Supplementary Information

Halogen···halogen *contra* C−H···halogen

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Experimental

Chloromethane, CH_3Cl, (m.p. 175.5 K, b.p. 249.1 K) and bromomethane, CH_3Br, (m.p. 179.5 K, b.p. 276.7 K) 99.5% purity from Sigma-Aldrich were used. For high-pressure studies they were loaded to a modified Merrill-Bassett (Bassett, W. A. (2009). *High Press. Res.* **29**, 163-186) diamond-anvil cell (DAC) at cryogenic conditions and crystallized *in situ*. The DAC anvils were supported directly on the steel discs (Katrusiak, A. (2008). *Acta Cryst.* **A64**, 135-148). At 295 K CH_3Cl froze at 0.78 GPa and CH_3Br at 0.65 GPa in the form of polycrystalline mass filling whole volume of the high-pressure chamber. Pressure was calibrated by the ruby fluorescence method (Piermarini, G. J., Block, S., Barnett, J. D. & Forman, R. A. (1975). *J. Appl. Phys*. **46**, 2774-2780) with a Photon Control spectrometer with the accuracy of 0.02 GPa, before and after the X-ray diffraction measurements. The single-crystals of CH_3Cl and CH_3Br were obtained in isochoric conditions: after the crystallization pressure was increased and the DAC with the polycrystalline mass was heated using a hot-air gun till all but one grain melted. Then single crystal grew as the DAC was cooled slowly to room temperature and eventually filled the whole volume of the chamber. The progress and experimental details on growing the single crystals of CH_3Cl are shown in Figures S1-S4, and of CH_3Br in Figures S5-S9.

Diffraction data were collected at 295 K using a KM-4 CCD diffractometer with the graphite-monochromated MoK_α radiation. The DAC was centred by the gasket-shadow method (Budzianowski, A. & Katrusiak, A. (2004). *High-Pressure Crystallography*, edited by A. Katrusiak & P.F. McMillan, pp. 101-112. Dordrecht: Kluwer Academic Publishers). The *CrysAlisCCD* and *CrysAlisRED* programs (Oxford Diffraction (2004). Oxford Diffraction Ltd., Xcalibur CCD system, CrysAlis Software system, Version 1.171) were used for the data collection, determination of the *UB*-matrix, and for initial data reduction and *Lp* corrections for both the compounds. The reflections intensities have been accounted for the effect of

absorption of X-rays by the DAC, shadowing of the beams by the gasket edges, and absorption of the sample crystal itself (Katrusiak, A. (2003). *REDSHABS* – Program for correcting reflections intensities for DAC absorption, gasket shadowing and sample crystal absorption. Adam Mickiewicz University, Poznań, Poland; Katrusiak, A. (2004). *Z. Kristallogr*. **219**, 461-467). The crystal structures of CH_3Cl and CH_3Br were solved by direct methods and the H-atoms were located from molecular geometry in the CH_3Cl and CH_3Br phase β structures (Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112-122). In the CH_3Br phase α the H-atoms were located from molecular geometry at two disordered sites (AFIX 137) with the C–H bond length restrained to 0.96 Å (Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112-122). Details of structure refinements and crystal data are given in Table S1 (CH_3Cl) and Table S2 (CH_3Br).

