5182(6)	10.524(5)	90	116.48(7)	90	607.1(6)
21.24(6)	11.639(8)	5.5134(6)	10.508(5)	90	116.56(8)	90	603.2(6)
21.81(6)	11.604(9)	5.5143(7)	10.505(6)	90	116.61(9)	90	601.0(7)
22.31(4)	11.570(8)	5.5129(6)	10.496(5)	90	116.72(8)	90	598.0(6)
22.66(5)	11.546(8)	5.5082(6)	10.487(5)	90	116.73(8)	90	595.6(6)
23.07(3)	11.528(8)	5.5043(6)	10.470(5)	90	116.77(7)	90	593.2(6)
23.57(4)	11.499(8)	5.5018(6)	10.462(5)	90	116.86(8)	90	590.4(6)
24.11(4)	11.456(9)	5.5006(7)	10.448(6)	90	116.93(9)	90	587.0(7)
24.72(7)	11.418(10)	5.4988(7)	10.462(7)	90	116.94(10)	90	585.6(8)
25.50(7)	11.388(10)	5.4948(7)	10.438(7)	90	116.99(10)	90	582.0(8)
25.89(3)	11.344(10)	5.4993(7)	10.411(6)	90	117.06(10)	90	578.4(8)

Table S4 (continued).

Pressure (GPa)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
High-pressure structure (continued)							
26.19(2)	11.322(11)	5.5049(9)	10.404(7)	90	117.08(11)	90	577.3(9)
26.61(6)	11.286(12)	5.5013(10)	10.388(8)	90	116.90(12)	90	575.2(10)
27.54(6)	11.14(2)	5.535(2)	10.373(15)	90	117.0(2)	90	570.1(17)
Polymer structure							
28.21(11)	11.101(13)	5.545(3)	9.990(14)	90.64(7)	115.59(12)	88.70(6)	554(1)
29.04(12)	11.006(13)	5.553(3)	9.909(11)	90.76(8)	115.58(12)	88.33(7)	546(1)
29.66(5)	10.865(16)	5.548(4)	9.863(13)	90.87(9)	115.79(14)	88.39(9)	535(1)
30.12(3)	10.787(14)	5.544(4)	9.845(13)	90.85(10)	115.81(13)	88.52(9)	530(1)
30.91(14)	10.744(13)	5.533(5)	9.805(14)	91.00(10)	115.84(13)	88.48(9)	524(1)
31.79(16)	10.686(17)	5.531(4)	9.780(16)	91.03(10)	116.07(16)	88.45(9)	519(1)
32.46(6)	10.647(18)	5.516(4)	9.769(14)	91.04(10)	115.86(15)	88.61(9)	516(1)
31.58(5)	10.57(2)	5.523(5)	9.790(13)	91.06(10)	115.95(17)	88.89(11)	514(1)
29.91(10)	10.633(12)	5.548(4)	9.789(11)	91.11(8)	115.99(11)	88.60(8)	518.9(9)
27.0(2)	10.712(19)	5.585(6)	9.839(15)	90.90(13)	115.63(16)	88.38(12)	531(1)
22.3(2)	10.818(18)	5.626(4)	9.840(9)	90.97(9)	116.11(14)	89.16(9)	538(1)
16.74(14)	10.97(2)	5.699(5)	9.999(13)	91.19(10)	115.75(16)	88.63(10)	563(1)
10.78(18)	11.22(3)	5.779(7)	10.016(14)	91.00(13)	115.0(2)	88.61(14)	588(2)
6.0(4)	11.509(16)	5.875(5)	10.179(11)	91.02(11)	114.03(12)	88.70(10)	628(1)
6.0(4)	11.574(15)	5.887(4)	10.182(18)	90.92(9)	114.07(15)	88.79(8)	633(1)
1.28(2)	12.49(2)	6.106(6)	10.352(13)	90.70(10)	112.59(14)	89.29(11)	729(2)

Table S5: Pressure evolution of the intramolecular separations, *s* (Å) and N–N–C–C dihedral angles (°) of **azobenzene**, $C_{12}H_{10}N_2$.

