Supporting Information

Pressure-induced preference for solvation of 5,6-dimethylbenzimidazole

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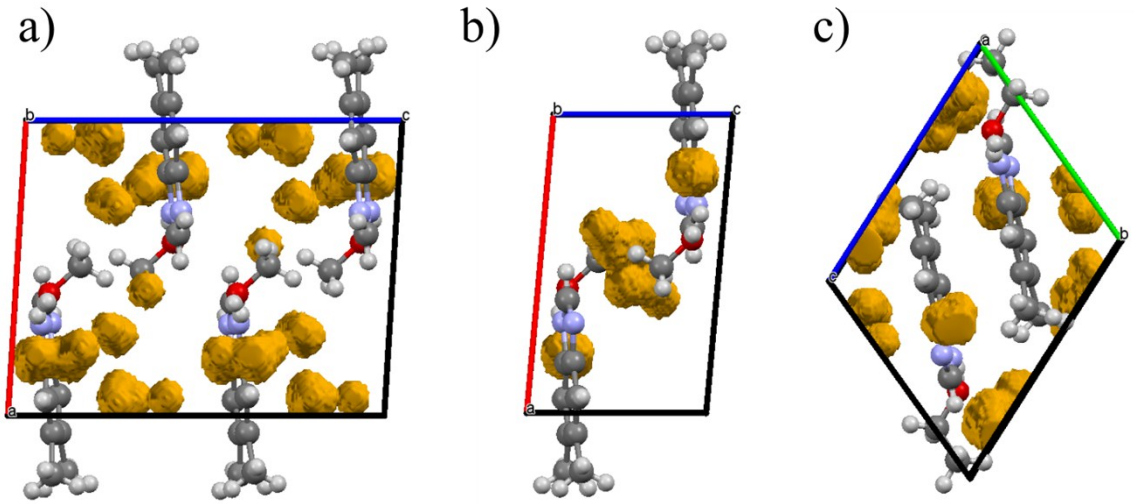


Figure S1. Molecular voids calculated with Mercury program (Probe Radius: 0.6 Å; Approx. Grid Spacing: 0.1 Å) for (a) dMBzIm·MeOH phase α at 0.92 GPa, void volume:44.07 Å^3 (4.8% of the unit-cell volume); (b) dMBzIm·MeOH phase β at 1.53 GPa, void volume: 14.98 Å^3 (3.4% of the unit-cell volume); (c) dMBzIm·EtOH at 0.84 GPa, void volume 32.88 Å^3 (6.5% of the unit-cell volume).

Table S1. The crystal data and experimental details of 5,6-dimethylbenzimidazole methanol (dMBzIm·MeOH) solvate.

		dMBzIm·MeOH phase *α*	**dMBzIm·MeOH phase *α***	**dMBzIm·MeOH phase *β***	**dMBzIm·MeOH phase *β***	**dMBzIm·MeOH phase *β***	**dMBzIm·MeOH phase *β***
Pressure (GPa)		0.92(2)	1.24(2)	1.53(2)	1.90(2)	2.19(2)	2.31(2)
Temperature (K)		296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Formula weight		178.23	178.23	178.23	178.23	178.23	178.23
Crystal colour		colourless	colourless	colourless	colourless	colourless	colourless
Crystal size (mm)		0.35x0.35x0.25	0.35x0.30x0.20	0.40x0.30x0.20	0.30x0.35x0.16	0.25x0.25x0.30	0.25x0.25x0.15
Crystal system		monoclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group		$P2_1/c$	$P2_1/c$	P-1	P-1	P-1	P-1
Unit cell (Å)	*a*	9.977(7)	9.960(12)	10.110(6)	10.037(2)	10.007(3)	10.027(10)
	b	7.1746(3)	7.1574(10)	7.1000(7)	7.0477(10)	7.0202(14)	7.0054(13)
	c	12.7576(6)	12.5790(8)	6.6984(10)	6.6292(10)	6.5889(12)	6.5581(12)
	α	90	90	114.720(12)	115.381(14)	115.903(19)	116.173(19)
	β	93.545(13)	93.71(2)	94.61(2)	94.711(14)	94.821(18)	94.86(3)
	γ	90	90	90.202(19)	90.103(14)	90.068(19)	90.02(4)
Volume (Å^3)		911.4(6)	894.8(11)	435.0(3)	421.88(13)	414.53(17)	411.6(4)
Z		4	4	2	2	2	2
D_x (g cm^{-3})		1.299	1.323	1.361	1.403	1.428	1.438
Wavelength MoKα, λ (Å)		0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Absorption (mm^{-1})		0.086	0.087	0.090	0.093	0.094	0.095
F(000) (e)		384	384	192	192	192.0	192
2Θ range (°)		6.4/56.306	8.638/54.346	7.944/53.754	6.404/56.478	6.458/55	6.486/55.736
Min./Max. indices h,k,l		-3/3,-9/9,-17/16	-3/3,-5/8,-16/16	-5/5,-8/8,-8/8	-8/8,-8/8,-7/7	-8/7,-8/7,-7/7	-3/3,-9/9,-8/8
Reflections collected		6238	2386	2321	2970	2025	1828
R_{int}		0.0520	0.0403	0.0329	0.1170	0.0389	0.1078
Independent reflections		617	451	437	520	451	419
Data/restraints/parameters		617/108/122	451/72/110	437/186/110	520/78/114	451/79/125	419/186/110
Goodness of fit on F^2		1.034	1.060	1.121	1.059	1.065	1.126
Final R indexes [I>=2$\sigma_{(I)}$]		R_1=0.0501, wR_2=0.1296	R_1=0.0644, wR_2=0.1532	R_1=0.0631, wR_2=0.1619	R_1=0.0612, wR_2=0.1529	R_1=0.0525, wR_2=0.1324	R_1=0.0757 wR_2=0.1960
Final R indexes [all data]		R_1=0.1064, wR_2=0.1788	R_1=0.1198 wR_2=0.2050	R_1=0.0834, wR_2=0.1812	R_1=0.0925, wR_2=0.1813	R_1=0.0896, wR_2=0.1587	R_1=0.1133, wR_2=0.2366
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})		0.12/-0.12	0.17/-0.14	0.18/-0.13	0.19/-0.16	0.16/-0.15	0.19/-0.22
Weighting scheme: x/y[a]		0.091/0.262	0.083/1.330	0.123/0.051	0.090/0.296	0.091/0.210	0.160/0.000
Extinction coefficient		–	–	–	–	–	–

