## SUPPORTING INFORMATION

# Uncommon halogen bond motifs in cocrystals of aromatic amines and 1,4-diiodotetrafluorobenzene

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#### **EXPERIMENTAL DETAILS**

#### MATERIALS

1,4-diiodotetrafluorobenzene (**tfib**) was obtained from Sigma-Aldrich. 4-aminoacetophenone (**4aap**), 3-aminoacetophenone (**3aap**) and 3-aminopyridine (**3ap**) were obtained from Merck. 3-aminobenzonitrile (**3abn**) was obtained from Acros Organics. 4-nitroaniline (**4noa**) was obtained from Kemika. 5-amino-2-methoxypyridine (**5a2mp**) was obtained from Alfa-Aesar. Tetrahydrofuran and acetonitrile were purchased from J. T. Baker. Methanol was purchased from Carlo Erba. Acetone and ethanol were purchased from Gram-Mol. Chloroform was purchased from Scharlau. Dichloromethane was purchased from Alkaloid. Benzene was purchased from T. T. T. *N*, *N*-dimethylformamide, copper(II) chloride tetrahydrate and iron(II) chloride tetrahydrate were purchased from Kemika. Chromium(III) chloride hexahydrate was purchased from Acros Organics. Nickel(II) chloride was purchased from Applichem Panreac.

#### **MECHANOCHEMICAL SYNTHESIS**

## 4aap + tfib screening, 2:1 amine : tfib molar ratio

A mixture of 20.0 mg **4aap** and 29.7 mg **tfib** was placed in a 10 mL stainless steel jar along with 15.0  $\mu$ L of acetonitrile, and two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

#### 4ab + tfib screening, 2:1 amine : tfib molar ratio

A mixture of 20.0 mg **4ab** and 20.4 mg **tfib** was placed in a 10 mL stainless steel jar along with 5.0  $\mu$ L of acetonitrile, and two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

## 4noa + tfib screening, 2:1 amine : tfib molar ratio

A mixture of 20.0 mg **4noa** and 29.1 mg **tfib** was placed in a 10 mL stainless steel jar along with 5.0  $\mu$ L of acetonitrile, and two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

### <u>**3ap** + tfib</u> screening, 2:1 amine : tfib molar ratio

A mixture of 20.0 mg **3ap** and 42.7 mg **tfib** was placed in a 10 mL stainless steel jar along with 5.0  $\mu$ L of acetonitrile, and two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

## <u>**3ap** + tfib</u> screening, 1:1 amine : tfib molar ratio

A mixture of 10.0 mg **3ap** and 42.7 mg **tfib** was placed in a 10 mL stainless steel jar along with 5.0  $\mu$ L of acetonitrile, and two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

## <u>**3abn** + tfib</u> screening, 2:1 amine : tfib molar ratio

A mixture of 20.0 mg **3abn** and 34.0 mg **tfib** was placed in a 10 mL stainless steel jar along with 5.0  $\mu$ L of acetonitrile, and two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

#### <u>**3abn** + tfib screening, 1:1 amine : tfib molar ratio</u>

A mixture of 20.0 mg **3abn** and 68.0 mg **tfib** was placed in a 10 mL stainless steel jar along with 10.0  $\mu$ L of acetonitrile, and two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

## 5a2mp + tfib screening, 2:1 amine : tfib molar ratio

A mixture of 40.0 mg **5a2mp** and 65.0 mg **tfib** was placed in a 10 mL stainless steel jar along with two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

#### **SOLUTION SYNTHESIS**

### (4aap)<sub>2</sub>(tfib) cocrystal

The cocrystal was obtained by dissolving a mixture of **4aap** (20.0 mg, 0.148 mmol) and **tfib** (30.0 mg, 0.0746 mmol) in 1.0 mL of hot methanol, and the subsequent cooling and solvent evaporation at room temperature.

#### (4ab)<sub>2</sub>(tfib) cocrystal

The cocrystal was obtained by dissolving a mixture of **4ab** (40.0 mg, 0.203 mmol) and **tfib** (40.0 mg, 0.100 mmol) in 2.0 mL of hot methanol, and the subsequent cooling and solvent evaporation at room temperature.

#### (3ap)(tfib) cocrystal

The (3ap)(tfib) cocrystal was obtained by recrystallizing 20.0 mg (0.0403 mmol) of the LAG sample (see the 1:1 molar ratio LAG screening experiment) from 25.0  $\mu$ L of acetonitrile.

### (3abn)(tfib) cocrystal

The cocrystal was obtained by recrystallizing 73.0 mg (0.140 mmol) of the LAG sample (see the 1:1 molar ratio LAG screening experiment) from 1.0 mL of hot butanone.