Pressure (GPa)	Intra-planar separation	N1–N1–C1–C2	N1–N1–C1–C6	Intraplanar separation	N2A–N2A–C7–C12	N2A–N2A–C7–C8	N2B–N2B–C7–C12	N2B–N2B–C7–C8
	Molecule A (N1)			**Molecule B (disordered, N2)**				
0.0001 [a]	0.369(3)	-161.86(11)	20.55(16)	0.200(3)	-170.37(12)	9.69(18)		
0.0001 [b]	0.316(3)	-164.24(13)	17.79(18)	0.161(5)	-173.3(3)	6.4(4)	-9.6(15)	171.5(9)
0.0001	0.332(10)	-163.9(5)	18.4(7)	0.16(2)	-174.3(7)	5.0(11)	-9(7)	172(4)
0.19(2)	0.332(11)	-163.3(5)	19.7(7)	0.18(2)	-173.1(7)	6.9(11)	-11(7)	171(4)
0.31(2)	0.339(9)	-162.9(5)	19.7(7)	0.188(18)	-172.8(6)	6.8(10)	-7(7)	173(4)
0.54(2)	0.338(8)	-162.5(4)	19.1(6)	0.188(15)	-172.0(5)	7.8(8)	-8(7)	172(4)
1.02(2)	0.323(8)	-162.5(4)	19.8(6)	0.216(14)	-170.6(4)	8.9(7)	-13(9)	169(5)
1.51(2)	0.326(8)	-162.1(4)	20.1(6)	0.231(14)	-169.7(5)	10.6(7)	-16(11)	168(6)
1.91(2)	0.323(8)	-161.9(4)	20.0(6)	0.247(14)	-169.6(4)	10.5(7)	-5(12)	174(6)
2.65(2)	0.300(8)	-161.7(4)	21.0(6)	0.278(13)	-168.4(4)	11.6(7)	-3(14)	174(7)
3.02(2)	0.294(8)	-161.7(4)	21.2(6)	0.275(15)	-168.1(4)	12.0(7)	-11(14)	170(7)
3.56(4)	0.281(8)	-161.7(4)	21.0(6)	0.294(12)	-167.5(4)	12.4(6)	-15(14)	167(7)
4.00(2)	0.267(8)	-161.8(4)	21.7(6)	0.313(12)	-167.0(4)	12.5(6)	-17(15)	165(8)
4.62(5)	0.265(8)	-162.2(4)	21.4(6)	0.321(13)	-166.7(4)	12.8(6)	-20(14)	164(8)
4.80(2)	0.258(8)	-162.2(4)	21.3(6)	0.323(13)	-166.5(4)	12.9(6)	-23(13)	162(7)
5.66(4)	0.242(8)	-162.0(4)	22.3(6)	0.336(14)	-165.9(4)	13.7(7)	-17(13)	166(6)
6.04(4)	0.232(8)	-162.2(4)	21.9(6)	0.341(14)	-165.8(4)	14.0(7)	-13(11)	167(6)
6.52(5)	0.226(8)	-162.1(4)	22.1(6)	0.357(14)	-165.3(5)	14.3(8)	-13(10)	167(5)
7.21(2)	0.213(9)	-162.3(4)	22.4(6)	0.370(15)	-164.9(5)	14.0(8)	-12(9)	167(5)
7.57(3)	0.211(9)	-162.3(4)	22.2(6)	0.380(15)	-165.0(5)	14.1(8)	-15(9)	165(5)
8.07(6)	0.201(10)	-162.5(5)	22.4(7)	0.397(16)	-164.4(6)	14.6(9)	-16(8)	164(4)
8.65(7)	0.186(10)	-162.8(5)	22.2(7)	0.409(18)	-164.1(6)	14.2(10)	-14(7)	165(4)
9.12(5)	0.181(10)	-162.8(5)	21.9(7)	0.420(18)	-164.0(6)	14.4(10)	-14(6)	165(3)
9.51(4)	0.174(10)	-162.8(5)	22.0(7)	0.432(18)	-163.8(7)	14.5(11)	-14(6)	165(3)
10.07(8)	0.163(12)	-163.3(6)	21.5(8)	0.45(2)	-163.7(8)	14.3(13)	-13(5)	165(3)
10.58(8)	0.147(12)	-163.6(6)	21.5(9)	0.47(2)	-163.6(9)	14.0(14)	-12(5)	165(3)
11.02(2)	0.142(13)	-163.8(6)	21.4(9)	0.49(3)	-163.6(10)	13.5(16)	-14(4)	163(3)
11.54(4)	0.132(14)	-164.1(7)	21.7(10)	0.50(3)	-163.8(11)	12.3(18)	-11(4)	165(2)
11.95(7)	0.134(17)	-164.2(8)	21.2(11)	0.55(3)	-163.5(12)	12(2)	-13(4)	163(2)
12.68(5)	0.17(2)	-165.5(11)	18.3(16)	0.52(5)	-163.8(15)	12(3)	-12(6)	164(3)
13.04(6)	0.13(3)	-164.0(13)	23.4(18)	0.52(5)	-162.8(17)	11(3)	-13(6)	162(4)
13.04(6) [c]	0.069(12)	-168.2(5)	18.2(9)	0.150(17)	172.2(4)	-13.5(7)		
13.57(4)	0.089(18)	-168.3(9)	19.1(12)	0.17(3)	172.4(7)	-13.7(11)		
14.12(10)	0.090(17)	-168.9(9)	18.0(13)	0.19(3)	172.2(7)	-14.1(12)		
14.67(2)	0.112(18)	-169.3(9)	19.6(13)	0.20(3)	172.6(8)	-14.7(12)		
14.93(3)	0.126(16)	-169.4(8)	19.0(11)	0.19(2)	171.7(7)	-15.7(11)		
15.55(7)	0.152(16)	-169.9(8)	18.7(11)	0.19(2)	171.7(7)	-15.7(11)		
16.27(8)	0.150(14)	-169.8(7)	18.1(10)	0.22(2)	170.8(6)	-16.6(10)		
16.75(10)	0.161(14)	-170.0(7)	17.5(10)	0.23(2)	171.0(6)	-16.5(9)		
17.25(8)	0.172(13)	-170.2(6)	17.6(8)	0.22(2)	171.0(5)	-16.5(8)		
17.62(7)	0.173(13)	-170.4(6)	17.4(8)	0.237(19)	171.0(5)	-16.7(8)		
17.98(4)	0.177(13)	-170.2(6)	17.3(9)	0.23(2)	170.7(5)	-17.1(8)		
18.51(7)	0.181(11)	-170.1(5)	17.7(8)	0.241(17)	171.0(5)	-16.7(7)		
18.97(4)	0.190(12)	-170.3(6)	17.9(8)	0.238(18)	170.9(5)	-16.5(7)		
19.63(9)	0.199(13)	-170.7(6)	17.0(9)	0.25(2)	170.7(6)	-17.1(9)		
20.15(4)	0.208(13)	-170.7(6)	17.0(9)	0.250(19)	171.0(5)	-16.8(8)		
20.57(5)	0.17(3)	-169.3(11)	17.4(17)	0.23(4)	170.0(9)	-15.3(15)		
21.24(6)	0.203(15)	-170.4(7)	17.8(10)	0.25(2)	171.4(6)	-16.9(9)		
21.81(6)	0.220(16)	-170.9(8)	17.5(11)	0.26(2)	171.6(7)	-17.1(10)		

