# Living in the Salt-Cocrystal Continuum: Indecisive Organic Complexes with Thermochromic Behaviour

## **Electronic Supporting Information**

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# S1. Crystallisation conditions

4-iodoaniline (4-IA) and 4-bromoaniline (4-BrA) are light-purple and beige crystalline solids, respectively, and 3,5-dinitrobenzoic acid (3,5-DNBA) is a light-yellow solid. Dissolution of 3,5-DNBA with 4-IA and 4-BrA resulted in pale-orange and yellow solutions. The  $\Delta$ pKa values for 3,5-DNBA with 4-IA and 4-BrA are 0.99 and 1.07, and thus complexes formed between them would fall into the salt-cocrystal continuum.

From 4-IA and 3,5-DNBA we obtained four 1:1 molecular complexes (1-3) and a methanol solvate (CSD refcode YIVHES)[1] *via* slow evaporation of the solvent. Cocrystallisation of 4-BrA and 3,5-DNBA yielded two molecular complexes (4 and 5), again *via* slow evaporation of solvent. Both sets of products included one ionic salt and one neutral form. In each of the products, the 4-haloaniline and 3,5-DNBA are present in the same 1:1 stoichiometry. The ionic molecular complexes invariably formed colourless crystals, whereas the crystals of the neutral and solvate forms were strongly coloured (red or orange).

4-iodo-2-methylaniline (4-I-2-MA), 4-bromo-2-methylaniline (4-Br-2-MA) and 4-chloro-2-methylaniline (4-Cl-2-MA) are light purple, light brown and light purple, respectively. Dissolution of 3,5-DNBA with 4-I-2-MA, 4-Br-2-MA and 4-Cl-2-MA resulted in pale-pink, yellow and orange solutions, respectively. The  $\Delta$ pKa values for 3,5-DNBA with 4-I-2-MA, 4-Br-2-MA are 0.84, 0.89 and 1.03, and thus again complexes formed between them would fall into the salt-corrystal continuum.

From the 1:1 cocrystallisation of the aniline with 3,5-DNBA, neutral and salt forms were obtained for 4-I-2-MA (**6** and **7**; CSD refcodes **YIVHUI** and **YIVHUI01**)[1] and 4-Br-2-MA (**8** and **9**), but only an ionic salt was formed with 4-CI-2-MA (**10**). Again, both forms occur with the same relative 1:1 stoichiometry, and the ionic complexes invariably formed colourless crystals whereas the neutral complexes were strongly coloured (red or orange).

All non-hydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were placed in calculated positions and refined as riding on the atoms to which they were bonded.

For the 4-XA ionic salt complexes, the hydrogen atoms of the two  $NH_3^+$  groups were located using Fourier difference maps and the H-atom positions allowed to freely refine with the  $U_{iso}$ constrained to 1.5  $U_{eq}$  of the N-atom to which they were bonded. For the neutral 4-XA cocrystals, the hydrogen atoms on the  $NH_2$  groups were identified and refined as above. The hydrogen atom of the carboxylic acid group was located using Fourier difference maps, and the position refined using a distance restraint of 0.9 Å and the  $U_{iso}$  of the H atom constrained to 1.5  $U_{eq}$  of the O atom to which it was bonded.

For the 4-X-2-MA compounds, the methyl group H atoms were located initially using Fourier difference maps and the bond distances and angles constrained to take standard values, with the  $U_{iso}$  of the H atoms constrained to 1.5  $U_{eq}$  of the C atom to which they were bonded. For the salts, the hydrogen atoms of the NH<sub>3</sub><sup>+</sup> group were identified using Fourier difference maps and the positions and isotropic displacement parameters allowed to freely refine. For the cocrystals, the hydrogen atoms of the NH<sub>2</sub> group were located and refined in the same manner. The hydrogen atom of the carboxylic acid group was located using Fourier difference maps and the position refined using a distance restraint (DFIX 0.9 Å) with the isotropic thermal parameters allowed to freely refine.

