Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Competition between hydrogen bonds and halogen bonds: A structural study

Janaka C. Gamekkanda ,[a] Abhijeet S. Sinha, [a] John Desper, [a] Marijana Đaković, [b] and Christer B. Aakeröy *[a]

[a] *Department of Chemistry, Kansas State University, Manhattan, KS, 66506, USA.*
[b] *Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia*

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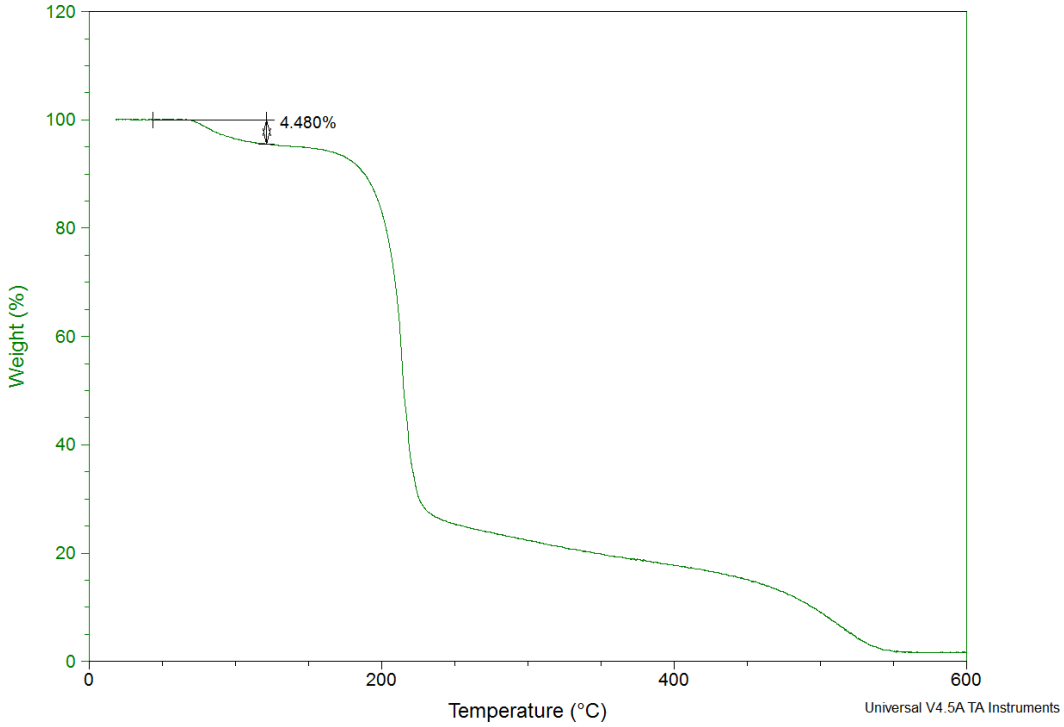