[a] Data collected at 100 K on a free crystal.

[b] Data collected at 298 K on a free crystal.

[c] High-pressure structure.

Table S5 (continued).

Pressure (GPa)	Intra-planar separation	N1–N1–C1–C2	N1–N1–C1–C6	Intraplanar separation	N2A–N2A–C7–C12	N2A–N2A–C7–C8	N2B–N2B–C7–C12	N2B–N2B–C7–C8
22.31(4)	0.224(15)	-171.2(7)	17.3(10)	0.26(2)	171.3(6)	-16.9(9)		
22.66(5)	0.221(13)	-170.8(6)	17.5(9)	0.262(19)	171.6(5)	-16.9(8)		
23.07(3)	0.231(14)	-170.8(7)	18.0(9)	0.27(2)	171.7(6)	-16.4(9)		
23.57(4)	0.234(13)	-170.8(6)	17.8(9)	0.267(19)	171.3(5)	-17.0(8)		
24.11(4)	0.229(15)	-171.0(7)	17.3(10)	0.28(2)	171.4(6)	-16.8(9)		
24.72(7)	0.261(17)	-171.2(8)	17.1(11)	0.29(3)	171.9(7)	-16.5(10)		
25.50(7)	0.242(18)	-171.1(8)	16.8(13)	0.29(3)	172.1(8)	-16.0(11)		
25.89(3)	0.225(19)	-170.7(9)	15.9(13)	0.30(3)	172.8(8)	-15.8(11)		
26.19(2)	0.23(2)	-171.0(11)	16.2(15)	0.30(3)	173.6(9)	-15.3(14)		
26.61(6)	0.24(3)	-170.4(12)	17.6(17)	0.32(4)	173.4(11)	-16.0(15)		
27.54(6)	0.27(4)	-173(2)	15(3)	0.40(6)	173.9(19)	-17(3)		
28.21(11)	0.25(6)	-169(3)	22(3)	0.55(9)	172(3)	-29(3)		

Table S6: Pressure evolution of the nearest-neighbour intermolecular C···C and C···N distances (Å) of **azobenzene**, $C_{12}H_{10}N_2$ across the phase transition at 13 GPa and in the high-pressure phase. Red: no significant interaction.