#### S1.1. 4-iodoaniline 3,5-dinitrobenzoic acid

The 4IA 3,5-DNBA molecular complexes were obtained under a range of crystallisation conditions, but not reproducibly, and single crystals were difficult to grow - repeated crystallisation trials would often result in the growth of a different form to that obtained under ostensibly the same conditions in a previous trial. In addition, mixtures were often obtained, either due to concomitant growth or spontaneous interconversion, making characterisation difficult.

Single crystals of molecular complex **1**, one of the ionic salts, could be grown reproducibly from 2-propanol at all the temperatures tested and crystallised as colourless needles. This molecular complex was the only product formed in this solvent, and the crystals were uniform. Below 30°C, crystallisation from ethanol, acetonitrile and ethyl acetate also yielded molecular complex **1**, but not reproducibly. In some crystallisation trials under these conditions (acetonitrile and ethanol, 4 °C and ambient temperature), the other salt polymorph **2** was obtained. However, growth of **2** was less common and single crystals were only grown in very small quantities, which suggests complex **2** is less stable than **1**.

Single crystals of molecular complex **3**, the neutral cocrystal, could be obtained from ethanol, acetonitrile and ethyl acetate with evaporation carried out between 30-60 °C. The complex crystallised as red blocks that were easily distinguishable from crystals of the two salt polymorphs. However, molecular complex **3** is metastable, and preservation of the crystals in this form was challenging. The stability of the crystals also appeared to be variable across different samples.

Many of the crystals were observed to transform spontaneously to a colourless polycrystalline phase under ambient conditions.

In the majority of samples, the red crystals of **3** transformed immediately upon exposure to ambient air, but in some cases the samples contained a mixture of red and colourless phases upon initial inspection of the vial. It is possible that the two phases had grown concomitantly, or that the sample had partially transformed immediately following crystallisation; however, the nature of the polycrystalline colourless phase suggested rapid transformation had occurred prior to inspection of the vial. Conversely, some single crystals of molecular complex **3** were stable for significant periods of time (up to one year at the time of writing). In general, the most stable crystals were obtained from ethanol and ethyl acetate, with evaporation between 40-60 °C. However, we never observed whole samples to remain as molecular complex **3**.

Given the lack of colour, it was considered possible that molecular complex **3** was transforming either to one of the known colourless salt polymorphs (**1** and **2**) or to an unknown salt.

#### 4-iodoanilinium 3,5-dinitrobenzoate Form I (1)

Molecular complex **1** was synthesised by slow evaporation of an ethanol solution at ambient temperature, yielding colourless needles.

#### 4-iodoanilinium 3,5-dinitrobenzoate Form II (2)

The synthesis of this complex has been reported previously[1] (CSD refcode YIVHAO).

#### 4-iodoaniline 3,5-dinitrobenzoic acid (3)

Molecular complex **3** was synthesised from ethyl acetate at 40 °C, yielding small red block crystals.

#### S1.2. 4-bromoaniline 3,5-dinitrobenzoic acid

The ionic form of molecular complex **4** was synthesised *via* slow evaporation at ambient temperature from all solvents. The highest-quality single crystals were obtained from ethanol. The molecular complex was obtained as colourless needles with identical morphology to the equivalent 4-IA 3,5-DNBA molecular complex (**1**).

The neutral molecular complex **5** was obtained *via* slow evaporation above room temperature. Single crystals suitable for single-crystal X-ray diffraction were obtained from acetonitrile at 40 °C. The complex formed orange blocks that were easily distinguishable from the salt form. However, similarly to 4-IA 3,5-DNBA, molecular complex **5** was highly metastable and preservation of the form was difficult, with spontaneous conversion to a polycrystalline colourless phase typically occurring immediately upon exposure to the ambient environment. Crystals of molecular complex **5** appeared much less stable than the equivalent neutral 4-IA 3,5-DNBA complex. Single crystal X-ray diffraction data was collected at low temperature on one crystal of the molecular complex, but the remaining crystals transformed to the colourless phase before further analysis could be conducted.

