Supporting Information

Ethynyl hydrogen bonds and iodoethynyl halogen bonds:

A case of synthon mimicry

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General Experimental Details

H NMR spectra were recorded on a Varian Unity plus 400 MHz spectrometer spectrometer in CDCl3. Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane or residual protiosolvent as internal reference and are reported as position (in ppm). Infrared spectroscopy analysis was carried out using Nicolet 380 FT-IR and melting point/decomposition point determination was done using Fisher-Johns melting point apparatus and are uncorrected. Tetramethyl pyrazine (TMP) and 1,2-bis(4-pyridyl)ethylene (BPE) were purchased from Sigma Aldrich and 4,4'-bipyridyl N,N'-dioxide (BNO) from Acros Organics.

Synthesis and Characterization of HPym and IPym

Synthesis of 5-bromo-2-aminopyrimidine

A solution of N-bromosuccinimide (5.2 g, 29.2 mmol) dissolved in methylene chloride (100 mL) was added dropwise to the solution of 2-aminopyrimidine (2.36 g, 24.8 mmol) dissolved in methylene chloride (50 mL) kept over an ice bath. After addition, the ice bath was removed and reaction mixture was stirred at room temperarture for 1 hr. Upon completion, the reaction was quenched with 10% sodium bicarbonate and 10% sodium sulfite solution. The mixture was filtered and the precipitate washed with water twice and dried to yield a white powder. (3.7 g, 86.2 %). M.P. > 250 ºC; ^{1}H NMR (δH; 200 MHz, $CDCl_3$): 8.31 (s, 2H), 5.09 (br, 2H).

Synthesis of 2-amino-5-trimethylsilanylethynylpyrimidine

5-bromo-2-aminopyrimidine (2.0 g, 11.5 mmol) was dissolved in triethylamine (30 mL) and degassed by bubbling nitrogen through the reaction mixture. TMS-acetylene (2.82 g, 28.7 mmol), $PdCl_2(PPh_3)_2$ (0.81 g, 1.15 mmol) and CuI (0.438 g, 2.30 mmol) were added and the mixture was refluxed at 70 ºC overnight. The solvent was removed by evaporation and the residue dissolved in diethyl ether (200 mL), was washed with 1 M HCl (50 mL) and brine (50 mL). The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent

was removed on a rotary evaporator and the residue was chromatographed on silica with hexane: ethyl acetate mixture as eluant to obtain a light brown colored powder. Upon recrystallization from methylene chloride, colorless crystals were obtained, (1.4 g, 63.6 %). ^{1}H NMR (δH; 200 MHz, $CDCl_3$): 8.40 (s, 2H), 5.21 (br, 2H), 0.26 (s, 9H).

Synthesis of 2-amino-5-ethynylpyrimidine (HPym)

2-amino-5-trimethylsilanylethynylpyrimidine (1.3 g, 6.8 mmol) and potassium carbonate (0.99 g, 7.20 mmol) were stirred in methanol at room temperature for 2 hrs. Upon completion, the solvent was removed by rotary evaporation and the residue dissolved in diethyl ether and washed with water (2 x 50 mL). The combined organic layers were dried over anhydrous magnesium sulfate and concentrated via rotary evaporation to obtain the product as yellow crystalline solid. (0.69 g, 85.1%). Dec. 148 ˚C. ^{1}H NMR (δH; 200 MHz, $CDCl_3$): 8.41 (s, 1H), 5.23 (br, 2H), 3.19 (s, 1H).

Synthesis of 2-amino-5-iodoethynylpyrimidine (IPym)

To a solution of 2-amino-5-ethynylpyrimidine (0.5 g, 4.2 mmol) dissolved in THF (50 mL), added dropwise simultaneously a concentrated solution of iodine in methanol (1.407 g, 5.54 mmol) and a 10% sodium hydroxide solution over 30 min, vigorously stirring. The mixture was stirred overnight, and quenched with 100 mL water upon which a light yellow color precipitate forms. The filtered solid washed with sodium bisulfite solution afforded pure pale yellow color powder, (0.82 g, 79.7%). Dec. 160 ˚C. ^{1}H NMR (δH; 200 MHz, $CDCl_3$): 8.38 (s, 1H), 5.21 (br, 2H).