#### (5a2mp)<sub>2</sub>(tfib) cocrystal

The cocrystal was obtained by dissolving **tfib** (24.0 mg, 0.0597 mmol) in a mixture of *n*-hexane and diethyl ether (1,5 mL, 2:1), mixing in **5a2mp** (15.0  $\mu$ L, 0.121 mmol), and the subsequent solvent evaporation at room temperature.

## (4noa)<sub>2</sub>(tfib) cocrystal

A variety of experimental parameters have been tested for obtaining the  $(4noa)_2(tfib)$  cocrystal (see Table S1). The single crystal was obtained by dissolving a mixture of the copper(II) chloride complex containing **4noa** (15.0 mg of the complex, 0.0365 mmol), and **tfib** (15.0 mg, 0.0373 mmol) in a solvent mixture of tetrahydrofuran and ethanol (1.5 mL,1:2), and the subsequent cooling and solvent evaporation at room temperature. The (**4noa**)<sub>2</sub>(**tfib**) cocrystal appeared as a green tinted yellow plate at the bottom of the crystallization vessel. The crystallization bulk corresponding to the cocrystal was obtained by dissolving a mixture of the copper(II) chloride complex containing **4noa** (15.0 mg of the complex, 0.0365 mmol), and **tfib** (15.0 mg, 0.0373 mmol) in 2.0 mL of acetone, and the subsequent solvent evaporation at room temperature.

#### THERMAL ANALYSIS

DSC measurements were performed on a Mettler-Toledo DSC823<sup>e</sup> module. The samples were placed in sealed aluminium pans (40  $\mu$ L) with three holes made on the top cover, and heated in flowing nitrogen (150 mL min<sup>-1</sup>) from 25 °C to 500 °C at a rate of 10 °C min<sup>-1</sup>. The data collection and analysis was performed using the program package STAR<sup>e</sup> Software 14.00.<sup>1</sup>

#### SINGLE-CRYSTAL X-RAY DIFFRACTION EXPERIMENTS

The crystal and molecular structures of the prepared samples were determined by single crystal X-ray diffraction. Details of data collection and crystal structure refinement are listed in Table S2. The diffraction data were collected at 295 K. Diffraction measurements were made on an Oxford Diffraction Xcalibur Kappa CCD X-ray diffractometer with graphite-monochromated MoK $\alpha$  ( $\lambda = 0.71073$ Å) radiation. The data sets were collected using the  $\omega$  scan mode over the  $2\theta$  range up to 54°. Programs CrysAlis CCD and CrysAlis RED were

employed for data collection, cell refinement, and data reduction.<sup>2</sup> The structures were solved by direct methods and refined using the SHELXS, SHELXT and SHELXL programs, respectively.<sup>3, 4</sup> The structural refinement was performed on F<sup>2</sup> using all data. The hydrogen atoms not involved in hydrogen bonding were placed in calculated positions and treated as riding on their parent atoms [d(C-H) = 0.93 Å and  $U_{iso}(H) = 1.2 U_{eq}(C)$ ] while the others were located from the electron difference map. The amino group hydrogen atoms in the (**3ap**)(**tfib**), (**4ab**)<sub>2</sub>(tfib) and (**4noa**)<sub>2</sub>(**tfib**) cocrystals were placed in calculated positions and then refined with the following restraints: d(N-H) = 0.891 Å, d(H to H) = 1.486 Å,  $U_{iso}(H) =$ 1.5  $U_{eq}(N)$ , while in the others they were located from the electron difference map. All calculations were performed using the WINGX crystallographic suite of programs.<sup>5</sup> The molecular structures of compounds are presented by ORTEP-3,<sup>5</sup> and their molecular packing projections were prepared by Mercury.<sup>6</sup>

#### **POWDER X-RAY DIFFRACTION EXPERIMENTS**

PXRD experiments on the samples were performed on a PHILIPS PW 1840 X-ray diffractometer with CuK $\alpha$ 1 (1.54056 Å) radiation at 40 mA and 40 kV. The scattered intensities were measured with a scintillation counter. The angular range was from 5 to 40° (2 $\theta$ ) with steps of 0.02 – 0.03°, and the measuring time was 0.2 – 0.5 s per step. Data collection and analysis was performed using the program package Philips X'Pert.<sup>7</sup>

#### References

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<sup>1.</sup> STARe Software V.14.00, MettlerToledo GmbH, 2015.