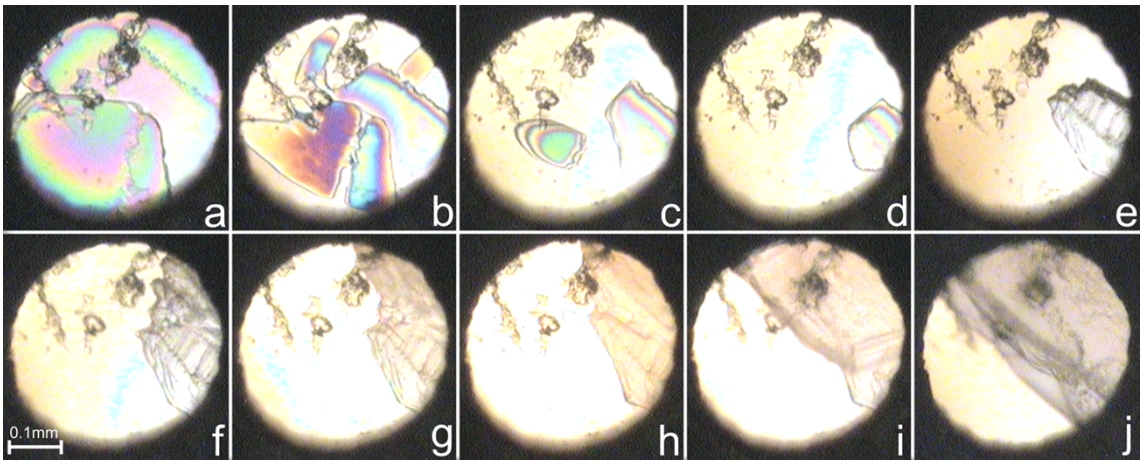

Figure S1. Stages of the CH_3Cl single-crystal growth inside the DAC chamber: (a) polycrystal grown isothermally at 316 K; (b) polycrystal-liquid equilibrium at 318 K; (d) one crystal seed at 323 K; (e-i) the single-crystal cooled to 306 K and (j) filling *ca*. half of the DAC chamber at 295 K and 1.22 GPa. The ruby chip for pressure calibration lies in the upper part of the DAC chamber.

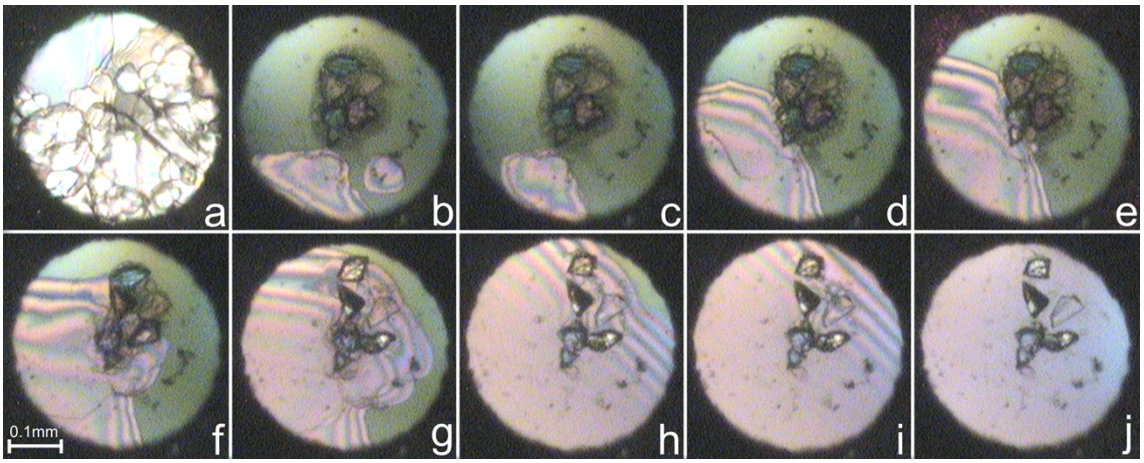

Figure S2. Stages of the CH_3Cl single-crystal growth inside the DAC chamber: (a) polycrystal grown isothermally at 298 K; (b) polycrystal-liquid equilibrium at 384 K; (c) one crystal seed at 385 K; (d-i) the single-crystal cooled to 372 K and (j) filling the DAC chamber at 295 K and 1.69 GPa. The ruby chips for pressure calibration lie in the central part of the DAC chamber.

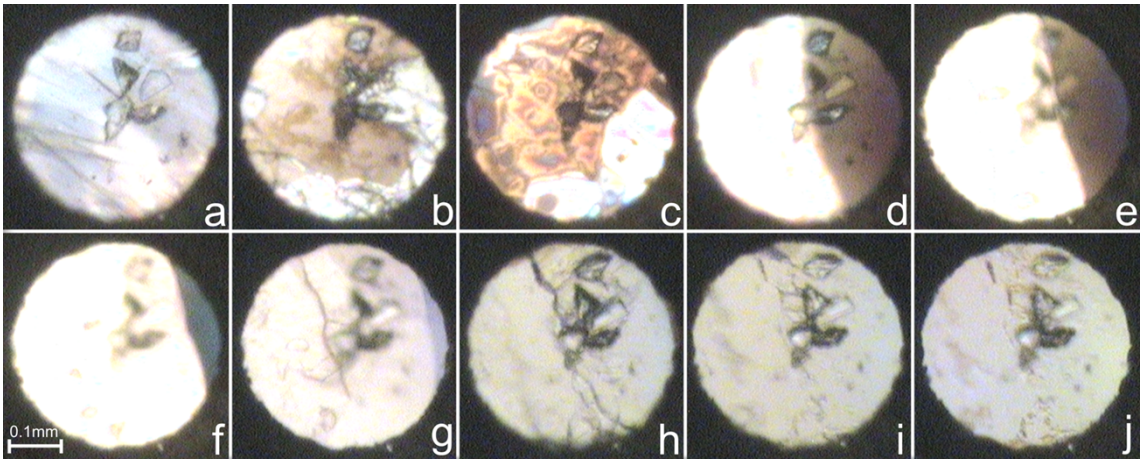

Figure S3. Stages of the CH_3Cl single-crystal growth inside the DAC chamber: (a) polycrystal grown isothermally at 323 K; (c) polycrystal-liquid equilibrium at 428 K; (d) one crystal seed at 430 K; (e-i) the single-crystal cooled to 384 K and (j) filling the DAC chamber at 295 K and 2.91 GPa. The ruby chips for pressure calibration lie in the central part of the DAC chamber.

