Supporting information

Impact and importance of electrostatic potential calculations for predicting structural patterns of hydrogen and halogen bonding

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Table 1IR table of grinding experiments of **A1** and **A2,** ✓ indicates a positive result and × indicates a negative result

Hydrogen bond donors	**A1**	**A2**
Succinic acid **(HB1)**	✓	✓
Adipic acid **(HB2)**	✓	✓
Suberic acid **(HB3)**	✓	✓
Sebacic acid **(HB4)**	✓	✓
Dodecanedioic acid **(HB5)**	✓	✓
Glutaric acid **(HB6)**	✓	✓
Pimelic acid **(HB7)**	×	✓
Azaleic acid **(HB8)**	×	×
2-fluorobenzoic acid **(HB9)**	✓	✓
2-nitrobenzoic acid **(HB10)**	✓	✓
P-hydroxybenzoic acid **(HB11)**	×	×
Benzoic acid **(HB12)**	×	×
Mixed donors	**A1**	**A2**
4-iodotetrafluorophenol **(D1)**	✓	✓
4-bromotetrafluorophenol **(D2)**	✓	✓
4-iodotetrafluorobenzoic acid **(D3)**	✓	✓
4-bromotetrafluorobenzoic acid **(D4)**	✓	✓

Halogen bond donors	**A1**	**A2**
Pentafluoroiodobenzene **(XB1)**	✓	✓
1,2-diiodotetrafluorobenzene **(XB2)**	×	✓
1,3,5-triiodotriflurobenzene **(XB3)**	✓	✓
1,4-diiodotetrafluorobenzene **(XB4)**	✓	✓
4,4'-diiodo-1,1'-biphenyloctafluorobenzene **(XB5)**	✓	×

Table 2 Crystallographic data for the co-crystals

Code	**A1:XB1**	**A1:XB4**	**A1:HB2**	**A1**	**A1:HB9**
Formula moiety	(C_6F_5I) $(C_{10}H_7N_3)$	$(C_6F_4I_2)$ $(C_{10}H_7N_3)_2$	$(C_{10}H_7N_3)_2$ $(C_6H_{10}O_4)$	$C_{10}H_7N_3$	$(C_{10}H_7N_3)$ $(C_7H_5O_2F)$
Empirical formula	$C_{16}H_7F_5IN_3$	$C_{26}H_{14}F_4I_2N_6$	$C_{26}H_{24}N_6O_4$	$C_{10}H_7N_3$	$C_{17}H_{12}FN_3O_2$
Molecular weight	463.15	740.23	484.51	169.19	309.30
Color, Habit	Colorless, Prism	Bronze, Plate	Colorless, Plate	Orange, Plate	Bronze, Prism
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group, *Z*	*P*2(1)/*c*, 4	$P\bar{1}$, 1	*P*2(1)/*c*, 2	*C*2/*c*, 24	*P*2(1)/*n*, 4
a, Å	7.8304(9)	6.6906(14)	6.9843(6)	10.9465(10)	6.3976(15)
b, Å	15.1834(18)	9.568(2)	25.501(2)	8.6731(8)	20.616(5)

c, Å	12.9152(15)	10.618(2)	6.8129(6)	50.527(5)	10.876(3)
α, º	90	64.954(6)	90	90	90
β, º	103.176(5)	79.728(5)	108.111(4)	93.861(4)	98.126(9)
γ, º	90	87.328(5)	90	90	90
Volume, Å^3	1495.1(3)	605.6(2)	1153.32(17)	4786.2(8)	1420.1(6)
Density, g/cm^3	2.058	2.030	1.395	1.409	1.447
T, ºK	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal size, min x mid x max	0.12 x 0.18 x 0.38	0.14 x 0.28 x 0.34	0.08 x 0.36 x 0.44	0.08 x 0.24 x 0.26	0.14 x 0.26 x 0.42
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	2.203	2.657	0.097	0.089	0.107
Trans min / max	0.4882 / 0.7779	0.4653 / 0.7074	0.9584 / 0.9923	0.9771 / 0.9929	0.9566 / 0.9852
θ_{min}, º	2.10	2.15	3.07	3.04	1.98
θ_{max}, º	32.62	33.04	32.05	30.03	32.62
Reflections					
collected	17912	15546	11766	21202	15510
independent	5100	4039	3681	6479	4619
observed	4227	3909	2796	3499	3314
R_{int}	0.0227	0.0325	0.0251	0.0823	0.0513
Threshold expression	> 2σ(*I*)	> 2σ(*I*)	> 2σ(*I*)	> 2σ(*I*)	> 2σ(*I*)
No. parameters	226	172	166	352	221
No. restraints	0	0	0	0	0
R_1 (observed)	0.0263	0.0181	0.0477	0.0697	0.0504
wR_2 (all)	0.0643	0.0464	0.1309	0.2101	0.1439
Goodness of fit (all)	1.070	1.105	1.097	1.065	1.104
ρ_{max}, ρ_{min}, e Å^{-3}	0.688, -0.540	0.426, -1.022	0.342, -0.252	0.616, -0.279	0.362, -0.252
2θ limit, º	31.00	31.00	30.00	27.50	30.00
Completeness to 2θ limit	0.934	0.965	0.983	0.976	0.984
Code	**A1:HB6**	**A1:D1**	**A2:XB3**	**A2:XB2**	
Formula moiety	$(C_{10}H_7N_3)_2$ $(C_5H_8O_4)$	$(C_{10}H_7N_3)_2$ $(C_7HF_4IO_2)$	$(C_6H_5N_3)$ $(C_6F_3I_3)$	$(C_6H_5N_3)$ $(C_6F_4I_2)$	
Empirical formula	$C_{25}H_{22}N_6O_4$	$C_{27}H_{15}F_4IN_6O_2$	$C_{12}H_5F_3I_3N_3$	$C_{12}H_5F_4I_2N_3$	
Molecular weight	470.49	658.35	628.89	520.99	
Color, Habit	Colorless, Needle	Bronze, Plate	Colorless, Prism	Colorless, Prism	
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	
Space group, *Z*	*Fdd*2, 8	*P*1, 1	*P*2(1)/*n*, 4	*P*2$_1$, 2	
a, Å	28.065(11)	6.6580(8)	9.3698(6)	8.1237(17)	
b, Å	36.966(14)	9.8155(11)	13.7351(9)	7.1542(15)	
c, Å	4.2708(16)	10.4663(13)	12.2408(8)	12.318(3)	
α, º	90	65.256(4)	90	90	
β, º	90	79.993(4)	90.6496(15)	92.502(7)	
γ, º	90	84.833(4)	90	90	
Volume, Å^3	4431(3)	611.63(13)	1575.23(18)	715.2(3)	
Density, g/cm^3	1.411	1.787	2.652	2.419	
T, ºK	120(2)	120(2)	120(2)	120(2)	
Crystal size, min x mid x max	0.04 x 0.06 x 0.38	0.16 x 0.42 x 0.44	0.32 x 0.38 x 0.40	0.08 x 0.14 x 0.36	

