Supplementary Information

Table S1 Crystal data and structure refinements details for high-pressure measurements of dabcoHI with methanol.

Formula		Dabco2HI:3CH_3OH $[C_6H_{14}N_2]^+2I^-$:3CH_3OH]	DabcoCH$_3$I:2CH_3OH $[C_7H_{15}N_2]^+I^-$:CH_3OH]
Pressure (GPa)		1.80(5) GPa	2.40(5) GPa
Temperature (K)		296(2)	296(2)
Formula weight (g/mol)		464.12	318.19
Wavelength (Å)		0.71073	0.71073
Crystal system		Monoclinic	Monoclinic
Space group		$P2_1/m$	$P2_1/m$
Unit cell dimensions (Å,°)	a	7.385(3)	8.88(2)
	b	7.782(5)	6.5844(4)
	c	12.82(8)	10.335(10)
	β	95.02(12)	108.69(19)
Volume (Å^3)		734(5)	572.6(15)
Z		2	2
Calculated density (g/cm^3)		2.101	1.845
Absorption coefficient (mm^{-1})		4.284	2.777
F(000)		448	320
Crystal size (mm)		0.26/0.10/0.10	0.42/0.27/0.09
θ-range for data collection (°)		2.77 to 28.92	2.64 to 29.20
Min/max indices: h, k, l		-10/10, -7/7, -4/4	-7/6, -9/9, -13/13
Reflect. Collected/ unique (R_{int})		639/281 (0.0847)	3760/328 (0.0683)
Refinement method		Full-matrix least-squares on F^2	
Completeness (%)		13.5	19.6
Data/restrains/parameters		281/7/47	328/5/42
Goodness-of-fit on F^2		1.386	1.086
Final R_1/wR_2 ($I>2\sigma_1$)		0.0617/0.1424	0.0396/0.0841
R_1/wR_2 (all data)		0.1172/0.1682	0.0413/0.0903
Weighting scheme[a)]		1/[sigma^2(Fo^2)+(0.0316*P)^2+23.92*P]	1/[sigma^2(Fo^2)+(0.0436*P)^2+2.81*P]
Largest diff. peak and hole (e.Å^{-3})		0.625/-0.672	0.296/-0.301

[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 Shortest intermolecular distances (Å,°) in dabco2HI:3CH3OH at 1.80 GPa/296 K.

DH···A	H···A	D···A	D-H···A	Symmetry codes
O(11)H···O(12)^{i}	2.02	2.79(7)	157.66	x,y,z
N(1)H···O(11)^{i}	2.23	2.93(4)	132.91	x,y,z; x,0.5-y,z
N(2)H···O(11)^{i}	2.39	3.06(5)	130.44	x-1,0.5-y,z; x-1,y,z
C(3)H···O(11)^{i}	2.70	3.12(5)	106.11	x,y,z
O(12)H···I(1)^{i}	2.70	3.51(8)	167.76	1-x,y-0.5,2-z
C(3)H···I(2)^{i}	3.01	3.80(7)	139.64	x,y,z
C(11)H···I(2)^{i}	3.02	3.95(6)	164.54	1-x,0.5+y,1-z
N(2)H···I(1)^{i}	3.14	3.69(8)	121.21	x-1,y,z
C(3)H···I(1)^{i}	3.15	3.92(7)	137.43	x,y,z
C(3)H···I(1)^{i}	3.16	3.70(6)	116.54	1-x,y-0.5,2-z
C(4)H···I(2)^{i}	3.16	3.86(7)	130.35	x,y,z
C(2)H···I(2)^{i}	3.18	3.59(11)	107.29	-x,0.5+y,1-z
C(4)H···I(1)^{i}	3.17	3.79(6)	123.22	x-1,y,z

Table S3 Shortest intermolecular distances (Å,°) in dabcoCH_3I:2CH_3OH at 2.40 GPa.

DH···A	H···A	D···A	D-H···A	Symmetry code
O(12)H···N(1)^{i}	1.92	2.74(4)	179.94	x,y,z
C(3)H···O(12)^{i}	2.34	3.16(1)	140.70	1-x,y-0.5,-z
C(4)H···O(11)^{i}	2.50	2.91(2)	105.40	1-x,y-0.5,-z
C(1)H···O(12)^{i}	2.56	3.31(1)	133.96	1-x,y-0.5,-z
C(3)H···O(11)^{i}	2.61	2.98(1)	103.33	1-x,y-0.5,-z
O(11)H···I(1)^{i}	2.70	3.48(4)	159.46	x,y,z
C(5)H···I(1)^{i}	3.03	3.97(2)	167.85	x,y,z-1
C(11)H···I(1)^{i}	3.06	4.02(3)	176.17	1-x,0.5+y,1-z
C(5)H···I(1)^{i}	3.10	4.02(2)	163.22	-x,0.5+y,-z