Electronic Supplementary Information

Straightening Out Halogen Bonds

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Experimental

All reagents were obtained from commercial sources and used without purification unless otherwise stated. Diethyl ether was dried before use by running through an alumina column on a PureSolv solvent purification system (Innovative Technologies). NMR spectra were obtained on a Bruker AV300 spectrometer. Mass spectra were collected on a Thermo Scientific LCQ Fleet ion trap instrument. ATR-FTIR spectra were collected on a PerkinElmer Spectrum 200 with diamond ATR attachment.

Single crystal X-ray diffraction data were collected on the MX1 beamline at the Australian Synchrotron,¹ using Si(111) double crystal-monochromated X-rays ($\lambda = 0.7108 \text{ Å}$) and operating at 100(2) K through the BluIce interface.² Data were indexed, integrated and reduced using XDS.³ Structures were solved using SHELXT⁴ and refined via full-matrix least-squares refinement against *F*² using SHELXL-2014⁵ implemented within the WinGX-32 or Olex2 graphical interface.^{6, 7} Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in idealised positions and refined using a riding model. The two ligand structures proved to have small twin components, while the THF solvate in *p*-bnpdH•0125THF was disordered over a symmetry position and was modelled with a rigid body.

Synthesis of 1,3-di(4-benzonitrile)-1,3-propanedione, p-bnpdH

An adaptation of the previous literature method was employed.⁸ 4-acetylbenzonitrile (0.5333 g, 0.0038 mol) was dissolved in anhydrous diethyl ether, placed under nitrogen and cooled in an ice bath before sodium methoxide (0.26 g, 0.00475 mol) in

methanol (40 mL) was added. Methyl-4-cyanobenzoate (0.6182 g, 0.0038 mol) dissolved in anhydrous diethyl ether (30 mL) was then added dropwise over a period of 30 minutes. The pale yellow mixture was allowed to warm to room temperature and left stirring overnight. This was acidified with concentrated hydrochloric acid (10 mL), producing a precipitate which was collected by filtration. The resulting yellow solid was washed with hot ethanol (5 x 20 mL). Yield 0.8132 g, 78 %. Recrystallisation from methanol yielded crystals of *p*-bnpdh suitable for diffraction (Figure S1), while recrystallisation from THF yielded single crystals of *p*-bnpdH•0125THF (Figure S2).

¹H NMR (300 MHz, DMSO-*d*₆) δ 16.63 (b, CH, 1H), δ 8.36 (dd, J = 8.7 Hz, Ar-H, 4H), δ 8.08 (dd, J = 8.8 Hz, Ar-H, 4H), δ 7.56 (s, CH, 1H). *m/z* (ESI-MS): 273.1 [L₁ – H]⁻. FTIR: 2229, 1586, 1534, 1488, 1291, 1223, 1119, 861, 833, 787, 694, 642, 544 cm⁻¹. Characterisation data is in agreement with previous literature.⁸

Crystallographic Data for *p*-bnpdH: Monoclinic, space group C2/c (no. 15), *a* = 7.1360(14) Å, *b* = 12.568(3) Å, *c* = 14.975(3) Å, β = 94.29(3)°, Å *V* = 1339.2(5) Å³, *Z* = 4, *T* = 100.15 K, μ = 0.091 mm⁻¹, *D*_c= 1.360 g/cm³, 1584 reflections measured (5.456° ≤ 2Θ ≤ 55.734°), 1584 unique (*R*_{int} = 0.1561, *R*_{sigma} = 0.0482) which were used in all calculations. The final *R*₁ was 0.1062 (I > 2σ(I)) and *wR*₂ was 0.3161 (all data). CCDC Deposition number 1976701



Figure S1. ORTEP diagram of monoclinic polymorph of *p*-bnpdH. Non-hydrogen atoms are shown as anisotropic displacement ellipsoids with 50% probability.

Crystallographic Data for *p*-bnpdH•0.125THF: Formula C35 H22 N4 O4.25 , M = 566.56, triclinic, space group $P^{\overline{1}}$, *a* = 3.8500(8) Å , *b* = 14.124(3) Å , *c* = 26.384(5) Å, *a* = 93.98(3)0, *β* = 91.69(3)0, *γ* = 92.08(3) 0, *V* = 1429.5(5) Å3, *D*_c = 1.316 g cm⁻³, *Z* = 2, temperature = 100(2) K, synchrotron = 0.7108 Å, μ = 0.089 mm⁻¹, 2 θ_{max} = 49.416, R_{sigma} = 0.0390, R_1 (F) 0.1192, wR_2 (F², all) 0.3645, GooF(all) 1.011, $D\rho_{min,max}$ 0.55 , -0.48 e⁻ Å⁻³. CCDC deposition number 1976896.



Figure S2. ORTEP diagram of asymmetric unit of of *p*-bnpdH·0.125THF. Non-hydrogen atoms are shown as anisotropic displacement ellipsoids with 50% probability.