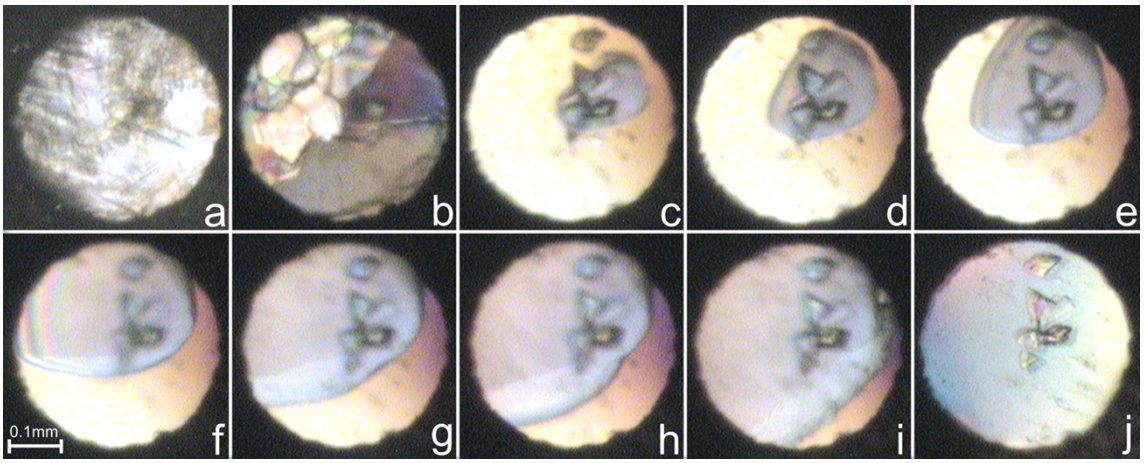

Figure S4. Stages of the CH_3Cl single-crystal growth inside the DAC chamber: (a) polycrystal grown isothermally at 353 K; (b) polycrystal-liquid equilibrium at 483 K; (c) one crystal seed at 485 K; (d-i) the single-crystal cooled to 456 K and (j) filling the DAC chamber at 295 K and 4.38 GPa. The ruby chips for pressure calibration lie in the central part of the DAC chamber.

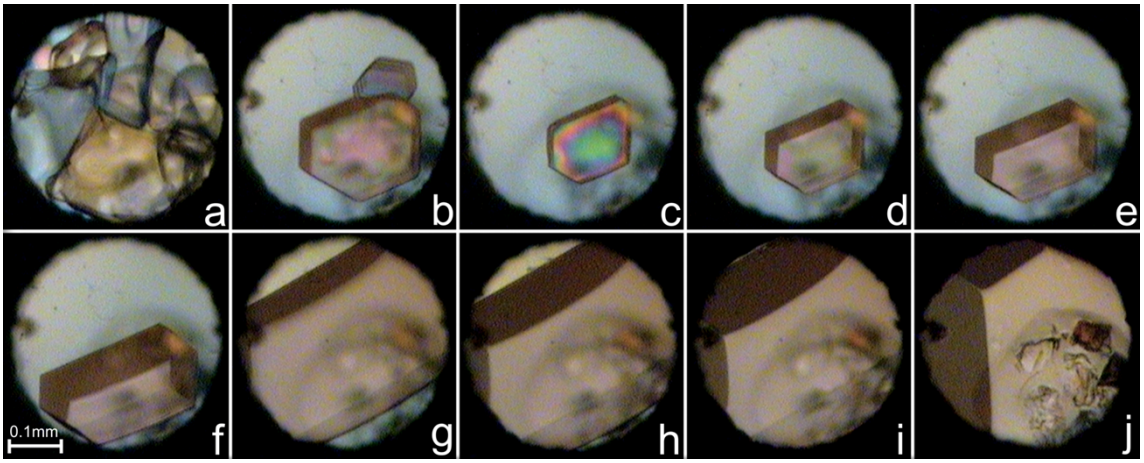

Figure S5. Stages of the CH_3Br phase α single-crystal growth inside the DAC chamber: (a) polycrystal grown isothermally at 321 K; (b) polycrystal-liquid equilibrium at 345 K; (c) one crystal seed at 347 K; (d-i) the single-crystal cooled to 327 K and (j) filling the DAC chamber at 295 K and 1.11 GPa. The ruby chips for pressure calibration lie in the central part of the DAC chamber.