Pressure (GPa)	C8···C12	C2···C6	C8···C11	C5···C12	C6···C10	C3···C6	C9···C12	C4···C8	C2···C5
10.58(8)	3.100	2.979	3.310	3.205	3.219	3.180	3.331	3.210	3.171
11.02(2)	3.092	2.967	3.301	3.196	3.212	3.168	3.323	3.192	3.159
11.54(4)	3.068	2.952	3.274	3.179	3.194	3.151	3.312	3.179	3.146
11.95(7)	3.058	2.938	3.270	3.161	3.195	3.134	3.307	3.163	3.136
12.68(5)	3.031	2.906	3.267	3.144	3.208	3.110	3.305	3.166	3.128
13.04(6)	3.019	2.887	3.250	3.153	3.196	3.097	3.336	3.169	3.124
13.04(6) [a]	2.824	2.810	2.982	2.972	3.014	2.953	3.043	3.065	2.977
13.57(4)	2.806	2.813	2.963	2.956	3.017	2.947	3.022	3.034	2.969
14.12(10)	2.785	2.790	2.950	2.946	3.014	2.922	2.994	3.011	2.952
14.67(2)	2.759	2.764	2.915	2.923	2.979	2.915	2.972	2.992	2.937
14.93(3)	2.754	2.763	2.909	2.917	2.970	2.913	2.974	2.997	2.939
15.55(7)	2.735	2.758	2.880	2.904	2.944	2.905	2.957	2.975	2.923
16.27(8)	2.728	2.739	2.863	2.882	2.925	2.884	2.944	2.951	2.905
16.75(10)	2.723	2.736	2.856	2.868	2.912	2.878	2.937	2.942	2.906
17.25(8)	2.707	2.727	2.834	2.860	2.893	2.868	2.918	2.926	2.891
17.62(7)	2.703	2.720	2.824	2.847	2.884	2.865	2.911	2.917	2.879
17.98(4)	2.694	2.713	2.815	2.835	2.872	2.847	2.905	2.908	2.876
18.51(7)	2.689	2.707	2.808	2.830	2.8862	2.853	2.896	2.894	2.864
18.97(4)	2.682	2.697	2.801	2.819	2.849	2.843	2.885	2.887	2.854
19.63(9)	2.671	2.693	2.787	2.807	2.832	2.836	2.873	2.868	2.842
20.15(4)	2.666	2.687	2.785	2.803	2.830	2.825	2.867	2.865	2.839
20.57(5)	2.672	2.671	2.781	2.788	2.821	2.818	2.864	2.852	2.832
21.24(6)	2.652	2.669	2.766	2.784	2.809	2.810	2.846	2.844	2.822
21.81(6)	2.641	2.664	2.758	2.782	2.795	2.813	2.833	2.839	2.807
22.31(4)	2.637	2.657	2.754	2.772	2.793	2.800	2.827	2.831	2.805
22.66(5)	2.632	2.655	2.746	2.763	2.787	2.797	2.821	2.824	2.804
23.07(3)	2.631	2.650	2.744	2.757	2.782	2.796	2.826	2.822	2.795
23.57(4)	2.623	2.644	2.733	2.745	2.777	2.786	2.817	2.815	2.793
24.11(4)	2.620	2.634	2.723	2.734	2.767	2.778	2.808	2.801	2.782
24.72(7)	2.615	2.637	2.711	2.720	2.750	2.765	2.800	2.791	2.782
25.50(7)	2.608	2.623	2.687	2.694	2.740	2.766	2.789	2.783	2.775
25.89(3)	2.591	2.621	2.668	2.679	2.740	2.758	2.772	2.773	2.776
26.19(2)	2.576	2.612	2.643	2.673	2.735	2.743	2.753	2.771	2.773
26.61(6)	2.578	2.609	2.628	2.656	2.738	2.748	2.749	2.770	2.783
27.54(6)	2.573	2.609	2.566	2.585	2.743	2.761	2.751	2.772	2.803
28.21(11)	2.550	2.559	2.466	2.454	2.765	2.641	2.662	2.783	2.836

[a] High-pressure structure.

Table S6 (continued).