Synthesis of [p-bnpdH •0.5(1,4-DITFB)]

1,4-DITFB (9.8 mg, 2.44x10⁻⁵ mol) and *p*-bnpdH (4.6 mg, 1.67x10⁻⁵ mol) were dissolved in acetone (10 mL) and 2 mL of water were added. Slow evaporation yielded pale yellow crystals suitable for X-ray analysis that were used directly in the crystallographic study (Figure S3). Due to the small quantity of material obtained no accurate mass nor additional analytical data were recorded.

Triclinic, space group *P*-1 (no. 2), *a* 12.591(3), *b* 13.280(3) Å, *c* 15.488(3) Å, *a* 109.22(3)°, β 90.54(3)° γ 111.68(10)°, *V* 2246.8(10) Å³, *Z* 4, μ 0.7108 mm⁻¹, *D_c* 1.453 g/cm³, 40 964 reflections measured (3.536° \leq 2 $\Theta \leq$ 56.568°), 9850 unique (*R*_{int} = 0.0293, *R*_{sigma} = 0.0251) which were used in all calculations. The final *R*₁ was 0.0413 (I > 2 σ (I)) and *wR*₂ was 0.01123 (all data). CCDC Deposition number 1976306.



Figure S3. ORTEP diagram of asymmetric unit of [*p*-bnpdH •0.5(1,4-DITFB)]. Non-hydrogen atoms are shown as anisotropic displacement ellipsoids with 50% probability.

CSD search parameters

All database searches were conducted using CSD version 5.40 (November 2018)⁹ using ConQuest 2.0.3.

N_{py}…halogen interactions

Searches were conducted for all crystal structures containing pyridyl N…halogen contacts, where the halogen is covalently bound to another atom. Crystal structures containing pyridyl groups with quaternary nitrogen atoms were were excluded from the search (Figure S4). This was found to be necessary to exclude pyridinium halide salts. Further filters applied include: R-factor <= 0.1, Non-disordered structures only, no errors, non-polymeric structures only, no ions, single-crystal structures only.

The search results were then manually screened to remove anomalous crystal structures, including haloalkane solvates, hypervalent iodine compounds, intramolecular close contacts, metal-halide complexes and incorrectly refined pyridinium halide salts, in addition to duplicate structures. These are special cases that do not display the types of intermolecular interaction that we were exploring in this study. This resulted in 820 unique crystal structures for further analysis.



Figure S4. ConQuest queries for N_{py}... halogen interactions.

C≡N…halogen interactions

Searches were conducted for all crystal structures containing C=N···halogen contacts, where the halogen is covalently bound to another atom. Crystal structures containing halogen···halogen interactions were excluded (Figure S5). Further filters applied include: R-factor <= 0.1, Non-disordered structures only, no errors, non-polymeric structures only, no ions, single-crystal structures only.

Manual screening was then applied in a similar manner to that used for the pyridyl analogue to remove anomalous search results and duplicate structures, resulting in 476 unique crystal structures.



Figure S5. ConQuest queries for C=N...halogen interactions.

Frequency analysis for ψ parameter



Figure S6. Frequency histogram for ψ parameter. Calculated ψ parameters are grouped in bins of 0.05. The two right-most bins contain all type α halogen bonds, while the remainder are type β . Py…X halogen bonds (orange) show a distinct trend towards type α interactions, whereas C=N…X halogen bonds (grey) display a broad distribution of values.



Figure S7. Normalised percentage frequency histogram for ψ parameter. Calculated ψ parameters are grouped in bins of 0.05. The two right-most bins contain all type α halogen bonds, while the remainder are type β . Py…X halogen bonds (orange) show a distinct trend towards type α interactions, whereas C=N…X halogen bonds (grey) display a broad distribution of values.



Figure S8. Frequency histogram for ψ parameter (Py…I halogen bonds only). Calculated ψ parameters are grouped in bins of 0.05. The two right-most bins contain all type α halogen bonds, while the remainder are type β .

Geometric and steric constraints in Py---I halogen bonds

While there is a clear trend towards type α interactions in Py…I halogen bonds, a number of interactions with $\psi < 0.7$ were observed. Examination of these crystal structures showed that this was generally due to geometric or steric constraints, where the formation of one linear halogen bond prevented the formation of another, or the formation of one linear halogen bond forces the formation of a non-linear interaction with an adjacent Lewis base. A clear example of this is in the series of halogen-bonded structures containing 1,10-phenanthroline and its derivatives, for example TAWFIJ (Figure S9).¹⁰ In these cases, bifurcated halogen-bonding occurs and the two ψ values are 0.72 and 0.66 respectively.



Figure S9. Bifurcated halogen bonding in the crystal structure of 1,4-DITFB and bathophenanthroline.¹⁰

Another example is $RUGSOD^{11}$ (Figure S10), in which a bulky group attached to C8 of a quinoline ring system prevents formation of a linear N···I halogen bond.



Figure S10. Halogen bonding in the RUGSOD¹¹ crystal structure.

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