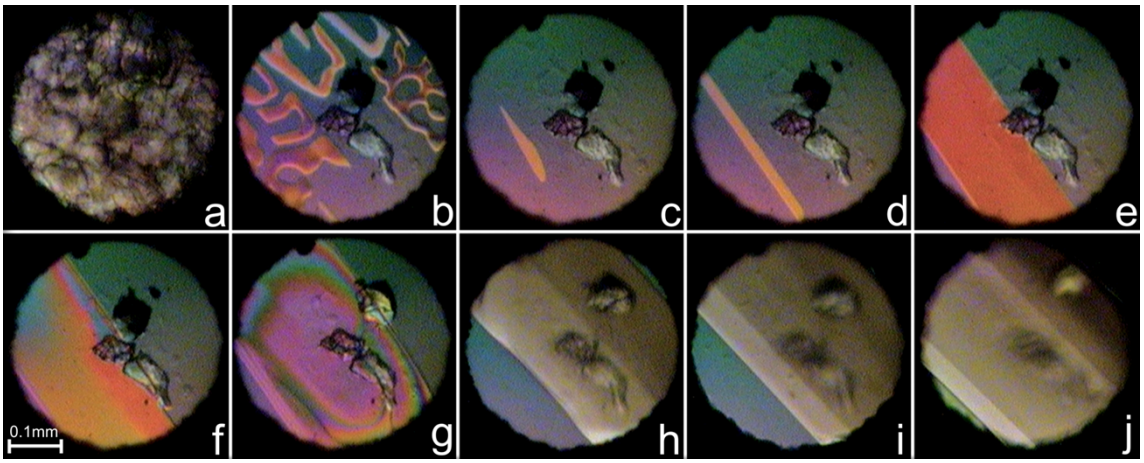

Figure S6. Stages of the CH_3Br phase α single-crystal growth inside the DAC chamber: (a) polycrystal grown isothermally at 313 K; (b) polycrystal-liquid equilibrium at 358 K; (c) one crystal seed at 360 K; (d-i) the single-crystal cooled to 341 K and (j) filling the DAC chamber at 295 K and 1.50 GPa. The ruby chips for pressure calibration lie in the central part of the DAC chamber.

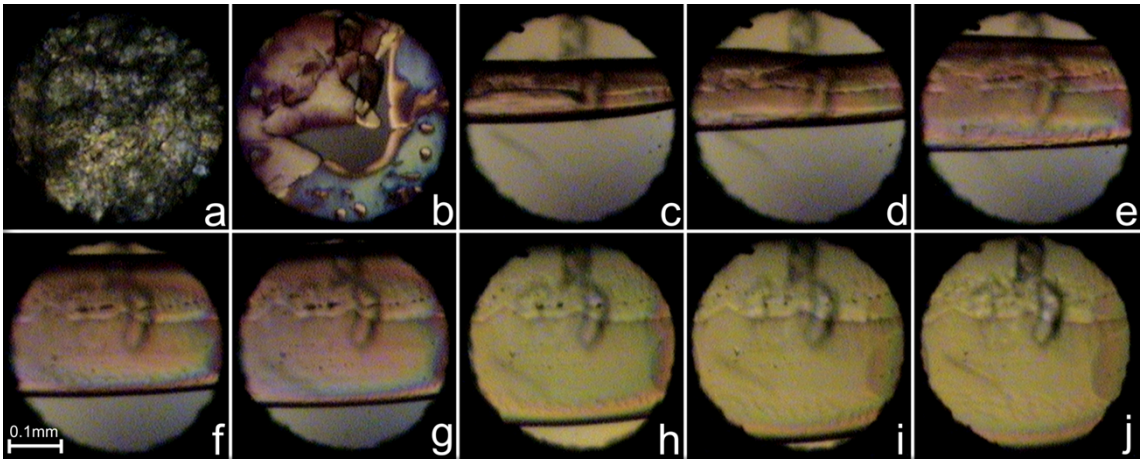

Figure S7. Stages of the CH_3Br phase β single-crystal growth inside the DAC chamber: (a) polycrystal grown isothermally at 303 K; (b) polycrystal-liquid equilibrium at 377 K; (c) one crystal seed at 381 K; (d-i) the single-crystal cooled to 365 K and (j) filling the DAC chamber at 295 K and 1.55 GPa. The ruby chips for pressure calibration lie in the upper part of the DAC chamber.