Pressure (GPa)	C1···C6	C8···C7	C9···C7	C10···N2	C4···N1
10.58(8)	3.061	3.100	3.076	3.119	2.944
11.02(2)	3.053	3.095	3.079	3.099	2.931
11.54(4)	3.048	3.079	3.088	3.074	2.917
11.95(7)	3.034	3.069	3.102	3.033	2.903
12.68(5)	2.998	3.042	3.098	3.010	2.866
13.04(6)	2.990	3.032	3.136	3.013	2.865
13.04(6) [a]	3.066	3.055	3.129	2.816	2.749
13.57(4)	3.069	3.041	3.111	2.794	2.750
14.12(10)				2.769	2.727
14.67(2)				2.745	2.717
14.93(3)				2.745	2.704
15.55(7)				2.722	2.694
16.27(8)				2.704	2.677
16.75(10)				2.694	2.666
17.25(8)				2.682	2.656
17.62(7)				2.673	2.652
17.98(4)				2.668	2.643
18.51(7)				2.656	2.641
18.97(4)				2.648	2.631
19.63(9)				2.638	2.621
20.15(4)				2.630	2.609
20.57(5)				2.630	2.616
21.24(6)				2.616	2.601
21.81(6)				2.609	2.589
22.31(4)				2.601	2.583
22.66(5)				2.592	2.584
23.07(3)				2.585	2.577
23.57(4)				2.578	2.566
24.11(4)				2.570	2.560
24.72(7)				2.556	2.549
25.50(7)				2.541	2.543
25.89(3)				2.522	2.542
26.19(2)				2.512	2.534
26.61(6)				2.508	2.529
27.54(6)				2.452	2.499
28.21(11)				2.452	2.523

[a] High-pressure structure.

Table S7: Pressure evolution of the π···π intermolecular distances (Å) and the angles between plane normals (°) of phenyl rings of molecule A of the **azobenzene**, $C_{12}H_{10}N_2$, high-pressure phase.

Pressure (GPa)	Centroid-centroid distance	Interplanar separation 1	Shift	Interplanar separation 2	Shift	Angle between planes
13.04(6)	3.996(4)	3.529(4)	1.875(8)	3.464(6)	1.993(7)	33.7(2)
13.57(4)	3.985(6)	3.509(7)	1.889(12)	3.461(10)	1.976(11)	33.5(3)
14.12(10)	3.970(7)	3.492(7)	1.889(11)	3.424(11)	2.009(11)	32.7(3)
14.67(2)	3.972(7)	3.485(7)	1.905(12)	3.395(10)	2.061(11)	31.6(3)
14.93(3)	3.970(6)	3.479(6)	1.914(10)	3.383(9)	2.078(9)	31.1(3)
15.55(7)	3.969(6)	3.469(6)	1.928(10)	3.360(9)	2.112(9)	30.2(3)
16.27(8)	3.957(5)	3.458(6)	1.923(9)	3.323(8)	2.147(8)	29.5(3)
16.75(10)	3.954(5)	3.451(5)	1.929(9)	3.311(8)	2.160(8)	29.1(2)
17.25(8)	3.948(5)	3.445(5)	1.928(8)	3.295(8)	2.175(7)	28.7(2)
17.62(7)	3.944(5)	3.439(5)	1.931(8)	3.282(8)	2.188(7)	28.4(2)
17.98(4)	3.937(5)	3.434(5)	1.926(9)	3.267(8)	2.197(8)	28.1(2)
18.51(7)	3.934(4)	3.429(4)	1.929(7)	3.259(7)	2.203(6)	27.9(2)
18.97(4)	3.926(4)	3.421(4)	1.926(7)	3.246(7)	2.209(6)	27.7(2)
19.63(9)	3.920(4)	3.413(5)	1.929(8)	3.231(7)	2.221(7)	27.3(2)
20.15(4)	3.913(4)	3.407(5)	1.924(8)	3.222(7)	2.221(7)	27.3(2)
20.57(5)	3.906(7)	3.411(8)	1.904(15)	3.210(12)	2.226(13)	27.4(4)
21.24(6)	3.902(5)	3.399(5)	1.916(9)	3.201(8)	2.231(8)	27.0(3)
21.81(6)	3.896(5)	3.391(5)	1.919(10)	3.189(8)	2.238(8)	26.7(3)
22.31(4)	3.890(5)	3.384(5)	1.920(9)	3.179(8)	2.243(8)	26.5(3)
22.66(5)	3.888(4)	3.382(5)	1.918(8)	3.175(7)	2.243(7)	26.5(2)
23.07(3)	3.883(4)	3.376(5)	1.919(9)	3.168(7)	2.245(7)	26.3(2)
23.57(4)	3.877(4)	3.372(5)	1.914(8)	3.159(7)	2.248(7)	26.2(2)
24.11(4)	3.870(4)	3.367(5)	1.908(9)	3.147(8)	2.253(8)	26.1(3)
24.72(7)	3.865(5)	3.355(6)	1.918(11)	3.135(9)	2.261(9)	25.6(3)
25.50(7)	3.860(5)	3.350(6)	1.918(11)	3.119(9)	2.275(9)	25.3(3)
25.89(3)	3.856(7)	3.347(7)	1.915(12)	3.107(12)	2.284(10)	25.1(4)
26.19(2)	3.852(9)	3.343(9)	1.913(15)	3.098(15)	2.289(12)	25.0(4)
26.61(6)	3.854(9)	3.345(9)	1.914(16)	3.101(15)	2.289(14)	25.0(5)
27.54(6)	3.860(14)	3.334(15)	1.95(3)	3.09(2)	2.31(2)	24.1(8)
28.21(11)	3.84(2)	3.28(2)	1.99(4)	2.99(4)	2.41(3)	21.0(11)