Generally, evaporation carried out between 30-60 °C yielded the polycrystalline colourless phase, or a mixture of this phase and a very small amount of **5**. Visually, the colourless phase matched that of the phase obtained upon spontaneous transformation, suggesting that rapid conversion of **5** had occurred prior to inspection of the vial.

#### 4-bromoanilinium 3,5-dinitrobenzoate (4)

Molecular complex **4** was synthesised by slow evaporation of an ethanol solution at room temperature, yielding colourless needles.

#### 4-bromoaniline 3,5-dinitrobenzoic acid (5)

Molecular complex **5** was synthesised by slow evaporation of an acetonitrile solution at 40 °C, yielding yellow/orange block crystals.

#### S1.3. 4-iodo-2-methylaniline 3,5-dinitrobenzoic acid

The 4-I-2-MA 3,5-DNBA molecular complexes **6** and **7** formed as colourless and red block crystals, respectively, making the two forms easily distinguishable visually. It was not possible to predict which molecular complex would form under a particular set of conditions, with both often forming concomitantly. Both **6** and **7** were obtained from multiple solvents at each of the evaporation temperatures tested and repeat crystallisation trials would often result in the formation of a different molecular complex to the previous trial. Furthermore, molecular complex **7** is metastable and preservation of the form was difficult, similar to the corresponding 4-IA 3,5-DNBA complex. The stability of the crystals also varied across the samples. Many of the red crystals of **7** were observed to

transform spontaneously to a polycrystalline colourless phase upon exposure to the ambient environment. Conversely, some crystals of **7** were stable for significant periods of time (up to one year at the time of writing). Typically, the most stable crystals were obtained from crystallisation above 30 °C.

## 4-iodo-2-methylanilinium 3,5-dinitrobenzoate (6)

The synthesis of this complex has been reported previously[1] (CSD refcode **YIVHUI**).

## 4-iodo-2-methylaniline 3,5-dinitrobenzoic acid (7)

The synthesis of this complex has been reported previously[1] (CSD refcode **YIVHUI01**).

## S1.4. 4-bromo-2-methylaniline 3,5-dinitrobenzoic acid

The molecular complexes of 4-Br-2-MA 3,5-DNBA (**8** and **9**) formed as colourless and orange block crystals, respectively. Similarly to 4-I-2-MA 3,5-DNBA, it was not possible to predict which form would result from a given set of crystallisation conditions - each molecular complex was obtained from a range of solvent/temperature systems and many repeat crystallisation trials often resulted in a different form to a previous trial.

However, single crystals of **9** were only obtained in one crystallisation trial (methanol, 40 °C); in all other cases the form was obtained only as a powder. Furthermore, molecular complex **9** is metastable, and thus preserving the form was difficult, with the samples typically transforming spontaneously to a colourless phase upon exposure to the ambient environment. However, it was possible to collect single-crystal X-ray diffraction data and to carry out HSM analysis on a single crystal of the molecular complex obtained from methanol at 40 °C prior to transformation.

## 4-bromo-2-methylanilinium 3,5-dinitrobenzoate (8)

Molecular complex **8** was synthesised by slow evaporation of a methanol solution at ambient temperature, yielding colourless block crystals.

#### 4-bromo-2-methylaniline 3,5-dinitrobenzoic acid (9)

Molecular complex  ${\bf 9}$  was synthesised by slow evaporation of a methanol solution at 40 °C, yielding orange block crystals.

#### S1.5. 4-chloro-2-methylaniline 3,5-dinitrobenzoic acid

In the cocrystallisation experiments with 4-Cl-2-MA and 3,5-DNBA, it was only possible to obtain ionic molecular complex **10**, which formed reproducibly as large single crystals in each of the crystallisation trials. Numerous repeat crystallisations were conducted, but no additional phases were observed.