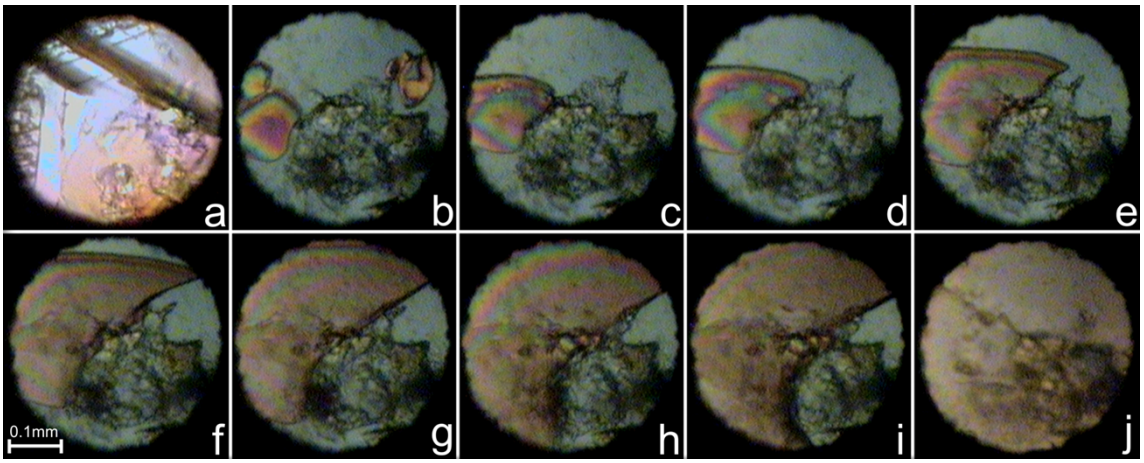

Figure S8. Stages of the CH_3Br phase β single-crystal growth inside the DAC chamber: (a) polycrystal grown isothermally at 298 K; (b) polycrystal-liquid equilibrium at 397 K; (c) one crystal seed at 399 K; (d-i) the single-crystal cooled to 394 K and (j) filling the DAC chamber at 295 K and 1.83 GPa. The ruby chips for pressure calibration lie in the central part of the DAC chamber.

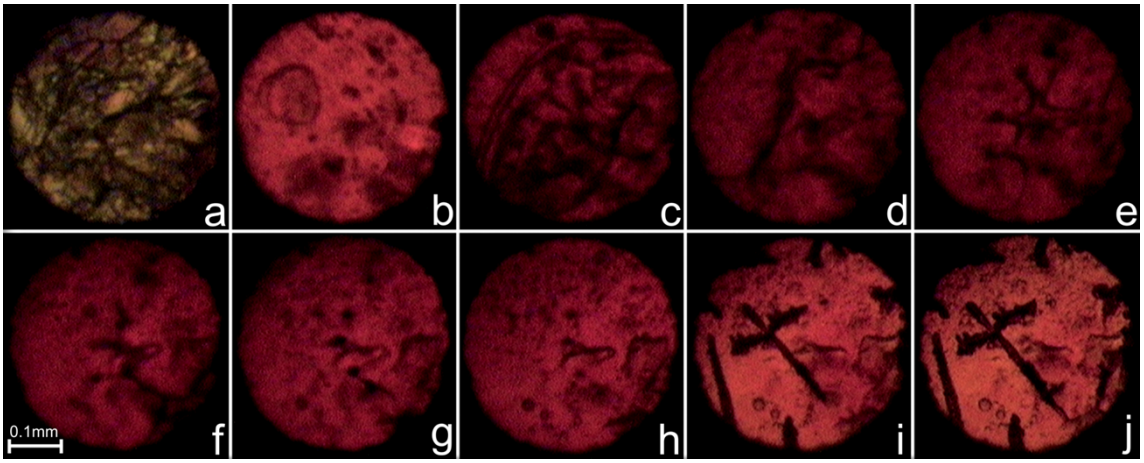

Figure S9. Stages of the CH_3Br phase β single-crystal growth inside the DAC chamber: (a) polycrystal grown isothermally at 406 K; (b) one crystal seed at 437 K; (c-i) the single-crystal cooled to 382 K and (j) filling the DAC chamber at 295 K and 2.85 GPa. The ruby chips for pressure calibration lie in the right part of the DAC chamber.