Table S8: Pressure evolution of the π···π intermolecular distances (Å) and the angles between plane normals (°) of phenyl rings of molecule B of the **azobenzene**, $C_{12}H_{10}N_2$, high-pressure phase. Red: no significant interaction.

Pressure (GPa)	Centroid-centroid distance	Interplanar separation 1	Shift	Interplanar separation 2	Shift	Angle between planes
13.04(6)	4.041(4)	3.537(6)	1.954(11)	3.450(8)	2.104(10)	31.7(3)
13.57(4)	4.019(7)	3.511(9)	1.955(17)	3.419(13)	2.112(15)	31.2(5)
14.12(10)	4.002(7)	3.481(9)	1.975(17)	3.374(13)	2.152(15)	29.8(5)
14.67(2)	3.991(7)	3.455(9)	1.998(17)	3.325(13)	2.208(14)	28.1(5)
14.93(3)	3.991(6)	3.452(8)	2.002(15)	3.315(12)	2.221(13)	27.7(4)
15.55(7)	3.976(6)	3.429(8)	2.013(15)	3.272(12)	2.258(13)	26.5(4)
16.27(8)	3.966(6)	3.404(8)	2.035(13)	3.236(11)	2.292(12)	25.2(4)
16.75(10)	3.962(5)	3.392(7)	2.048(12)	3.218(10)	2.311(11)	24.5(4)
17.25(8)	3.949(5)	3.377(7)	2.047(12)	3.188(10)	2.33(1)	23.9(4)
17.62(7)	3.944(5)	3.369(6)	2.049(11)	3.176(10)	2.338(10)	23.6(3)
17.98(4)	3.938(5)	3.364(7)	2.048(12)	3.164(10)	2.345(10)	23.3(4)
18.51(7)	3.391(4)	3.352(6)	2.053(10)	3.147(9)	2.355(9)	22.9(3)
18.97(4)	3.924(4)	3.343(6)	2.054(10)	3.131(9)	2.364(9)	22.5(3)
19.63(9)	3.914(4)	3.329(7)	2.058(12)	3.11(1)	2.376(10)	22.0(4)
20.15(4)	3.909(4)	3.322(7)	2.060(12)	3.10(1)	2.381(10)	21.8(3)
20.57(5)	3.904(7)	3.324(12)	2.05(2)	3.094(18)	2.381(18)	21.9(7)
21.24(6)	3.896(5)	3.306(7)	2.062(13)	3.074(11)	2.395(11)	21.2(4)
21.81(6)	3.889(5)	3.297(8)	2.063(14)	3.058(12)	2.403(12)	20.8(4)
22.31(4)	3.882(5)	3.292(7)	2.058(13)	3.049(11)	2.403(10)	20.8(4)
22.66(5)	3.877(4)	3.286(6)	2.056(11)	3.042(10)	2.404(9)	20.7(3)
23.07(3)	3.876(4)	3.283(7)	2.060(12)	3.038(11)	2.407(10)	20.5(4)
23.57(4)	3.867(4)	3.274(6)	2.058(11)	3.023(9)	2.412(9)	20.3(3)
24.11(4)	3.860(5)	3.264(7)	2.061(12)	3.009(11)	2.417(10)	19.9(4)
24.72(7)	3.854(5)	3.247(8)	2.075(15)	2.985(12)	2.437(12)	19.1(5)
25.50(7)	3.842(6)	3.239(9)	2.066(16)	2.970(14)	2.437(13)	19.0(5)
25.89(3)	3.289(7)	3.231(10)	2.054(17)	2.951(15)	2.439(13)	18.8(5)
26.19(2)	3.818(9)	3.226(12)	2.04(2)	2.934(18)	2.442(16)	18.7(6)
26.61(6)	3.812(9)	3.216(13)	2.05(2)	2.93(2)	2.444(18)	18.5(7)
27.54(6)	3.788(14)	3.19(2)	2.04(4)	2.90(3)	2.43(3)	18.2(11)
28.21(11)	3.75(2)	3.20(3)	1.97(5)	2.91(5)	2.37(4)	19.8(16)