Figure S1. TGA trace of **D1**.H_2O

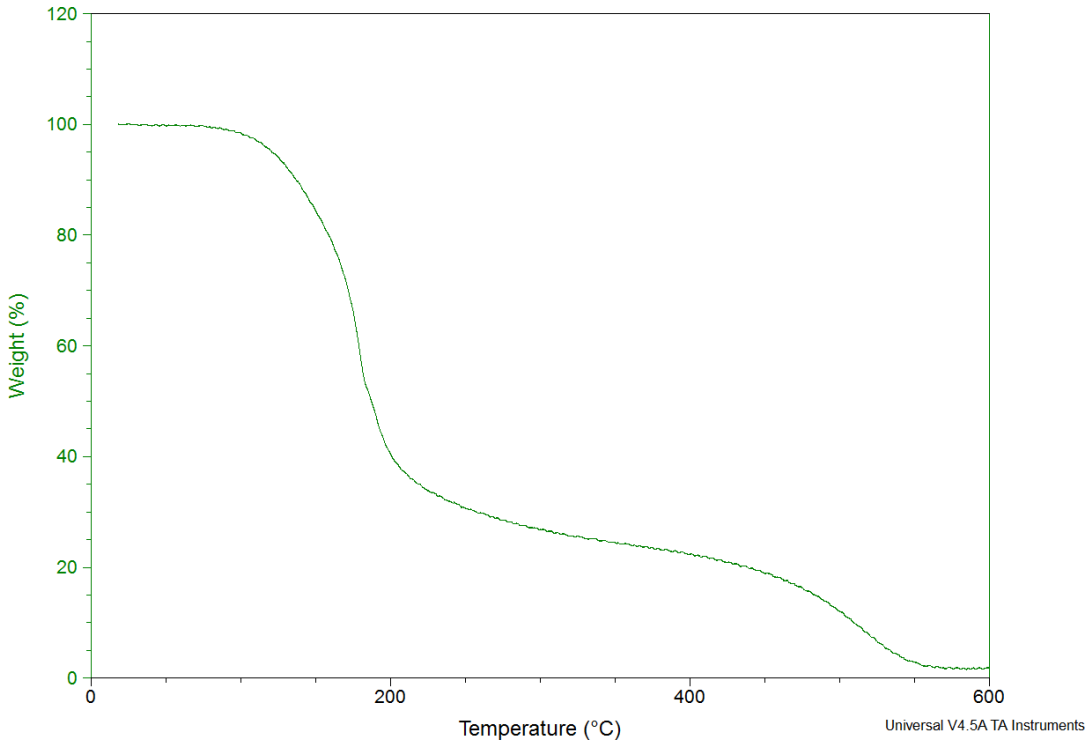

Figure S2. TGA trace of **D2**

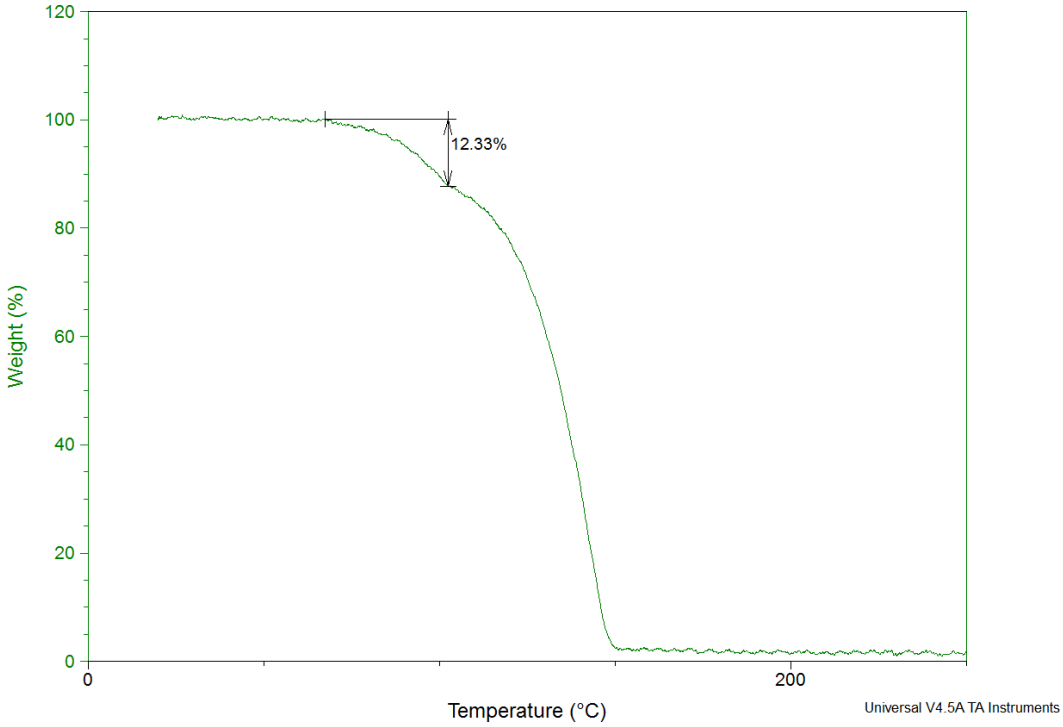