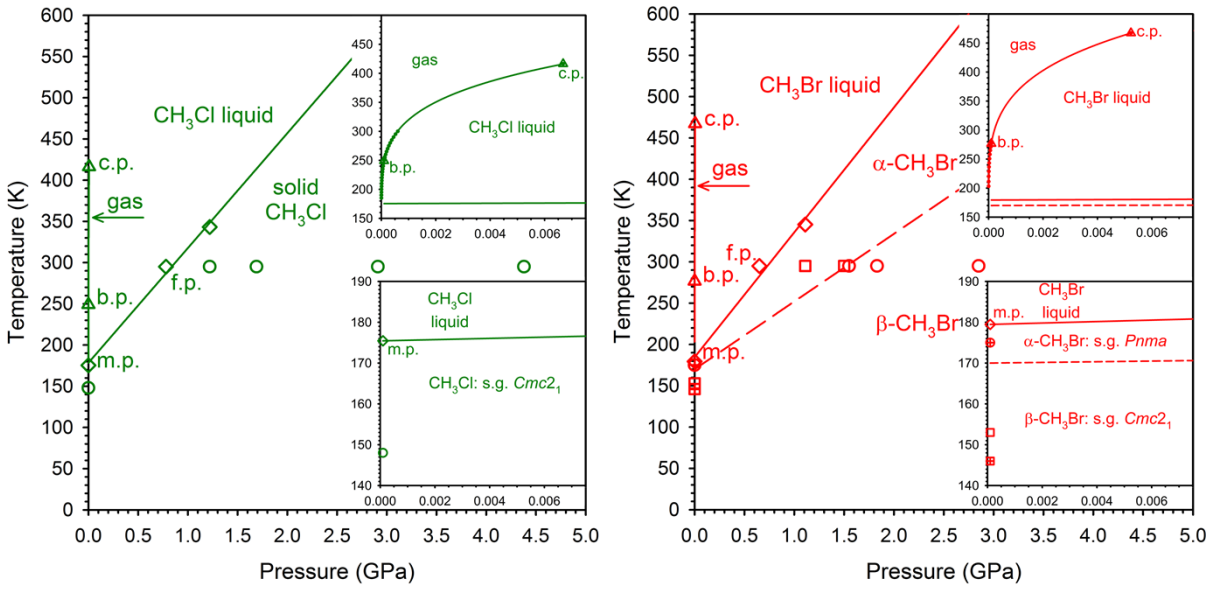

Figure S10. Phase diagrams of CH_3Cl (green) and CH_3Br (red): the boiling points at 0.1 MPa (249.1 and 276.7 K; b.p.), melting points at 0.1 MPa (175.5 and 179.5 K; m.p.) and the critical points (c.p. 6.68 MPa/416.3 K and 5.23 MPa/467.2 K) after (Egan, C. J. & Kemp, J. D. (1938). *J. Am. Chem. Soc.* **60**, 2097-2101; Lide, D. R. *CRC Handbook of Chemistry and Physics*, 90th ed., CRC Press Inc., Boca Raton, FL, 2010); the freezing points (f.p.) at 295 K from our DAC experiment; the freezing lines obtained from the m.p. at 0.1 MPa, f.p. at 0.78 GPa/295 K and 0.65 GPa/295 K and from melting points at 1.22 GPa and 1.11 GPa (our optical observations of CH_3Cl and CH_3Br melting in the DAC − spectroscopic pressure calibration and temperature measured by a thermocouple – diamonds); diffractometric determinations of CH_3Cl (green circles), CH_3Br phase α (red squares), CH_3Br phase β (red circles), CD_3Br phase α (red square crossed) and CD_3Br phase β (red circle crossed); The red dashed line shows the solid-solid border between phases α-CH_3Br and β-CH_3Br. The enhanced gas-liquid regions are shown in the upper insets: the experimental vapour-pressure data (green and red circles after Egan, C. J. & Kemp, J. D. (1938). *J. Am. Chem. Soc.* **60**, 2097-2101; Lide, D. R. *CRC Handbook of Chemistry and Physics*, 90th ed., CRC Press Inc., Boca Raton, FL, 2010) and the gas-liquid boundary extrapolation (green and red lines); the enhanced liquid-solid regions are shown in the lower insets. Note that the boiling lines were determined below 0.1 MPa, however short of reaching the triple points.

Table S1. Crystal data and details of the refinements of CH_3Cl at 1.22, 1.69, 2.91 and 4.38 GPa (all at 295 K).