starting material	solvent or solvent mixture	result
1:1 CuCl <sub>2</sub> ( <b>4noa</b> ) <sub>2</sub> + <b>tfib</b>	tetrahydrofuran : ethanol, 1:2	cocrystal
1:1 CuCl <sub>2</sub> ( <b>4noa</b> ) <sub>2</sub> + <b>tfib</b>	acetone	cocrystal bulk
reactant mixture	methanol	mixture
reactant mixture	ethanol	mixture
reactant mixture	acetonitrile	mixture
reactant mixture	acetone	mixture
reactant mixture	tetrahydrofuran	mixture
reactant mixture	chloroform	mixture
reactant mixture	dichloromethane	mixture
reactant mixture	tetrahydrofuran : ethanol, 1:1	mixture
reactant mixture	tetrahydrofuran : ethanol, 1:2	mixture
reactant mixture	benzene : ethanol, 2:1	mixture
reactant mixture	dichloromethane : ethanol, 1:1	mixture
LAG sample	tetrahydrofuran : ethanol, 1:2	mixture
LAG sample	N, N-dimethylformamide	mixture

 Table S1. Crystallization and recrystallization attempts for the (4noa)<sub>2</sub>(tfib) cocrystal.

	(4aap) <sub>2</sub> (tfib)	(4ab) <sub>2</sub> (tfib)	$(4noa)_2(tfib)$	(3ap)(tfib)	(3abn)(tfib)	( <b>5a2mp</b> ) <sub>2</sub> ( <b>tfib</b> )
Molecular formula	$(C_8H_9NO)_2(C_6I_2F_4)$	$(C_{13}H_{11}NO)_2(C_6I_2F_4)$	$(C_6H_6N_2O_2)_2(C_6I_2F_4)$	$(C_5H_6N_2)(C_6I_2F_4)$	$(C_7H_6N_2)(C_6I_2F_4)$	$(C_6H_8N_2O)_2(C_6I_2F_4)$
$M_{ m r}$	672.2	796.4	678.1	496.0	520.0	650.2
Crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	P-1	$P 2_1/n$	P-1	$P  2_1/n$	P-1	$P 2_1/n$
Crystal data:						
<i>a</i> / Å	6.1553(3)	8.4300(7)	9.4529(6)	7.5682(17)	8.4368(10)	6.0259(3)
b/Å	9.6907(6)	5.6597(4)	10.6844(8)	13.372(3)	8.4962(2)	8.6495(4)
<i>c</i> / Å	10.8382(5)	31.140(2)	12.1719(17)	14.198(2)	11.8803(10)	20.3527(13)
$\alpha$ / °	113.014(5)	90	96.727(2)	90	100.565(11)	90
$eta/\circ$	96.686(4)	94.781(7)	112.766(4)	105.457(1)	107.57	93.507(5)
$\gamma/\circ$	104.202(5)	90	103.570(6)	90	105.95	90
$V/\text{\AA}^3$	560.28(6)	1480.5(2)	1071.86(19)	1384.9(5)	746.97(11)	1058.82(10)
Ζ	1	2	2	4	2	2
$D_{ m calc}$ / g cm <sup>-3</sup>	1.992	1.786	2.101	2.379	2.312	2.039
$\lambda(MoK_{\alpha})$ / Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T/K	295	295	295	295	295	295
Crystal size / mm <sup>3</sup>	0.54 x 0.45 x 0.14	0.74 x 0.29 x 0.10	0.60 x 0.28 x 0.11	0.61 x 0.31 x 0.16	0.63 x 0.34 x 0.15	0.46 x 0.25 x 0.17
$\mu / \mathrm{mm}^{-1}$	2.862	2.182	3.002	4.574	4.246	3.027
<i>F</i> ( <i>000</i> )	322	772	644	912	480	620
Refl. collected/unique	7170 / 2381	14877 / 3213	11446 / 3771	6550 / 2281	7773 / 3215	6366 / 2077
Data/restraints/parameters	154	196	301	178	196	143
$\Delta ho_{ m max}$ , $\Delta ho_{ m min}$ / e Å <sup>-3</sup>	0.410; -0.703	0.621; -0.428	0.795; -0.809	0.993; -1.067	0.478; -0.766	0.793; -0.795
$R[F^{2}>4\sigma(F^{2})]$	0.020	0.033	0.037	0.053	0.027	0.029
$wR(F^2)$	0.049	0.090	0.141	0.139	0.059	0.092
Goodness-of-fit, S	1.078	0.898	0.818	0.922	0.882	0.995