X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	0.099	1.380	5.979	4.437
Trans min / max	0.9633 / 0.9960	0.5820 / 0.8094	0.1984 / 0.2506	0.642 / 0.718
θ_{min}, °	5.81	2.17	2.23	2.510
θ_{max}, °	31.67	31.85	32.07	32.045
Reflections				
collected	5500	22351	16602	10644
independent	2425	6827	4882	4292
observed	1620	6772	4468	4187
R_{int}	0.0599	0.0215	0.0256	0.0233
Threshold expression	> 2σ(I)	> 2σ(I)	> 2σ(I)	> 2σ(I)
No. parameters	162	324	190	190
No. restraints	1	75	0	1
R_1 (observed)	0.0533	0.0257	0.0288	0.0180
wR_2 (all)	0.1260	0.0626	0.0598	0.0502
Goodness of fit (all)	0.986	1.050	1.210	1.113
ρ_{max}, ρ_{min}, e Å^{-3}	0.226, -0.218	0.760, -0.300	0.681, -1.055	0.898, -0.710
2θ limit, °	30.00	30.00	30.00	30.00
Completeness to 2θ limit	0.963	0.907	0.989	0.997

Crystallography Experimental Details

All datasets were collected on a Bruker APEX II system using MoKα radiation. Data were collected using APEX2 software.[1] Initial cell constants were found by small widely separated "matrix" runs. Data collection strategies were determined using COSMO.[2] Scan speed and scan widths were chosen based on scattering power and peak rocking curves. All datasets were collected at -153 °C using an Oxford Cryostream low-temperature device.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT,[3]using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. Lorenz and polarization corrections were applied. Multi-scan absorption corrections were performed with SADABS.[4]

Data were reduced with SHELXTL.[5] The structures were solved in all cases by direct methods without incident. Except as noted, hydrogen atoms were located in idealized positions and were treated with a riding model. All non-hydrogen atoms were assigned anisotropic thermal parameters. Refinements continued to convergence, using the recommended weighting schemes.

A1HB6: Coordinates of the carboxylic acid proton H31 was allowed to refine.

A1HB9: The asymmetric unit contains one molecule each of the triazole-based ligand and aromatic carboxylic acid. The aromatic carboxylic acid molecule is disordered over two closely related positions. The same coordinates have been utilized for atoms occupying the same site using the EXYZ command. Thermal parameters for closely located atoms were pairwise constrained using the EADP command. Coordinates of the carboxylic acid proton H31 was allowed to refine.

A1HB2: Coordinates of the carboxylic acid proton H31 was allowed to refine.

A1D1: The asymmetric unit contains two molecules of the triazole-based ligand and one molecule of the aromatic carboxylic acid. The aromatic carboxylic acid molecule is disordered over two closely related positions, thus representing different orientations. Relative populations were allowed to refine. Thermal parameters for closely located atoms were pairwise constrained using EADP commands. Geometry of the aromatic ring was restrained using the SAME command. The bond distances were fixed to idealized distances using the DFIX command.

References

1. APEX2 v2013.10-0, © 2013, Bruker Analytical X-ray Systems, Madison, WI.
2. COSMO v1.61, © 1999 - 2009, Bruker Analytical X-ray Systems, Madison, WI.
3. SAINT v8.34a, © 1997 - 2013, Bruker Analytical X-ray Systems, Madison, WI.
4. SADABS v2012/1, © 2012, Bruker Analytical X-ray Systems, Madison, WI.
5. SHELXTL v2008/4, © 2008, Bruker Analytical X-ray Systems, Madison, WI.