Table S9: Unit-cell parameters of the molecular and polymer phases of **azobenzene** obtained from single-crystal X-ray diffraction data of crystals (cry) 1 and 2, and from DFT calculations.

Pressure (GPa)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
Molecular high-pressure structure							
27.54(6) cry 1	11.37(4)	5.4748(8)	10.291(15)	90	116.8(3)	90	572(3)
28.21(11) cry 1	11.26(5)	5.4851(12)	10.25(2)	90	116.6(4)	90	566(4)
27.54(6) cry 2	11.14(2)	5.535(2)	10.373(15)	90	117.0(2)	90	570.1(17)
30 DFT	11.2720	5.4153	10.2419	90	117.33	90	555.42
Polymer structure							
30.12(3) cry 1	10.745(14)	5.533(2)	9.831(9)	89.84(5)	115.47(11)	89.36(6)	527.6(9)
30.12(3) cry 2	10.787(14)	5.544(4)	9.845(13)	90.85(10)	115.81(13)	88.52(9)	530(1)
30 polymer I DFT	10.2988	5.5182	10.2018	90	118.15	90	511.18
30 polymer II DFT	9.7678	5.3372	9.9761	90	121.24	90	444.69

Table S10: Unit cell parameters and atomic coordinates (*x y z*) of the molecular structure of **azobenzene** computed at 30 GPa. Atomic coordinates were taken from the computational output files and the structure was transformed from space group *P*1 to $P2_1/c$.

Space group: $P2_1/c$
a = 11.2720 Å, b = 5.4153 Å, c = 10.2419 Å, α = 90.0°, β = 117.33°, γ = 90.0°

N1	0.48915	0.11162	0.50779
C1	0.41965	0.14254	0.58567
C2	0.37985	0.37774	0.59621
H2	0.39923	0.52187	0.53668
C3	0.32598	0.41734	0.68981
H3	0.30348	0.59601	0.71552
C4	0.31821	0.22873	0.77316
H4	0.28120	0.26933	0.84860
C5	0.35942	0.99517	0.76411
H5	0.36225	0.85590	0.83964
C6	0.40716	0.95115	0.66685
H6	0.44280	0.77490	0.65560
N2	0.99156	0.11179	0.98205
C7	0.92107	0.14461	0.83438
C8	0.90296	0.95353	0.73832
H8	0.93668	0.77652	0.78514
C9	0.85108	-0.00112	0.59215
H9	0.84448	0.86048	0.51406
C10	0.81800	0.23627	0.54588
H10	0.78139	0.27425	0.43325
C11	0.83542	0.42481	0.64042
H11	0.81600	0.60564	0.59644
C12	0.88560	0.38174	0.78722
H12	0.90775	0.52368	0.86842

Table S11: Unit cell parameters and atomic coordinates (*x y z*) of the polymer I structure of **azobenzene** computed at 30 GPa. Atomic coordinates were taken from the computational output files and the structure was transformed from space group *P*1 to $P2_1/c$.

