Supplementary Information

Table S1 Crystal data and structure refinements details for chloro-, dichloro- and trichloroacetonitrile.

Compound		CH_2ClCN	$CHCl_2CN$	CCl_3CN
Pressure (GPa)		1.30(5)	1.00(5)	0.90(5)
Temperature (K)		296(2)	296(2)	296(2)
Formula weight		75.50	109.94	144.39
Wavelength (Å)		0.71073	0.71073	0.71073
Crystal system		Orthorhombic	Monoclinic	Tetragonal
Space group		*Pbca*	$P2_1/c$	$I4_1cd$
Unit cell dimensions (Å,°)	*a*	7.7821(16)	5.9360(12)	15.251(2)
	b	7.0635(14)	17.940(4)	15.251(2)
	c	11.620(2)	7.5470(15)	8.1219(16)
	β	90.00	92.44(3)	90.00
Volume ($Å^3$)		638.7(2)	803.0(3)	1889.0(5)
Z		8	8	16
Calculated density (g/cm^3)		1.570	1.819	2.031
Absorption coefficient (mm^{-1})		0.904	1.394	1.759
F(000)		304	432	1120
Crystal size (mm)		0.33/0.33/0.15	0.40/0.40/0.10	0.40/0.40/0.25
θ-range for data collection (°)		4.27 to 29.14	2.93 to 29.96	2.67 to 29.29
Min/max indices: *h*, *k*, *l*		-9/8,-9/8, -11/11	-8/8, -5/5, -10/10	-7/7, -20/20, -10/10
Reflect. collected/unique/R_{int}		3723/467/0.0429	5955/640/0.1656	5562/822/0.1219
Completeness/θ_{max} (%,°)		54.4/29.14	27.2/29.96	64.5/29.29
Refinement method		Full-matrix least-squares on F^2		
Data/restrains/parameters		467/0/37	640/0/61	822/1/55
Goodness-of-fit on F^2		1.068	1.081	1.125
Final R_1/wR_2 ($I>2\sigma_1$)		0.0493/0.0995	0.0794/0.1439	0.0636/0.1613
R_1/wR_2 (all data)		0.0580/0.1043	0.2091/0.1994	0.0707/0.1724
Weighting scheme[a)]		$w=1/(\sigma^2(F_o^2)+(0.0434*P)^2+0.48*P)$	$w=1/(\sigma^2(F_o^2)+(0.0772*P)^2+0.00*P)$	$w=1/(\sigma^2(F_o^2)+(0.0915*P)^2+9.56*P)$
Max. ΔF peak and hole ($e.Å^{-3}$)		0.148/-0.249	0.272/-0.299	0.538/-0.527

[a)] $w=1/(\sigma^2 F_o^2+w_1^2*P^2+w_2*P)$, where $P=(\mathrm{Max}(F_o^2,0)+2*F_c^2)/3$

Table S2 The shortest intermolecular distances (Å) and angles (°) in chloro- and dichloroacetonirile.

	CH_2ClCN[a)] 1.30 GPa/296 K	Contact type[*)]	$CHCl_2CN$[b)] 1.00 GPa/296 K	Contact type[*)]
H···N^{i}/C···N(1)^{i}/C-H···N^{i}	2.60/3.22(1)/122		2.39/3.08(3)/127	
H···N^{ii}/C···N^{ii}/C-H···N^{ii}	2.62/3.37(1)/135		2.48/3.12(3)/123	
H···N^{iii}/C···N^{iii}/C-H···N^{iii}	2.63/3.28(1)/124		2.52/3.17(3)/124	
H···N^{iv}/C···N^{iv}/C-H···N^{iv}			2.54/3.23(3)/128	
H···Cl^{v}/C···Cl^{v}/C-H···Cl^{v}	2.79/3.53(1)/133		2.77/3.53(1)/135	
H···Cl^{vi}/C···Cl^{vi}/C-H···Cl^{vi}			2.91/3.60(2)/129	
Cl···Cl^{vii}/C-Cl···Cl^{vii}	3.82(1)/76	type I	3.50(1)/116	type I
Cl···Cl^{viii}/C-Cl···Cl^{viii}	3.82(1)/69	type I	3.50(1)/136	type I
Cl···Cl^{ix}/C-Cl···Cl^{ix}			3.52(1)/161	type II
Cl···Cl^{x}/C-Cl···Cl^{x}			3.52(1)/97	type II
Cl···Cl^{xi}/C-Cl···Cl^{xi}			3.58(1)/80	type II
Cl···Cl^{xii}/C-Cl···Cl^{xii}			3.58(1)/152	type II
Cl···Cl^{xiii}/C-Cl···Cl^{xiii}			3.58(1)/126	type I
Cl···Cl^{xiv}/C-Cl···Cl^{xiv}			3.58(1)/123	type I
Cl···N^{xv}/C-Cl···N^{xv}	3.39(1)/156		3.41(3)/66	