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

Table S1 - continued. The crystal data and experimental details of 5,6-dimethylbenzimidazole ethanol (dMBzIm·EtOH) solvate.

		dMBzIm·EtOH	**dMBzIm·EtOH**	**dMBzIm·EtOH**	**dMBzIm·EtOH**
Pressure (GPa)		0.84(2)	1.20(2)	1.50(2)	2.17(2)
Temperature (K)		296(2)	296(2)	296(2)	296(2)
Formula weight		192.26	192.26	192.26	192.26
Crystal colour		colourless	colourless	colourless	colourless
Crystal size (mm)		0.35x0.35x0.20	0.30x0.25x0.20	0.25x0.20x0.15	0.20x0.20x0.18
Crystal system		triclinic	triclinic	triclinic	triclinic
Space group		*P*-1	*P*-1	*P*-1	*P*-1
Unit cell (Å)	*a*	7.081(2)	7.0242(16)	7.0048(7)	6.926(3)
	b	8.559(2)	8.496(2)	8.453(3)	8.343(4)
	c	9.604(3)	9.475(2)	9.3834(12)	9.223(4)
	α	67.00(2)	66.75(2)	66.49(2)	66.57(5)
	β	81.82(2)	81.96(2)	81.840(9)	81.99(4)
	γ	71.19(2)	71.38(2)	71.705(18)	72.07(5)
Volume (Å^3)		507.1(3)	492.3(2)	483.6(2)	465.2(4)
Z		2	2	2	2
D_x (g cm^{-3})		1.259	1.297	1.320	1.373
Wavelength MoKα, λ (Å)		0.71073	0.71073	0.71073	0.56085
Absorption (mm^{-1})		0.082	0.085	0.086	0.057
F(000) (e)		208	208	208	208
2Θ range (°)		5.408/58.8	6.918/56.344	7.818/54.43	7.202/60.322
Min./Max. indices h,k,l		-6/6,-11/11,-10/10	-6/6,-11/11,-10/10	-8/8,-6/6,-11/11	-12/12,-8/8,-16/16
Reflections collected		3791	3470	2897	7509
R_{int}		0.1837	0.1240	0.0513	0.1460
Independent reflections		620	582	575	1350
Data/restraints/parameters		620/197/120	582/168/119	575/84/132	1350/84/120
Goodness of fit on F^2		1.089	1.119	1.155	1.081
Final R indexes [I>=2σ$_{(I)}$]		R_1=0.0905, wR_2=0.2311	R_1=0.0957, wR_2=0.2530	R_1=0.0571, wR_2=0.1414	R_1=0.1112, wR_2=0.2820
Final R indexes [all data]		R_1=0.1535, wR_2=0.3014	R_1=0.1410, wR_2=0.3100	R1 = 0.0833, wR2 = 0.1608	R_1=0.2012, wR_2=0.3637
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})		0.18/-0.14	0.21/-0.17	0.16/-0.17	0.31/-0.32
Weighting scheme: x/y[a]		0.153/0.277	0.188/0.236	0.077/0.286	0.20/-
Extinction coefficient		–	–	0.104135	0.386845