Figure S3. TGA trace of **D3**.H_2O

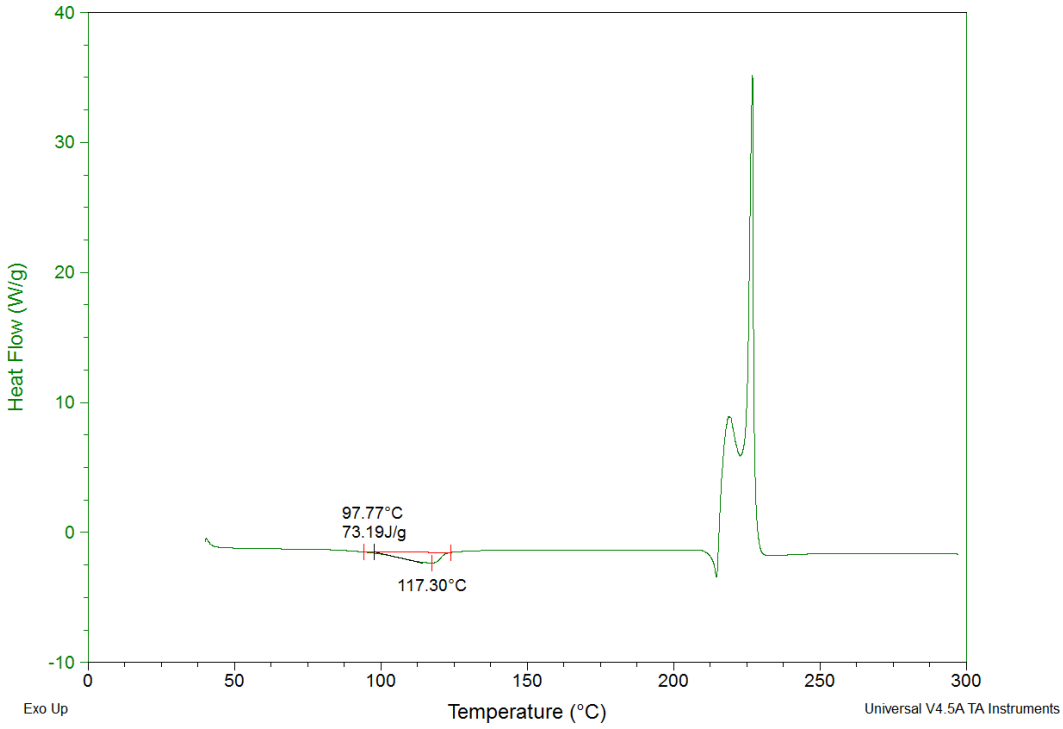

Figure S4. DSC trace of **D1**.H_2O.