	CH_3Cl	**CH_3Cl**	**CH_3Cl**	**CH_3Cl**
Pressure (GPa)	1.22(2)	1.69(2)	2.91(2)	4.38(2)
Temperature (K)	295(2)	295(2)	295(2)	295(2)
Formula weight	50.48	50.48	50.48	50.48
Crystal colour	colourless	colourless	colourless	colourless
Crystal size (mm)	0.27 x 0.26 x 0.20	0.25 x 0.25 x 0.20	0.25 x 0.25 x 0.20	0.28 x 0.28 x 0.20
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$
Unit cell dimensions (Å; °) a =	6.314(10)	6.183(10)	6.018(5)	5.967(15)
b =	5.031(9)	4.904(5)	4.832(11)	4.708(4)
c =	7.334(9)	7.317(17)	7.035(11)	6.984(15)
Volume (Å^3)	232.9(6)	221.9(7)	204.6(6)	196.2(7)
Z	4	4	4	4
D_x (g cm^{-3})	1.440	1.511	1.639	1.709
Wavelength MoKα, λ (Å)	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	1.19	1.25	1.35	1.41
F(000) (e)	104	104	104	104
2θ max (°)	54.56	53.82	55.32	55.36
Min./Max. indices h,k,l	-7/7, -3/3, -9/9	-7/7, -5/5, -4/4	-7/7, -3/3, -8/7	-4/4, -5/5, -6/6
Reflections collected/unique	472/120	469/94	416/103	408/69
R_{int}	0.0453	0.0409	0.0226	0.0390
Observed reflections (I>2σ(I))	107	82	98	66
Data/parameters	120/13	94/13	103/14	69/14
Goodness of fit on F^2	1.216	1.283	1.111	1.278
Final R_1 indices (I>2σ(I))	0.0302	0.0140	0.0128	0.0208
R_1/wR_2 indices (all data)	0.0357/0.0530	0.0190/0.0216	0.0136/0.0221	0.0212/0.0476
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0.12, -0.10	0.06, -0.07	0.07, -0.08	0.11, -0.12
Flack parameter	0.1(3)	0.37(17)	0.2(2)	0.7(4)
Weighting scheme: x; y[a]	0; 0.36	0.0055; 0.01	0.0068; 0.06	0.0266; 0.04
Absorption corrections	DAC, gasket and sample crystal	DAC, gasket and sample crystal	DAC, gasket and sample crystal	DAC, gasket and sample crystal
DAC transmission min/max	0.91 / 0.99	0.91 / 1.00	0.91 / 0.99	0.91 / 0.99
Gasket shadowing min/max	0.52 / 0.90	0.52 / 0.92	0.56 / 0.90	0.60 / 0.91
Sample transmission min/max	0.74 / 0.76	0.75 / 0.78	0.75 / 0.78	0.74 / 0.76

[a] $w = 1/(\sigma^2(Fo^2)+x^2P^2+yP)$, where $P=(\mathrm{Max}(Fo^2, 0)+2Fc^2)/3$.

Table S2. Crystal data and details of the refinements of CH_3Br at 1.11, 1.50, 1.55, 1.83 and 2.85 GPa (all at 295 K).

	CH_3Br phase α	**CH_3Br phase α**	**CH_3Br phase β**	**CH_3Br phase β**	**CH_3Br phase β**
Pressure (GPa)	1.11(2)	1.50(2)	1.55(2)	1.83(2)	2.85(2)
Temperature (K)	295(2)	295(2)	295(2)	295(2)	295(2)
Formula weight	94.94	94.94	94.94	94.94	94.94
Crystal colour	colourless	colourless	colourless	colourless	colourless
Crystal size (mm)	0.27 x 0.27 x 0.20	0.28 x 0.28 x 0.20	0.28 x 0.27 x 0.16	0.24 x 0.24 x 0.18	0.24 x 0.24 x 0.16
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$
Unit cell dimensions (Å; °) *a* =	4.372(5)	4.331(3)	6.387(9)	6.378(10)	6.236(5)
b =	6.375(5)	6.358(5)	5.163(5)	5.133(9)	5.017(6)
c =	9.196(9)	9.142(6)	7.492(5)	7.413(9)	7.394(19)
Volume (Å^3)	256.3(4)	251.8(3)	247.1(5)	242.7(6)	231.3(7)
Z	4	4	4	4	4
D_x (g cm^{-3})	2.460	2.505	2.553	2.598	2.726
Wavelength MoKα, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	15.63	15.91	16.21	16.50	17.32
F(000) (e)	176	176	176	176	176
2θ max (°)	54.82	54.56	53.58	53.88	54.06
Min./Max. indices *h,k,l*	-3/3, -8/8, -10/10	-5/5, -6/6, -6/6	-2/2, -6/6, -9/9	-5/5, -5/5, -7/7	-7/7, -6/6, -2/2
Reflections collected/unique	987/125	868/75	492/115	463/121	468/73
R_{int}	0.0629	0.0387	0.0479	0.0346	0.0265
Observed reflections (I>2σ(I))	95	70	89	97	65
Data/parameters	125/15	75/15	115/14	121/13	73/13
Goodness of fit on F^2	1.053	1.041	1.171	1.196	1.123
Final R_1 indices (I>2σ(I))	0.0253	0.0139	0.0390	0.0273	0.0145
R_1/wR_2 indices (all data)	0.0416/0.0484	0.0200/0.0243	0.0473/0.0756	0.0363/0.0545	0.0171/0.0325
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0.22, -0.23	0.13, -0.15	0.29, -0.32	0.38, -0.29	0.10, -0.13
Flack parameter	–	–	0.57(19)	0.44(15)	0.40(11)
Weighting scheme: x; y[a]	0.0217; 0.14	0.0122; 0	0.0240; 2.40	0.0226; 0.47	0.0156; 0.26
Absorption corrections	DAC, gasket and sample crystal	DAC, gasket and sample crystal	DAC, gasket and sample crystal	DAC, gasket and sample crystal	DAC, gasket and sample crystal
DAC transmission min/max	0.91 / 0.99	0.91 / 1.00	0.92 / 0.99	0.91 / 1.00	0.91 / 1.00
Gasket shadowing min/max	0.55 / 0.91	0.54 / 0.95	0.66 / 0.90	0.56 / 0.94	0.60 / 0.93
Sample transmission min/max	0.03 / 0.04	0.03 / 0.04	0.05 / 0.07	0.04 / 0.05	0.04 / 0.06