Space group: $P2_1/c$
a = 10.2988 Å, b = 5.5182 Å, c = 10.2018 Å, α = 90.0°, β = 118.15°, γ = 90.0°

N1	0.49204	0.11368	0.52026
C1	0.44286	0.13255	0.61461
C2	0.43337	0.38243	0.65573
H2	0.42487	0.50228	0.56783
C3	0.32364	0.40971	0.70547
H3	0.30305	0.58855	0.73048
C4	0.30282	0.23655	0.78084
H4	0.26571	0.29267	0.85626
C5	0.31058	0.97762	0.76078
H5	0.35996	0.88792	0.86848
N2	0.97564	0.11499	0.98666
C6	0.41799	0.93485	0.69995
H6	0.40244	0.77754	0.63367
C7	0.91831	0.16573	0.85003
C8	0.94339	0.98522	0.75865
H8	0.91394	0.81738	0.79024
C9	0.85138	0.03710	0.60183
H9	0.81597	0.89646	0.51895
C10	0.82564	0.26785	0.56621
H10	0.75408	0.32679	0.45760
C11	0.88905	0.46118	0.67810
H11	0.83976	0.62441	0.61990
C12	0.85581	0.41083	0.80383
H12	0.91909	0.53083	0.89642

Table S12: Unit cell parameters and atomic coordinates (*x y z*) of the polymer II structure of **azobenzene** computed at 30 GPa. Atomic coordinates were taken from the computational output files and the structure was transformed from space group *P*1 to $P2_1/c$.

Space group: $P2_1/c$
a = 9.7678 Å, b = 5.3372 Å, c = 9.9761 Å, α = 90.0°, β = 121.24°, γ = 90.0°

N1	0.46338	0.11211	0.50812
C1	0.36914	0.09019	0.58584
C2	0.38592	0.36610	0.64724
H2	0.36249	0.47998	0.54973
C3	0.30327	0.44981	0.73271
H3	0.38163	0.59476	0.80217
C4	0.35035	0.26325	0.85738
H4	0.25699	0.24471	0.87848
C5	0.35345	0.98865	0.81944
H5	0.41894	0.88970	0.92777
C6	0.43306	0.91853	0.72882
H6	0.39383	0.74167	0.67560
N2	0.96598	0.12659	0.97269
C7	0.84991	0.10515	0.80849
C8	0.91972	0.95952	0.73013
H8	0.89901	0.77652	0.75479
C9	0.83862	0.00587	0.55269
H9	0.89972	0.88143	0.51534
C10	0.86334	0.28082	0.53634
H10	0.74743	0.33527	0.45064
C11	0.89991	0.44639	0.66936
H11	0.85943	0.61761	0.60613
C12	0.81790	0.38757	0.75719
H12	0.88609	0.49205	0.86396

Table S13: C–C, C–N, and N–N bond lengths (Å) of the molecular, the polymer I, and the polymer II structure of **azobenzene** computed at 30 GPa.

C/N–C/N (Å)	Molecular	Polymer I	Polymer II
Molecule A			
C1–C2	1.371	1.458	1.571
C2–C3	1.367	1.449	1.514
C3–C4	1.360	1.306	1.469
C4–C5	1.365	1.451	1.518
C5–C6	1.353	1.521	1.514
C1–C6	1.376	1.491	1.530
C1–N1	1.361	1.286	1.484
N1–N1	1.258	1.355	1.446
Molecule B			
C7–C8	1.377	1.468	1.494
C8–C9	1.356	1.452	1.539
C9–C10	1.362	1.316	1.510
C10–C11	1.358	1.471	1.476
C11–C12	1.362	1.501	1.495
C7–C12	1.366	1.476	1.570
C7–N2	1.359	1.262	1.434
N2–N2	1.254	1.345	1.480
Intermolecular bonds			
C2–C6		1.571	1.570
C8–C11		1.537	1.511
C5–C12		1.562	1.533
C3–C7			1.568
C1–C9			1.839
C4–N1			1.484
C10–N2			1.520

Table S14: Coordinates of the reciprocal and real unit cell axes of the two azobenzene crystals loaded in the DAC for data collection at 0.19(2) GPa with respect to an orthogonal reference system. The frame of reference (xyz) is shown in Figure S7; the x axis corresponds to the direction of the incident X-ray beam, while the crystals inside the DAC lie on the perpendicular plane yz.

Crystal 1							
Reciprocal (Å^{-1})	x	y	z	Real (Å)	x	y	z
a*	-0.04197	-0.07532	-0.02469	a	-1.1635	-11.54121	-3.31327
b*	-0.01495	-0.04658	0.16751	b	0.48778	1.53139	-5.50009
c*	-0.07117	0.00833	-0.00399	c	-13.2606	7.12681	0.79875
Crystal 2							
Reciprocal (Å^{-1})	x	y	z	Real (Å)	x	y	z
a*	0.04794	0.02034	-0.07301	a	2.55775	0.95544	-11.75155
b*	-0.07171	0.15913	-0.00267	b	2.35264	-5.22248	0.0897
c*	0.06361	0.02893	0.0162	c	11.14078	5.16737	8.75637