# **Table S2.** General and crystallographic data for the prepared cocrystals.

Table	<b>S3</b> .	Geo	ometric	pai	rameters	for	the	hale	ogen	bonds	in	prepared	cocry	stals.	Dis	stances
betwee	en se	elect	atoms	in a	contact	are	denc	oted	as d,	while	the	correspon	nding a	angle	is r	narked
with $\alpha$																

compound	<b>D</b> –I····A	<i>d(D</i> –I) / Å	<i>d</i> (I··· <i>A</i> ) / Å	<i>α</i> /°	symmetry operator
(4aap) <sub>2</sub> (tfib)	C10–I1…O1	2.086(2)	2.889(2)	178	<i>x</i> , <i>y</i> –1, <i>z</i>
(4ab) <sub>2</sub> (tfib)	C15–I1····C3	2.078(4)	3.456(4)	167	<i>x</i> –1, <i>y</i> –1, <i>z</i>
(4noa) <sub>2</sub> (tfib)	C14–I1…O1	2.102(11)	3.09(1)	161	<i>x</i> , <i>y</i> –1, <i>z</i>
	C14–I1…O2	2.102(11)	3.38(1)	159	<i>x</i> , <i>y</i> –1, <i>z</i>
	C16–I2···O3	2.100(12)	3.36(1)	158	<i>x</i> , <i>y</i> , <i>z</i>
	C16–I2····O4	2.100(12)	3.18(1)	163	<i>x</i> , <i>y</i> , <i>z</i>
(3ap)(tfib)	C6–I1…N1	2.106(7)	2.805(8)	175	x-1/2, 3/2-y, z+1/2
	C9–I2…I2	2.065(8)	3.782(1)	141	-x, 2-y, 1-z
(3abn)(tfib)	C12–I1…N2	2.082(3)	3.041(3)	168	<i>x</i> , <i>y</i> +1, <i>z</i> +1
	C9–I2····C6	2.061(3)	3.359(3)	171	<i>x</i> , <i>y</i> +1, <i>z</i> +1
(5a2mp) <sub>2</sub> (tfib)	C8–I1…N2	2.093(6)	2.964(7)	179	<i>x</i> –1, <i>y</i> , <i>z</i>

Table S4	4. Geo	metric	para	meters	for	the	hydr	ogen	bonds	in	prepared	cocrystals.	Distances
between	select	atoms	in a c	contact	are	den	oted	as d,	while	the	correspor	iding angle	is marked
with $\alpha$ .													

compound	<b>D</b> –H···A	<i>d</i> ( <i>D</i> −H) / Å	<i>d</i> (H…A) / Å	<i>d(D−</i> H··· <i>A</i> ) / Å	α/°	symmetry operator
(4aap) <sub>2</sub> (tfib)	C6–H6…F1	0.930(3)	2.517(2)	3.286(3)	140	1-x, 1-y, -z
(4ab) <sub>2</sub> (tfib)	N1–H1N…O1	0.88(6)	2.04(5)	2.920(6)	175	<i>x</i> –1, <i>y</i> , <i>z</i>
	N1-H2N…N1	0.86(5)	2.56(5)	3.433(7)	175	-x-1/2, y+1/2, 1/2-z
	С5-Н5…О1	0.930(4)	2.611(4)	3.298(6)	131	1/2-x, y+1/2, 1/2-z
(4noa) <sub>2</sub> (tfib)	N2–H2N…O3	0.89(8)	2.42(9)	3.138(17)	138	<i>x</i> –1, <i>y</i> , <i>z</i>
	N4–H3N…O2	0.88(15)	2.40(15)	3.15(2)	142	<i>x</i> , <i>y</i> +1, <i>z</i>
	N2–H1N…F2	0.89(3)	2.66(9)	3.109(16)	112	<i>x</i> –1, <i>y</i> , <i>z</i>
	N4–H4N…F4	0.87(13)	2.32(13)	3.126(17)	153	<i>x</i> , <i>y</i> +1, <i>z</i>
	С5 <b>–</b> Н5…F3	0.930(15)	2.617(9)	3.221(17)	123	<i>x</i> , <i>y</i> , <i>z</i>
	С6 <b>–</b> Н6…F3	0.930(14)	2.632(8)	3.230(16)	122	<i>x</i> , <i>y</i> , <i>z</i>
	C11–H11…F1	0.930(14)	2.563(8)	3.182(15)	124	<i>x</i> , <i>y</i> , <i>z</i>
(3ap)(tfib)	С6 <b>–</b> Н6…F1	0.930(3)	2.517(2)	3.286(3)	140	1-x, 1-y, -z
(3abn)(tfib)	N2-H2N…N1	0.89(6)	2.22(6)	3.099(6)	170	<i>x</i> –1, <i>y</i> , <i>z</i>
	N2–H1N…F2	0.78(6)	2.71(6)	3.480(5)	166	x, 1–y, z
(5a2mp) <sub>2</sub> (tfib)	N2–H2N…N1	0.90(6)	2.36(6)	3.257(6)	172	3/2- <i>x</i> , <i>y</i> +1/2, 1/2- <i>z</i>
	С6Н1С…О1	0.960(6)	2.740(3)	3.369(6)	124	2-x, 1-y, 1-z