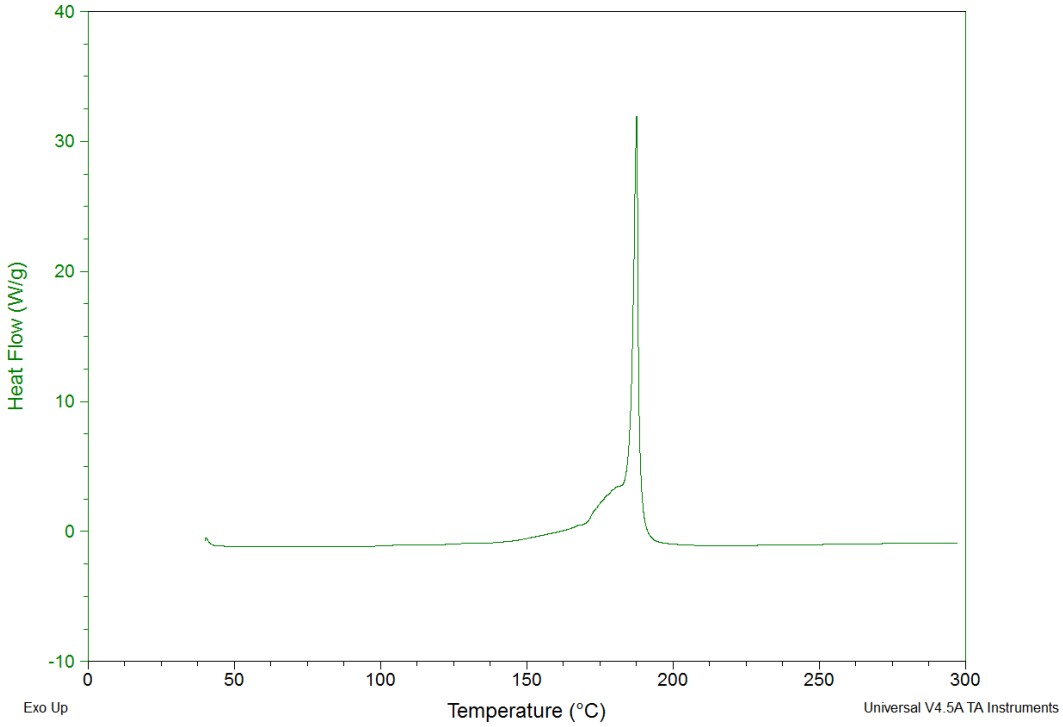

Figure S5. DSC trace of **D2**.

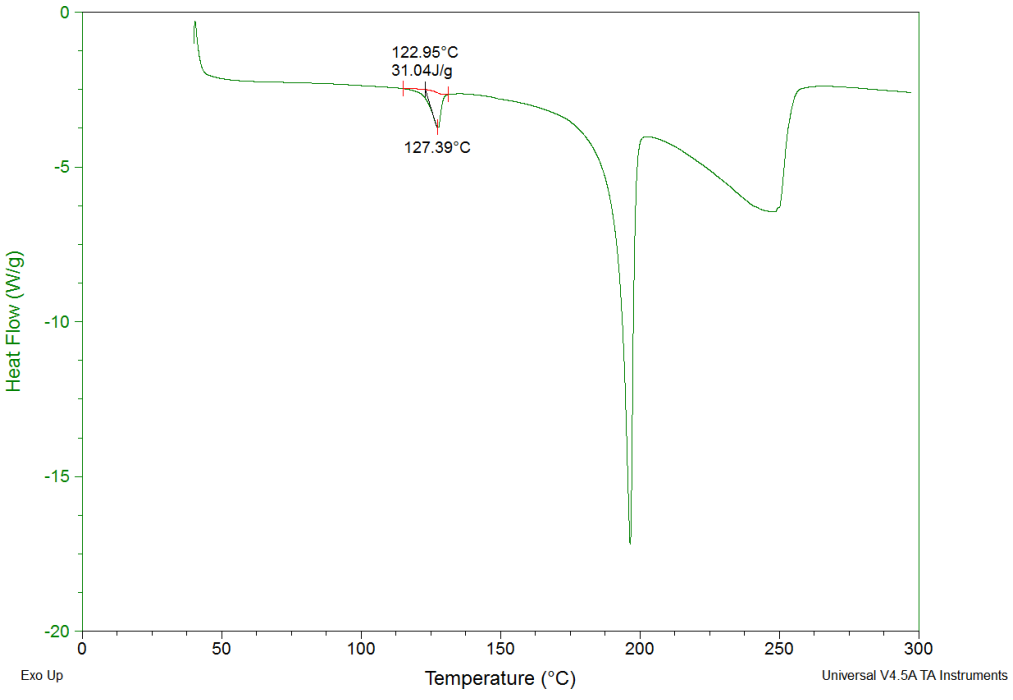

Figure S6. DSC trace of **D3**.H_2O.