Synthesis and characterization of co-crystals

Synthesis of IPym·TMP

2-amino-5-iodoethynylpyrimidine (IPym) (0.010 g, 0.041 mmol) and tetramethylpyrazine (TMP) (0.003 g, 0.020 mmol) were dissolved in methanol: THF 1:1 mixture in a 2 dram borosilicate vial and allowed for slow evaporation at ambient conditions. After three days colorless plate shaped crystals were obtained. M.p. 108-110 ˚C.

Synthesis of IPym·BPE

2-amino-5-iodoethynylpyrimidine (IPym) (0.010 g, 0.041 mmol) and 1,2-bis(4-pyridyl)ethylene (BPE) (0.004 g, 0.020 mmol) were dissolved in methanol:THF 1:1 mixture in a 2 dram borosilicate vial and allowed for slow evaporation at ambient conditions. After two days colorless plate shaped crystals were obtained. Dec. 171℃

Synthesis of HPym·TMP

2-amino-5-ethynylpyrimidine (HPym) (0.010 g, 0.084 mmol) and tetramethylpyrazine (TMP) (0.034 g, 0.25 mmol) were dissolved in methanol in a 2 dram borosilicate vial and allowed for slow evaporation at ambient conditions. After seven days colorless plate shaped crystals were obtained. Dec. 112 ˚C.

Synthesis of HPym·BPE

2-amino-5-ethynylpyrimidine (HPym) (0.010 g, 0.084 mmol) and 1,2-bis(4-pyridyl)ethylene (BPE) (0.046 g, 0.25 mmol) were dissolved in methanol in a 2 dram borosilicate vial and allowed for slow evaporation at ambient conditions. After five days gold color plate shaped crystals were obtained. M.p. 135-137 ˚C.

IR data based on grinding experiments– Table S1

	IR bands of pure donor (cm^{-1})	IR bands of the co-crystal (cm^{-1})
IPym·TMP	2175	2163
IPym·BPE	2175	2166
IPym·BNO	2175	2156
IPym·BP	2175	2169
IPym·PZ	2175	2161
HPym·TMP	2159	2168
HPym·BPE	2159	2155
HPym·BNO	2159	2151
HPym·BP	2159	2155
HPym·PZ	2159	2147

X-ray data were collected on a Bruker APEX II CCD diffractometer at 120 K using, a fine-focus molybdenum Kα tube. Data were collected using APEX2[(a)] software. Initial cell constants were found by small widely separated "matrix" runs. Scan speed and scan width were chosen based on scattering power and peak rocking curves.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT,[(b)] 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. All datasets were corrected for absorption using SADABS.[(c)] Laué symmetry, space group, and unit cell contents were found with XPREP.

Data were reduced with SHELXTL.[(d)] The structures were solved in all cases by direct methods without incident. Except where indicated, hydrogens were assigned to idealized positions and were allowed to ride. Heavy atoms were refined with anisotropic thermal parameters. Absorption correction was carried out on all datasets.

Ipym The molecule sits on a crystallographic mirror plane. All hydrogens were located in idealized positions. Attempts to account for the residual electron density in the vicinity of the iodine, either with more sophisticated absorption correction or with molecular disorder, were unsuccessful.

Ipym·TMP The asymmetric unit contains one alkyne and one half-pyrazine. All hydrogens were located in idealized positions.

Ipym·BPE The asymmetric unit contains one alkyne and one half-ethylene. Coordinates of the amine hydrogens H32A & H32B were allowed to refine.

Hpym·TMP The asymmetric unit contains one alkyne and one half-pyrazine. The two unique methyl groups were rotationally disordered and were each treated as two species. All hydrogens were located in idealized positions. Coordinates of the amine hydrogens H12A & H12B and the ethynyl hydrogen H18 were allowed to refine.

Hpym·BPE The asymmetric unit contains two alkynes and two half-ethylenes. These molecules were grouped into two different residues for consistent numbering. One of the two half-ethylenes was disordered and was modeled as two species. Geometries of the two species were restrained with the "SAME" command and thermal parameters were pairwise constrained with the "EADP" command. For both residues, coordinates of the amine hydrogens H12A & H12B and the ethynyl hydrogen H18 were allowed to refine.