# 4-chloro-2-methylanilinium 3,5-dinitrobenzoate (10)

Molecular complex **10** was synthesised by slow evaporation of an acetonitrile solution at ambient temperature, yielding colourless block crystals.

	1	<b>2</b> [1]	3	4	5
Formula	(C <sub>6</sub> H <sub>7</sub> NI) <sup>+</sup> (C <sub>7</sub> H <sub>3</sub> N <sub>2</sub> O <sub>6</sub> ) <sup>−</sup>	$(C_6H_7NI)^+ (C_7H_3N_2O_6)^-$	(C <sub>6</sub> H <sub>6</sub> NI) (C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> O <sub>6</sub> )	(C <sub>6</sub> H <sub>7</sub> NBr)⁺ (C <sub>7</sub> H <sub>3</sub> N <sub>2</sub> O <sub>6</sub> )⁻	(C <sub>6</sub> H <sub>6</sub> NBr) (C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> O <sub>6</sub> )
<i>M</i> [g mol <sup>-1</sup> ]	431.14	431.14	431.14	384.15	384.15
T [K] (radiation)	100(2) (Mo Kα)	100(2) (Mo Kα)	150(2) (Mo Kα)	150(2) (Cu Kα)	100(2) (Mo Kα)
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	ρĪ	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	ρĪ
a [Å]	6.7588(1)	6.0536(7)	7.2766(3)	6.7937(1)	7.3332(10)
b [Å]	12.0929(2)	10.5285(16)	7.3862(3)	11.9574(1)	13.937(2)
<i>c</i> [Å]	36.4619(5)	24.444(3)	14.2883(5)	35.8729(3)	15.611(2)
α[°]	90	90	99.348(3)	90	65.133(5)
β [°]	90	90	103.7125(4)	90	82.758(6)
γ [°]	90	90	90.271(3)	90	83.330(6)
V [ų]	2980.16(8)	1558.0(4)	735.39(5)	2914.13(5)	1432.5(3)
Ζ	8	4	2	8	4
$ ho_{cal}$ [g cm <sup>-3</sup> ]	1.922	1.838	1.947	1.751	1.781
μ [mm <sup>-1</sup> ]	2.185	2.090	2.214	4.205	2.907
θ range [°]	3.065-26.366	3.16-27.47	2.798-27.484	4.444-66.600	3.045-27.485
Ref. collected	15628	10999	10639	14999	34237
Independent	6082	3552	3391	5107	6545
Observed > $2\sigma$	5960	3349	2740	4983	5473
R <sub>int</sub>	0.0159	0.0299	0.0574	0.0345	0.0408
Completeness [%]	99.6	99.7	99.9	99.9	99.8
Parameters	433	220	217	433	433
Flack parameter	-0.016(5)	-0.02(2)	-	-0.028(7)	-
GooF	1.071	1.154	1.081	1.044	1.143
R <sub>1</sub> (obs)	0.0205	0.0211	0.0460	0.0390	0.0324
R <sub>1</sub> (all)	0.0213	0.0249	0.0633	0.0397	0.0403
wR <sub>2</sub> (all)	0.0476	0.0449	0.1099	0.1067	0.0879
$Q_{\text{max}}, Q_{\text{min}} [e \text{ Å}^{-3}]$	1.172, -0.902	0.560, -0.357	0.876, -0.585	1.205, -0.690	0.878, -0.652