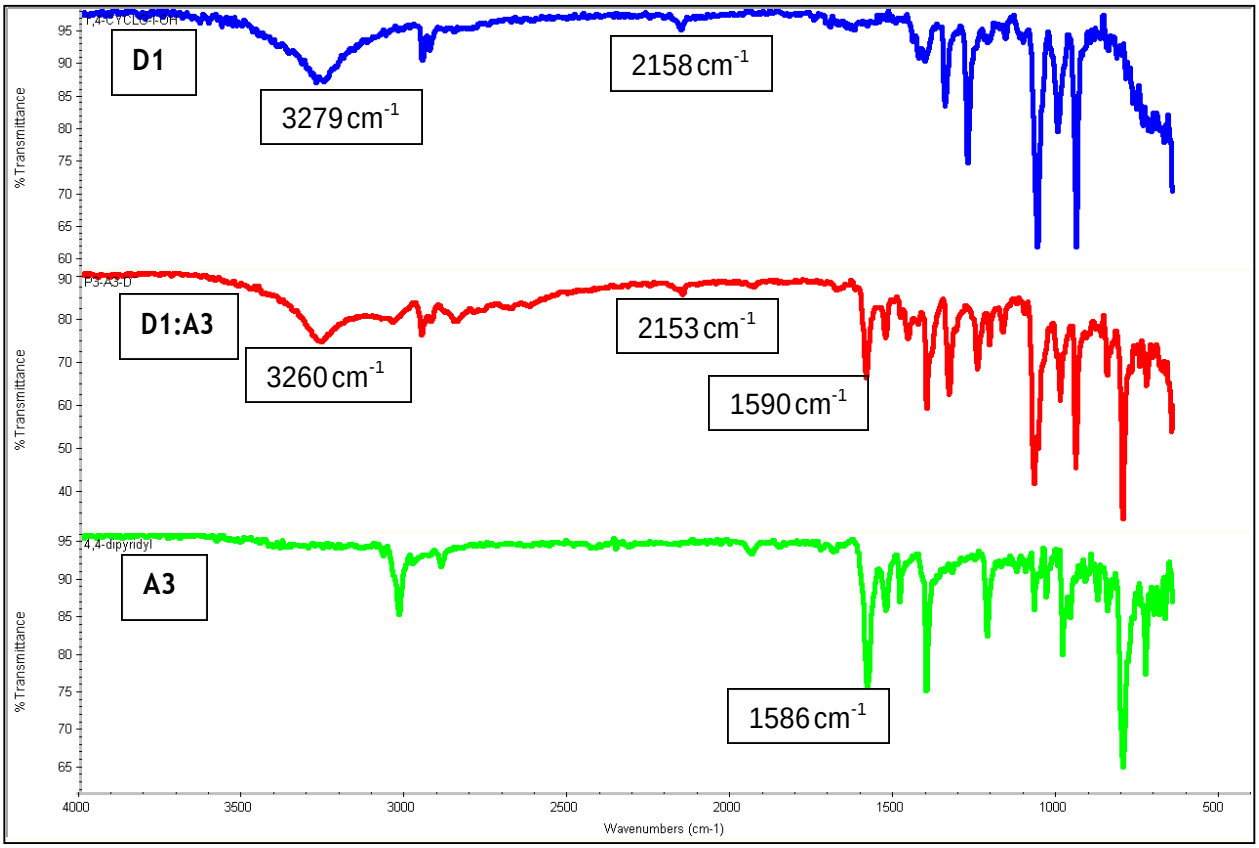

Figure S7. IR spectrums of **D1**, **A3** and **D1:A3**.

Crystallography Experimental Details

Datasets were collected on a Bruker Kappa APEX II system using MoKα radiation (**D1:A5**; **D2**), or on a Bruker SMART APEX II system using MoKα radiation (**D3**; **D1:A3; D1:A4**; **D3:A5**). Data were collected using APEX2 software.[i] Initial cell constants were found by small widely separated "matrix" runs. Data collection strategies were determined using COSMO.[ii] Scan speed and scan widths were chosen based on scattering power and peak rocking curves. Datasets were collected at -45 °C (**D3**; **D1:A3; D1:A4**; **D3:A5**), -143 °C(**D2**), and -153 °C (**D1:A5**) using an Oxford Cryostream low-temperature device.

For the above datasets, unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT,[iii] 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.[iv]

For the above datasets, data were reduced with SHELXTL.[v] 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.

Also, datasets for **D1**, **D2:A3**, and **D3:A3** were collected on an Oxford Diffraction Xcalibur four-circle kappa geometry single-crystal diffractometer with Sapphire 3 CCD detector, using a graphite monochromated MoKα radiation, and applying the CrysAlisPro Software system[vi] at 23 °C.

Data reduction, including Lorentz and polarization corrections as well as absorption correction, was done by CrysAlisPro program.[vi] The structures were solved by direct methods implemented in the SHELXS-2014/7 program.[vii] The coordinates and the anisotropic displacement parameters for all non-hydrogen atoms were refined by full-matrix least-squares methods based on F^2 using the SHELXS-2014/7 program.[vii] Except as noted, hydrogen atoms were located in idealized positions and were treated with a riding model.