Hpym The molecule sits on a crystallographic mirror plane. Coordinates of the unique amine hydrogen H11 were allowed to refine.

(a) APEX2 v2013.10.0 © 2005 - 2013, Bruker AXS, Madison, WI.
(b) SAINT v8.34a, © 1997 - 2013, Bruker AXS, Madison, WI.
(c) SADABS v2012.1, © 1997 - 2012, Bruker AXS, Madison, WI.
(d) SHELXTL v2008/4, © 2008 , Bruker AXS, Madison, WI.

Code	Ipym	Ipym·TMP	Ipym·BPE	Hpym	Hpym·TMP	Hpym·BPE
Formula moiety	$C_6H_4IN_3$	$(C_6H_4IN_3)_2$ $(C_8H_{12}N_2)$	$(C_6H_4IN_3)_2$ $(C_{12}H_{10}N_2)$	$C_6H_5N_3$	$(C_6H_5N_3)_2$ $(C_8H_{12}N_2)$	$(C_6H_5N_3)_2$ $(C_{12}H_{10}N_2)$
Empirical formula	$C_6H_4IN_3$	$C_{20}H_{20}I_2N_8$	$C_{24}H_{18}I_2N_8$	$C_6H_5N_3$	$C_{20}H_{22}N_8$	$C_{24}H_{20}N_8$
Molecular weight	245.02	626.24	672.26	119.13	374.46	420.48
Color, Habit	colourless plate	colourless plate	colourless plate	colourless plate	colourless plate	gold plate
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group, Z	Cmca, 8	P-1, 1	P2(1)/c, 2	P2(1)/m, 2	P-1, 1	P-1, 2
a, Å^3	7.6148(9)	5.7837(5)	19.625(2)	4.3404(7)	5.7849(18)	5.9068(6)
b, Å^3	7.8988(8)	6.1130(5)	7.5472(7)	7.7073(12)	6.0656(18)	11.5286(12)
c, Å^3	24.473(3)	16.4016(14)	8.2583(8)	8.6344(15)	14.756(5)	15.8169(16)
α, °	90.00	98.086(4)	90.00	90.00	79.742(8)	104.471(4)
β, °	90.00	92.180(4)	100.950(4)	91.363(9)	88.831(8)	93.042(5)
γ, °	90.00	101.892(4)	90.00	90.00	80.342(7)	95.934(4)
Volume, Å^3	1472.0(3)	560.46(8)	1200.9(2)	288.76(8)	502.2(3)	1033.84(18)
Density, g/cm^3	2.211	1.855	1.859	1.370	1.238	1.351
Temperature, °K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal size, min x mid x max	0.06 x 0.32 x 0.44	0.06 x 0.22 x 0.26	0.06 x 0.22 x 0.34	0.12 x 0.32 x 0.38	0.06 x 0.38 x 0.46	0.14 x 0.38 x 0.44
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	4.272	2.830	2.649	0.091	0.080	0.086
Absorption corr	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Trans min / max	0.2551 / 0.7836	0.5266 / 0.8486	0.4662 / 0.8572	0.9664 / 0.9892	0.9642 / 0.9952	0.9631 / 0.9880
θ_{min}, °	1.66	2.51	2.90	2.36	1.40	1.33
θ_{max}, °	30.59	31.04	32.04	32.56	31.39	31.84
Reflections						
collected	9305	10398	13808	4825	8079	24212
independent	1202	3427	3865	1000	2920	6280
observed	976	3028	3303	795	2009	4100
Threshold expression	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)
R1 (observed)	0.0865	0.0319	0.0242	0.0416	0.0463	0.0573
*w*R$_2$ (all)	0.1975	0.0919	0.0567	0.1299	0.1365	0.1814
Goodness of fit (all)	1.064	1.069	1.058	1.067	1.099	1.098
Δρ max / min	6.360 / -2.946	1.685 / -0.692	0.829 / -0.514	0.325 / -0.303	0.181 / -0.209	0.397 / -0.317
2θ limit	30.00	30.00	30.00	30.00	30.00	30.00
Completeness to 2θ limit	0.997	0.983	0.988	0.998	0.961	0.965