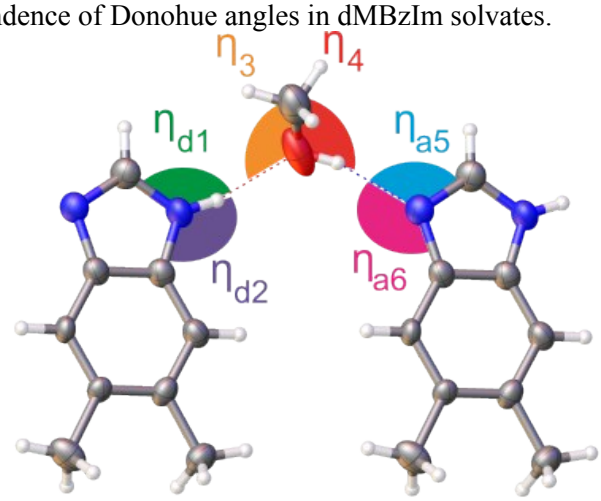
[a] $w = 1/(\sigma^2(Fo^2)+x^2P^2+yP)$, where $P=(\mathrm{Max}(Fo^2, 0)+2Fc^2)/3$.

Table S2. Pressure dependence of unit-cell volume (V), molecular volume (V/Z) of dMBzIm solvates and the volume of solvate molecules, estimated from compressibility of the solvents (Bridgman, P. W. *Proc. Am. Acad. Arts Sci.* **1942**, *74*, 399).

	Pressure (GPa)	V (Å³)	V/Z (Å³)	V_{MeOH}/V_{EtOH}*
dMBzIm·MeOH phase α	0.92(2)	911.4(6)	227.85(7)	50.86
	1.24(2)	894.8(11)	223.71(2)	49.38
dMBzIm·MeOH phase β	1.53(2)	435.0(3)	217.5(4)	48.38
	1.90(2)	421.88(13)	210.9(4)	46.63
	2.19(2)	414.53(17)	207.26(5)	45.90
	2.31(2)	411.6(4)	205.87(5)	45.28
dMBzIm·EtOH	0.84(2)	507.1(3)	253.5(5)	74.02
	1.20(2)	492.3(2)	246.1(5)	70.45
	1.50(2)	483.6(2)	241.8(4)	69.45
	2.17(2)	465.2(4)	232.6(8)	66.74

*Volume of MeOH and EtOH subtracted from solvates volume in order to calculate pure dMBzIM volumes (see Fig. 6).

Table S3. Pressure dependence of Donohue angles in dMBzIm solvates.



	Pressure (GPa)	η_{d1}	η_{d2}	η_3	η_4	η_{a5}	η_{a6}
dMBzIm·MeOH phase α	0.92(2)	123.7(10)	128.2(8)	107.0(3)	106.2(3)	122.5(10)	126.4(8)
	1.24(2)	121.5(13)	132.1(8)	108.4(5)	105.2(5)	123.6(13)	127.0(7)
dMBzIm·MeOH phase β	1.53(2)	120.5(15)	128.7(7)	99.0(6)	113.2(4)	119.1(6)	131.5(15)
	1.90(2)	118.2(8)	134.1(7)	99.3(7)	113.2(7)	119.6(9)	133.9(3)
	2.19(2)	118.1(9)	130.6(8)	96.6(6)	114.5(6)	119.1(1)	134.6(4)
	2.31(2)	118.7(16)	132.2(7)	96.8(7)	115.3(6)	118.2(11)	135.0(8)
dMBzIm·EtOH	0.84(2)	127.2(10)	126.809(17)	112.43(2)	101.33(3)	113.7(8)	139.5(10)
	1.20(2)	127.6(8)	127.3(7)	109.8(7)	103.4(10)	114.4(6)	141.1(9)
	1.50(2)	127.6(5)	127.6(5)	111.0(4)	101.3(4)	112.5(6)	142.0(3)
	2.17(2)	127.2(4)	125.8(3)	109.7(3)	102.0(4)	112.5(5)	142.5(2)

Table S4. Pressure dependence of voids volume in dMBzIm solvates. All voids were calculated with

Mercury program with Grid Spacing of 0.6 Å and Approx. Grid Spacing of 0.1 Å.

	Pressure (GPa)	V (Å^3)	% of the unit-cell volume
dMBzIm	0.11(2)	499.62	20.2
	0.22(2)	432.16	18.0
	0.33(2)	426.59	17.4
	0.64(2)	363.28	15.6
dMBzIm·MeOH phase α	0.92(2)	44.07	4.8
	1.24(2)	34.00	3.8
dMBzIm·MeOH phase β	1.53(2)	14.98	3.4
	1.90(2)	11.96	2.8
	2.19(2)	10.10	2.4
	2.31(2)	4.00	1.0
dMBzIm·EtOH	0.84(2)	32.88	6.5
	1.20(2)	20.42	4.1
	1.50(2)	12.62	2.6
	2.17(2)	8.74	1.9