# Table S1.1 Crystallographic data for molecular complexes 1-5.

	<b>6</b> [1]	<b>7</b> [1]	8	9	10
Formula	(C <sub>7</sub> H <sub>9</sub> NI) <sup>+</sup> (C <sub>7</sub> H <sub>3</sub> N <sub>2</sub> O <sub>6</sub> ) <sup>-</sup>	(C <sub>7</sub> H <sub>8</sub> NI) (C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> O <sub>6</sub> )	(C <sub>7</sub> H <sub>9</sub> NBr) <sup>+</sup> (C <sub>7</sub> H <sub>3</sub> N <sub>2</sub> O <sub>6</sub> ) <sup>-</sup>	(C <sub>7</sub> H <sub>8</sub> NBr) (C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> O <sub>6</sub> )	(C <sub>7</sub> H <sub>9</sub> NCl) <sup>+</sup> (C <sub>7</sub> H <sub>3</sub> N <sub>2</sub> O <sub>6</sub> ) <sup>-</sup>
<i>M</i> [g mol <sup>-1</sup> ]	445.17	445.17	398.18	398.18	353.72
T [K] (radiation)	100(2) (Μο Κα)	100(2) (Mo Kα)	150(2) (Μο Κα)	150(2) (Mo Kα)	150(2) (Mo Kα)
Space group	P2 <sub>1</sub>	рĪ	P2 <sub>1</sub>	рĪ	P2 <sub>1</sub>
a [Å]	10.7563(9)	8.534(3)	10.4081(4)	7.1802(4)	10.2583(6)
b [Å]	5.7898(4)	8.769(3)	5.8338(2)	7.2420(4)	5.8537(3)
<i>c</i> [Å]	13.3632(9)	11.882(8)	13.2672(5)	14.7292(6)	13.2818(9)
α [°]	90	111.035(8)	90	87.048(4)	90
β [°]	107.858(8)	101.327(7)	107.035(4)	88.078(4)	106.933
γ[°]	90	95.273(7)	90	89.926(5)	90
V [ų]	792.12(10)	800.9(7)	770.23(5)	764.46(7)	762.98(8)
Ζ	2	2	2	2	2
$ ho_{cal}$ [g cm <sup>-3</sup> ]	1.866	1.846	1.717	1.730	1.540
μ [mm <sup>-1</sup> ]	2.058	2.036	2.706	2.727	0.288
θ range [°]	3.203 - 27.473	3.209 - 27.483	2.949 - 29.514	2.816 - 30.410	2.969 - 27.461
Ref. collected	18081	18691	7649	11434	5839
Independent	3620	3661	3622	4107	3155
Observed > $2\sigma$	3583	3500	3192	3061	2630
R <sub>int</sub>	0.0206	0.0189	0.0361	0.0452	0.0321
Completeness [%]	99.7	99.8	99.8	99.9	99.8
Parameters	230	230	230	230	230
Flack parameter	-0.011(4)	-	0.003(7)	-	0.05(6)
GooF	1.095	1.135	1.033	1.068	1.044
R <sub>1</sub> (obs)	0.0131	0.0175	0.0385	0.0490	0.0431
R <sub>1</sub> (all)	0.0133	0.0185	0.0488	0.0766	0.0589
wR <sub>2</sub> (all)	0.0332	0.0462	0.0613	0.1058	0.0785
Q <sub>max</sub> , Q <sub>min</sub> [e Å <sup>-3</sup> ]	0.412, -0.246	0.515, -0.234	0.515, -0.389	1.339, -0.839	0.193, -0.224

 Table S1.2 Crystallographic data for molecular complexes 6-10.

# S2. Crystallographic discussion

#### S2.1. 4-haloanilinium 3,5-dinitrobenzoate molecular complexes

Two polymorphs of 4-iodoanilinium 3,5-dinitrobenzoate, **1** and **2**,[1] and a single complex of 4-bromoanilinium 3,5-dinitrobenzoate, **4**, were formed. Molecular complexes **1** and **4** are isomorphous. All three molecular complexes have a 1:1 stoichiometry and are ionic salts, with full proton transfer from the carboxylic acid group of 3,5-DNBA to the amine group of 4-XA. The C-O distances indicate a delocalisation of charge across the carboxylate group. All three grow as colourless crystals and crystallise in the orthorhombic space group  $P2_12_12_1$ . The asymmetric units of molecular complexes **1** and **4** contain two independent 4-iodoanilinium cations and two independent 3,5-dinitrobenzoate anions, whereas the asymmetric unit of molecular complex **2** contains one each of the cation and anion.