D1 - Coordinates of the hydroxy proton H10, and the water proton H20 were allowed to refine.

D2 - Coordinates of the hydroxy protons H10 and H14 were allowed to refine.

D3 - Coordinates of the hydroxy protons H4 and H10, and the water protons H13A and H13B were allowed to refine.

D1:A3 - Coordinates of the hydroxy protons H7, H11 and H21 were allowed to refine.

D1:A4 - Coordinates of the hydroxy protons H7 and H11 were allowed to refine.

D1:A5 - The asymmetric unit contains one molecule each of the iodoethynyl-based target molecule and the pyridine-based co-former. The entire pyridine-based co-former is disordered over two closely related positions, thus representing different orientations. Relative populations were allowed to refine. Thermal parameters 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.

D2:A3 - Coordinates of the hydroxy protons H10 and H20 were allowed to refine.

D3:A3 - Coordinates of the hydroxy protons H10 and H20 were allowed to refine.

D3:A5 - Coordinates of the hydroxy proton H13 was allowed to refine.

Table S1. Crystallographic data for the ligands and their co-crystals.

Code	**D1**	**D2**	**D3**	**D1:A3**	**D1:A4**
Formula moiety	$C_{10}H_{10}I_2O_2$, H_2O	$C_{10}H_{10}I_2O_2$	$C_{10}H_{12}O_2$, H_2O	$C_{10}H_{10}I_2O_2$, $C_{10}H_8N_2$	$C_{10}H_{10}I_2O_2$, $C_{12}H_{10}N_2$
Empirical formula	$C_{10}H_{12}I_2O_3$	$C_{10}H_{10}I_2O_2$	$C_{10}H_{14}O_3$	$C_{20}H_{18}I_2N_2O_2$	$C_{22}H_{20}I_2N_2O_2$
Molecular weight	434.00	415.98	182.21	572.16	598.20
Color, Habit	Pale yellow, Prism	Colorless, Needle	Colorless, Rectangular	Colorless, Irregular	Colorless, Rectangular
Crystal system	Tetragonal	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group, *Z*	*P*4(2)/*m*, 2	*P*2(1)/*c*, 4	*P*2(1)/*c*, 4	*P*$\bar{1}$, 4	*P*$\bar{1}$, 2
a, Å	8.5167(5)	11.1961(17)	9.9472(12)	7.7674(8)	7.8373(7)
b, Å	8.5167(5)	11.5073(18)	6.1399(8)	10.0010(10)	11.6273(11)
c, Å	8.8404(9)	9.2386(15)	16.775(2)	26.238(3)	12.6853(12)
α, º	90	90	90	81.2340(10)	93.5792(12)
β, º	90	100.613(4)	104.248(2)	89.2680(10)	96.5739(11)
γ, º	90	90	90	85.8440(10)	107.2327(11)
Volume, Å^3	641.23(10)	1169.9(3)	993.0(2)	2009.1(3)	1091.15(18)
Density, g/cm^3	2.243	2.362	1.219	1.892	1.821
T, ºK	296(2)	130(2)	228(2)	228(2)	228(2)
Crystal size, min x mid x max	0.210 x 0.230 x 0.520	0.110 x 0.188 x 0.370	0.230 x 0.260 x 0.480	0.180 x 0.220 x 0.390	0.140 x 0.290 x 0.370
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	4.891	5.350	0.089	3.147	2.901
Trans min / max	0.27 / 1.00	0.24 / 0.59	0.96 / 0.98	0.37 / 0.60	0.41 / 0.69
θ_{min}, º	4.61	2.86	2.50	2.07	2.33
θ_{max}, º	32.65	29.58	33.54	33.46	33.33
Reflections					
collected	5381	22544	13268	27960	15152
independent	1152	3266	3686	14217	7687
observed	891	3030	2678	10970	6045
Threshold expression	> 2*σ*(*I*)	> 2*σ*(*I*)	> 2*σ*(*I*)	> 2*σ*(*I*)	> 2*σ*(*I*)
R_1 (observed)	0.0294	0.0203	0.0455	0.0473	0.0289
wR_2 (all)	0.0741	0.0443	0.1308	0.1070	0.0659
Goodness of fit (all)	1.078	1.091	1.032	1.149	1.034
ρ_{max}, ρ_{min}, e Å^{-3}	0.947, -1.114	1.085, -1.799	0.355, -0.226	1.433, -1.219	1.070, -1.031
Completeness to 2*θ* limit	0.994	0.994	0.940	0.905	0.910