[a)]Symmetry codes for CH_2ClCN: (i) 0.5-*x*,0.5+*y*,*z*; (ii) 1-*x*,-*y*,-*z*; (iii) 0.5+*x*,0.5-*y*,-*z*; (v) 0.5+*x*,*y*,0.5-*z*; (vii) 1-*x*, *y*+-0.5,0.5-*z*; (viii) 1-*x*,*y*-0.5,0.5-*z*; (xv) *x*,0.5-*y*,0.5+*z*

[b)]Symmetry codes for $CHCl_2CN$: (i) *x*,1.5-*y*,0.5+*z*; (ii) 1-*x*,1.5-*y*,0.5+*z*; (iii) *x*,1.5-*y*,*z*-0.5; (iv) *x*,1.5-*y*,*z*-0.5; (v) 1+*x*,*y*,*z*; (vi) *x*,*y*,*z*; (vii) 1+*x*,*y*,*z*; (viii) *x*-1,*y*,*z*; (ix) 1-*x*,1-*y*,-*z*; (x) 1-*x*,1-*y*,-*z*; (xi) *x*-1,*y*,*z*-1; (xii) 1+*x*,*y*,1+*z*; (xiii) *x*-1,*y*, *z*; (xiv) 1+*x*,*y*,*z*; (xv) 1+*x*,1.5-*y*,0.5+*z*

[*)] G. R. Desiraju, R. Parthasarathy, J. Am. Chem. Soc. 1989, **111**, 8725.

Table S3 The shortest intermolecular distances (Å) and angles (°) in trichloroacetonirile.

	CCl_3CN[a)] 0.90 GPa/296 K	Contact type[*)]
Cl···Cl^{i}/C-Cl···Cl^{i}	3.50(1)/108	type II
Cl···Cl^{ii}/C-Cl···Cl^{ii}	3.50(1)/174	type II
Cl···Cl^{iii}/C-Cl···Cl^{iii}	3.52(1)/112	type I
Cl···Cl^{iv}/C-Cl···Cl^{iv}	3.52(1)/118	type I
Cl···N^{v}/C-Cl···N^{v}	3.21(1)/167	
Cl···N^{vi}/C-Cl···N^{vi}	3.23(1)/171	

[a)] Symmetry codes for CCl_3CN: (i) -*x*,*y*,*z*-0.5; (ii) -*x*,*y*,0.5+*z*; (iii) -*x*,-*y*,*z*; (iv) –*x*,-*y*,*z*; (v) *y*,0.5-*x*,*z*-0.75; (vi) *y*,*x*-0.5,*z*-0.25

[*)] G. R. Desiraju, R. Parthasarathy, J. Am. Chem. Soc. 1989, **111**, 8725.

Table S4 The shortest intermolecular distances (Å) and angles (°) in acetonitrile polymorphs α and β.

	α–CH_3CN[a)] 0.57 GPa/296 K	β–CH_3CN[b)] 0.63 GPa/296 K	β–CH_3CN[b)] 1.50 GPa/296 K
H···N^{i}/C···N(1)^{i}/C-H···N^{i}	2.640/3.600(4)/177.53	2.760(6)/3.721(2)/171(2)	2.618(4)/3.574(3)/169(2)
H···N^{ii}/C···N(1)^{ii}/C-H···N^{ii}	2.705/3.633(6)/162.71	2.760(6)/3.721(2)/171(2)	2.618(4)/3.574(3)/169(2)
H···N^{iii}/C···N(1)^{iii}/C-H···N^{iii}	3.070/4.021(6)/170.91	2.772(6)/3.740(4)/175(4)	2.610(5)/3.579(3)/178(3)

[a)]Symmetry codes for phase α: (i) 1+x, 1.5-y, z-0.5; (ii) 1-x, y-0.5, 1.5-z; (iii) 2-x, y-0.5, 1.5-z; (iv) x, 1.5-y, 0.5+z; (v) 1-x, 1-y, 1-z

[b)]Symmetry codes for phase β: (i) -0.5+x, 0.5-y, z-0.5; (ii) 0.5-x, 0.5-y, 0.5+z; (iii) x, y-1, z; (iv) -x, 1-y, 0.5+z; (v) -x, -y, 0.5+z