**Figure S2.1.1** (a) Moderate strength N-H···O hydrogen bonds linking the two 4-XA cations and four 3,5-DNBA anions and (b) hydrogen-bonded chain with a backbone of stacked 4-XA cations, connecting adjacent chains *via* short C-X···O contacts found in **1** and **4**; (c) the contrasting stacking in **2**.

In all three molecular complexes, the 3,5-DNBA molecules are approximately planar and each hydrogen atom of the tetrahedral  $NH_3^+$  group of the 4-haloanilinium cations participates in hydrogen bonding to the oxygen atom of a carboxylate group on an adjacent 3,5-dinitrobenzoate anion. The charge-assisted hydrogen bonding directs a three-dimensional network. An  $R_4^3$ (10) hydrogen-bonded

ring that includes two H atoms from each independent  $NH_3^+$  group and two carboxylate groups is formed (Figure S2.1.1(a)).

This four-molecule units extend along the crystallographic *a*-axis through two further hydrogen bonds to form a continuous hydrogen-bonded chain. In **1** and **4**, a stack of parallel 4-haloanilinium cations form the backbone of the chain (Figure S2.1.1(b)). The halogen atom of one cation forms a short contact with one of the nitro group oxygen atoms in an adjacent 3,5-DNBA chain (I···O = 3.312(3) and Br···O = 3.184(4) Å, compared to the sum of the van der Waals radii of the two atoms of 3.50 and 3.37 Å, respectively).

In molecular complex **2**, there is no stacking of the 4-IA molecules, and instead the cations are oriented away from each other and on opposing sides of the chain (Figure S2.1.1(c)). The iodine atoms form halogen bonds with one of the carboxylate oxygen atoms with an I···O distance of 2.987(2) Å, which is significantly shorter than the sum of the van der Waals radii of the two atoms (3.5 Å) and weaker than the halogen bond in **1**. This interaction links the individual hydrogen-bonded chains along the direction of the crystallographic *b*-axis (Figure S2.1.1(c)).

All three complexes also contain  $O_{nitro} \cdots O_{nitro}$  and  $O_{nitro} \cdots \pi$  interactions between 3,5-DNBA anions. Overall, the three-dimensional hydrogen bonding arrangement results in non-layered crystal structures, and there are no  $\pi \cdots \pi$  stacking interactions between 4-XA and 3,5-DNBA molecules. Projection down the crystallographic *b*-axis shows the alternating sections of 4-XA and 3,5-DNBA molecules (Figure S2.1.2).



Figure S2.1.2 Contrasting packing in complexes 1 and 4 (a) and complex 2 (b).

#### S2.2. 4-haloaniline 3,5-dinitrobenzoic acid

The neutral molecular complexes are not isomorphous, but the overall crystal packing in each is very similar. Both **3** and **5** crystallise in the triclinic space group  $P^{1}$ . The molecular components are neutral and crystallise in a 1:1 ratio. The asymmetric unit of **3** contains one molecule of each component, while the asymmetric unit of **5** contains two independent molecules of each component. In both complexes, the carboxylic acid groups of 3,5-DNBA are close to coplanar

3,5-DNBA molecules form dimers through moderate strength O-H···O hydrogen bonds between the strongest hydrogen bond donors and acceptors, resulting in  $R_2^2(8)$  hydrogen bonded rings typical for carboxylic acid groups. The dimers are formed between equivalent coplanar molecules.