[a] $w = 1/(\sigma^2(Fo^2)+x^2P^2+yP)$, where $P=(\mathrm{Max}(Fo^2, 0)+2Fc^2)/3$.

Table S3. Atomic coordinates ($\cdot 10^4$), U_{eq} and U_{iso} ($Å^2 \cdot 10^3$) for CH_3Cl at 1.22, 1.69, 2.91 and 4.38 GPa.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
1.22 GPa/295 K				
Cl1	0	1338(5)	2494(4)	67(1)
C1	0	3717(18)	4228(4)	54(3)
H1	0	5463	3700	82
H2	1242	3497	4969	82
H3	−1242	3497	4969	82
1.69 GPa/295 K				
Cl1	0	1289(1)	2460(4)	56(1)
C1	0	3762(4)	4263(4)	37(1)
H1	0	5562	3748	55
H2	1268	3524	5004	55
H3	−1268	3524	5004	55
2.91 GPa/295 K				
Cl1	0	1228(2)	2523(3)	38(1)
C1	0	3906(12)	4199(3)	44(2)
H1	0	5657	3555	66
H2	1303	3765	4981	66
H3	−1303	3765	4981	66
4.38 GPa/295 K				
Cl1	0	1199(2)	2521(8)	42(1)
C1	0	3856(10)	4202(8)	32(5)
H1	0	5668	3571	47
H2	1314	3693	4988	47
H3	−1314	3693	4988	47

Table S4. Atomic coordinates ($\cdot 10^4$), U_{eq} and U_{iso} ($Å^2 \cdot 10^3$) for CH_3Br at 1.11, 1.50, 1.55, 1.83 and 2.85 GPa.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
1.11 GPa/295 K				
Br1	1537(3)	2500	964(1)	59(1)
C1	3299(31)	2500	−939(10)	61(4)
H11	3099	1130	−1361	74
H12	5426	2864	−874	74
H13	2258	3507	−1537	74
1.50 GPa/295 K				
Br1	1538(1)	2500	964(1)	52(1)
C1	3449(14)	2500	−904(10)	54(4)
H11	3689	1078	−1237	64
H12	5439	3158	−836	64
H13	2185	3265	−1583	64
1.55 GPa/295 K				
Br1	0	1207(3)	2464(17)	54(3)
C1	0	3859(29)	4259(17)	63(31)
H1	0	5530	3697	95
H2	1227	3687	4989	95
H3	−1227	3687	4989	95
1.83 GPa/295 K				
Br1	0	1205(2)	2446(13)	57(1)
C1	0	3774(32)	4277(13)	59(5)
H1	0	5473	3736	88
H2	1229	3576	5012	88
H3	−1229	3576	5012	88
2.85 GPa/295 K				
Br1	0	1166(3)	2391(28)	43(3)
C1	0	4010(14)	4332(28)	44(79)
H1	0	5739	3775	66
H2	1257	3820	5070	66
H3	−1257	3820	5070	66