**Figure S1.** Molecular structure of  $(4aap)_2(tfib)$  showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.



**Figure S2.** Molecular structure of  $(4ab)_2(tfib)$  showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.



**Figure S3.** Molecular structure of  $(4noa)_2(tfib)$  showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, strong hydrogen and halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.



**Figure S4.** Molecular structure of (3ap)(tfib) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.



**Figure S5.** Molecular structure of (**3abn**)(**tfib**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.



**Figure S6.** Molecular structure of  $(5a2mp)_2(tfib)$  showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.



Figure S7. PXRD pattern of pure 4aap reactant.



Figure S8. PXRD pattern of pure 4ab reactant.



Figure S9. PXRD pattern of pure 4noa reactant.



Figure S10. PXRD pattern of pure 3ap reactant.



Figure S11. PXRD pattern of pure 3abn reactant.



Figure S12. PXRD pattern of pure tfib reactant.



**Figure S13.** PXRD patterns of: a) **tfib**, b) **4aap**, c) product obtained by grinding a mixture with a 2:1 molar ratio of **4aap** to **tfib** in a ball mill for 15 min in the presence of 15  $\mu$ L of acetonitrile, d) bulk product obtained from the solution synthesis experiment.



**Figure S14.** PXRD patterns of: a) **tfib**, b) **4ab**, c) product obtained by grinding a mixture with a 2:1 molar ratio of **4ab** to **tfib** in a ball mill for 15 min in the presence of 5.0  $\mu$ L of acetonitrile, d) bulk product obtained from the solution synthesis experiment.



**Figure S15.** PXRD patterns of: a) **tfib**, b) **4noa**, c) product obtained by grinding a mixture with a 2:1 molar ratio of **4noa** to **tfib** in a ball mill for 15 min in the presence of 5.0  $\mu$ L of acetonitrile, d) bulk product obtained from the solution synthesis experiment.



**Figure S16.** PXRD patterns of: a) **tfib**, b) **3ap**, c) product obtained by grinding an equimolar mixture of **3ap** and **tfib** in a ball mill for 15 min in the presence of 5.0  $\mu$ L of acetonitrile, d) bulk product obtained from the solution synthesis experiment.





**Figure S18.** PXRD patterns of: a) **tfib**, b) product obtained by grinding a mixture with a 2:1 molar ratio of **5a2mp** and **tfib** in a ball mill for 15 min, c) bulk product obtained from the solution synthesis experiment.



Figure S19. DSC curve of the pure tfib reactant.



Figure S20. DSC curve of the pure 4aap reactant.



Figure S21. DSC curve of the pure 4ab reactant.



Figure S22. DSC curve of the pure 4noa reactant.



Figure S23. DSC curve of the pure 3ap reactant.



Figure S24. DSC curve of the pure 3abn reactant.



Figure S25. DSC curve of the (4aap)<sub>2</sub>(tfib) cocrystal.



Figure S26. DSC curve of the (4ab)<sub>2</sub>(tfib) cocrystal.



Figure S27. DSC curve of the (4noa)<sub>2</sub>(tfib) cocrystal.



Figure S28. DSC curve of the (3ap)(tfib) cocrystal.



Figure S29. DSC curve of the (3abn)(tfib) cocrystal.



Figure S30. DSC curve of the (5a2mp)<sub>2</sub>(tfib) cocrystal.

**Table S5.** Endothermic peak onsets of the used reactants and obtained cocrystals.

compound	T <sub>e</sub> / °C				
tfib	80.0; 106.4				
4аар	90.2; 102.9				
(4aap) <sub>2</sub> (tfib)	92.2				
4ab	123.1				
( <b>4ab</b> ) <sub>2</sub> ( <b>tfib</b> )	77.6; 87.4				
4noa	149.0				
(4noa) <sub>2</sub> (tfib)	106.5; 115.6				
Зар	63.1				
(3ap)(tfib)	55.9				
3abn	53.5				
(3abn)(tfib)	93.4				
(5a2mp) <sub>2</sub> (tfib)	72.6				