Code	**D1:A5**	**D2:A3**	**D3:A3**	**D3:A5**
Formula moiety	$C_{10}H_{10}I_2O_2$, $C_{12}H_{12}N_2$	$C_{10}H_{10}I_2O_2$, $C_{10}H_8N_2$	$C_{10}H_{12}O_2$, $C_{10}H_8N_2$	$C_{10}H_{12}O_2$, $C_{12}H_{12}N_2$
Empirical formula	$C_{22}H_{22}I_2N_2O_2$	$C_{20}H_{18}I_2N_2O_2$	$C_{20}H_{20}N_2O_2$	$C_{22}H_{24}N_2O_2$
Molecular weight	600.21	572.16	320.38	348.43
Color, Habit	Colorless, Plate	Pale yellow, block	Pale yellow, plate	Colorless, Irregular
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group, *Z*	*P*$\bar{1}$, 2	*P*2(1)/*c*, 4	*P*$\bar{1}$, 2	*P*2(1)/*n*, 2
a, Å	7.8440(14)	9.5108(4)	5.9239(5)	11.5202(15)
b, Å	11.568(2)	10.5838(6)	12.3895(9)	7.7849(10)
c, Å	12.755(2)	22.0298(8)	13.2181(8)	11.8577(16)
a, º	92.124(6)	90	110.998(6)	90
β, º	97.154(6)	100.451(4)	96.684(6)	114.559(2)
γ, º	109.722(6)	90	99.359(6)	90
Volume, Å^3	1077.1(3)	2180.74(18)	877.44(12)	967.2(2)
Density, g/cm^3	1.851	1.743	1.213	1.196
T, ºK	120(2)	296(2)	296(2)	228(2)
Crystal size, min x mid x max	0.080 x 0.380 x 0.440	0.27 x 0.55 x 0.59	0.16 x 0.54 x 0.59	0.160 x 0.280 x 0.380
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	2.939	2.899	0.078	0.077
Trans min / max	0.36 / 0.80	0.458 / 1.000	0.817/1.000	0.97 / 0.99
θ_{min}, º	1.62	4.36	4.39	3.23
θ_{max}, º	30.59	27.00	26.99	28.28
Reflections				
collected	22664	14205	9747	9913
independent	6403	4769	3841	2395
observed	5625	3558	2595	1878
Threshold expression	> 2σ(*I*)	> 2σ(*I*)	> 2σ(*I*)	> 2σ(*I*)
R_1 (observed)	0.0297	0.0564	0.0518	0.0457
wR_2 (all)	0.0734	0.1540	0.1109	0.1210
Goodness of fit (all)	1.037	1.042	1.012	1.039
ρ_{max}, ρ_{min}, e Å^{-3}	1.735, -1.034	2.259, -1.564	0.173, -0.169	0.313, -0.280
Completeness to 2θ limit	0.966	0.996	0.995	0.998

[i] APEX2 v2013.10-0, © 2013, Bruker Analytical X-ray Systems, Madison, WI.

[ii] COSMO v1.61, © 1999 - 2009, Bruker Analytical X-ray Systems, Madison, WI.

[iii] SAINT v8.34a, © 1997 - 2013, Bruker Analytical X-ray Systems, Madison, WI.

[iv] SADABS v2012/1, © 2012, Bruker Analytical X-ray Systems, Madison, WI.

[v] SHELXTL v2008/4, © 2008, Bruker Analytical X-ray Systems, Madison, WI.

vi Oxford Diffraction, Xcalibur CCD System, CrysAlis Software System, Version 1.171.37, Oxford Diffraction Ltd., 2014.

vii (a) Sheldrick, G. M. (2014). SHELX-2014. University of Göttingen, Germany.

(b) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112–122.