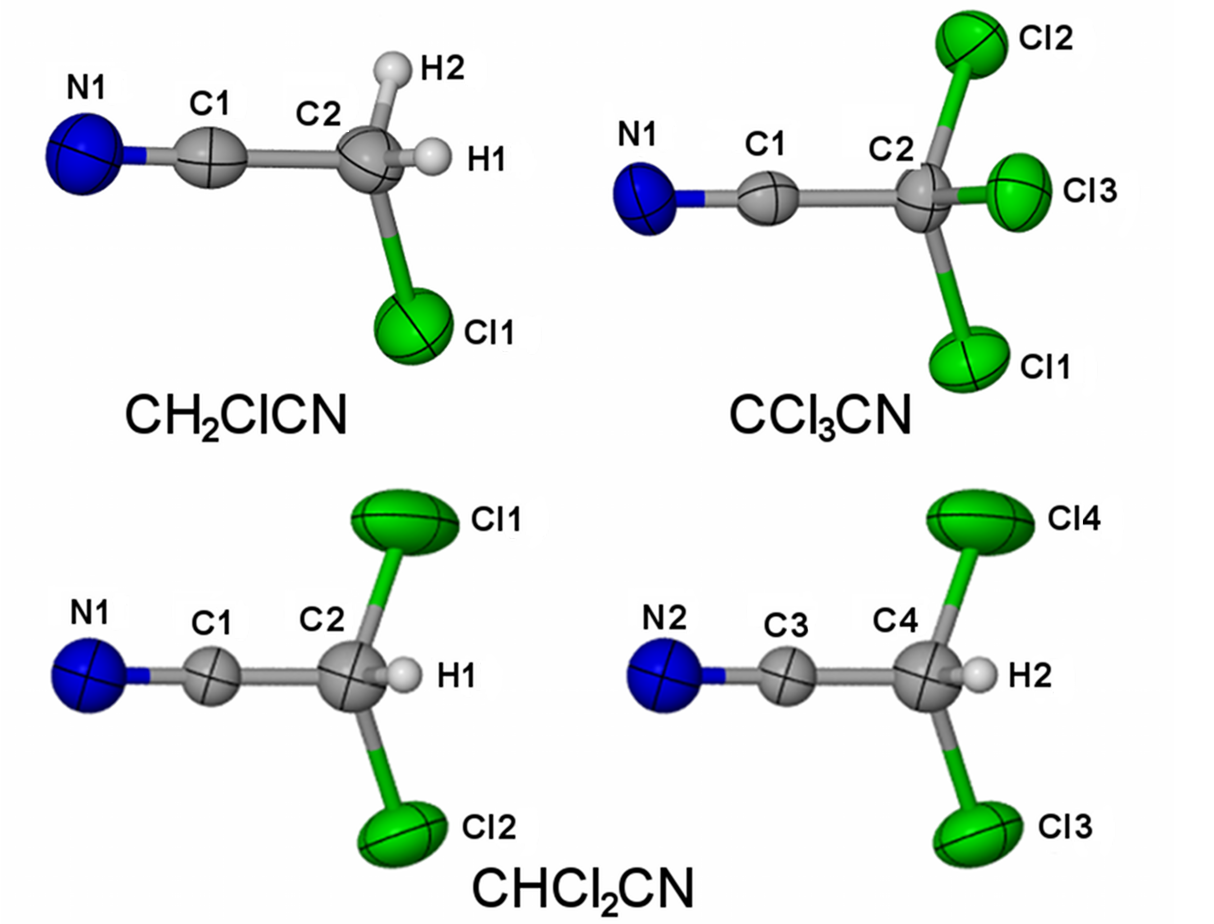

Figure S1. ORTEP drawings of the CH_2ClCN, $CHCl_2CN$ and CCl_3CN molecules determined at high pressure. Thermal ellipsoids have been drawn at the 50% probability level.

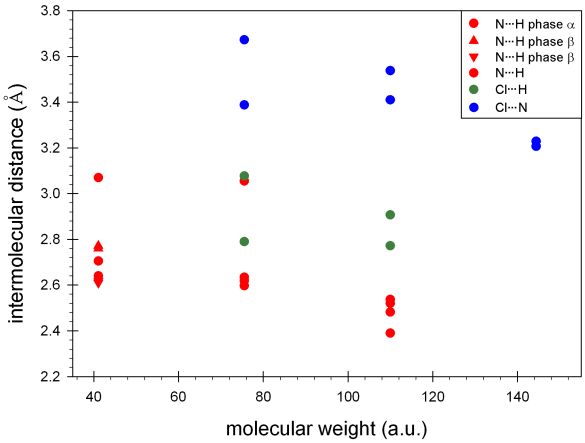

Figure S2. The shortest intermolecular distances in acetonitrile, chloro-, dichloro- and trichloroacetonitrile plotted against their molecular weight.