In both molecular complexes, alternating rows of the 4-haloaniline molecules and 3,5-DNBA dimers interact to form planar two-dimensional sheets. However, the intermolecular interactions and molecular orientations of the 4-XA molecules within the chains differ between the two complexes

(Figure S2.2.1) - in **3**, pairs of 4-IA molecules are in opposite orientations, whereas in **5** the 4-BrA molecules are in similar orientations across the chain.



**Figure S2.2.1** Two-dimensional planar sheets in molecular complex **3** (a), showing the N-H···O and C H···O hydrogen bonds, and molecular complex **5** (b) showing the N-H···O and C-H···O hydrogen bonds and C-Br···O halogen interactions.

In molecular complex **3**, 3,5-DNBA dimers interact with one another through weak C-H···O hydrogen bonds to form a hydrogen-bonded chain of 3,5-DNBA molecules (Figure S2.2.1(a)). The 4-IA molecules form moderate-to-weak N-H···O hydrogen bonds through both H atoms to nitro group O atoms of the 3,5-DNBA molecules to form sheets. The iodine atoms do not participate in halogen interactions.

In molecular complex **5**, each sheet incorporates both independent 4-BrA molecules and both 3,5-DNBA molecules. Unlike molecular complex **3**, there are no interactions between adjacent 3,5-DNBA dimers. The H atoms of the amine groups on both 4-BrA molecules are involved in moderate to weak N-H···O hydrogen bonds with nitro group O atoms (Figure 3.2.1 (b)). In addition, each of the bromine atoms are involved in short C-Br···O halogen bonds with nitro group oxygen atoms (Br1···O9 = 3.261(1) and Br2···O6 = 3.368(2) Å, compared to the sum of the van der Waals radii of Br and O of

3.37 Å). There are also further weak C-H···O hydrogen bonds between the aromatic hydrogen atoms of 4-BrA molecules and nitro/carboxylic acid group oxygen atoms (C···O =  $\sim$ 3.3-3.5 Å).

Within the sheets, the interactions between the 4-XA molecules and the hydrogen-bonded 3,5-DNBA dimers are all weak or close to weak in nature (i.e. on the borderline between moderate and weak hydrogen bonds, and close to the sum of the van der Waals radii for hydrogen bonds). This highlights the poor hydrogen-bond donating ability of the NH<sub>2</sub> donor groups and may also explain why the neutral complex is the least stable form. In general, however, the hydrogen bonds in **3** are slightly stronger than those in **5**. In both complexes, the planar sheets stack to form a layered structure, with alternately stacked 4-XA (electron-donor) and 3,5-DNBA (electron-acceptor) molecules forming mixed stack columns; it is these aromatic donor…acceptor interactions that dominate the packing arrangement in the structures. There are very similar intermolecular separations of  $\sim$ 3.36 and  $\sim$ 3.32 Å between stacked 4-XA and 3,5-DNBA molecules in **3** and **5**, respectively.

## S2.3. 4-halo-2-methylanilinum 3,5-dinitrobenzoate complexes

The 4-halo-2-methylanilinium 3,5-dinitrobenzoate molecular complexes **6**,[1] **8** and **10** are isomorphous. They form as colourless block crystals and crystallise in the triclinic space group  $P^{1}$ . The components of the molecular complexes are ionic, with full proton transfer from the carboxylic acid group of 3,5-DNBA to the amine group of 4-X-2-MA. The two components crystallise in a 1:1 ratio, with one molecule of each component in the asymmetric unit.

There is a delocalisation of the charge across the carboxylate groups. Similarly to the ionic forms of 4-XA 3,5-DNBA, moderate strength N-H···O hydrogen bonds form between the NH<sub>3</sub><sup>+</sup> group of 4-X-2-MA and the oxygen atoms of the 3,5-DNBA carboxylate groups, resulting in  $R_4^3$ (10) hydrogenbonded rings (Figure S2.3.1). The methyl group is only involved in one weak hydrogen bond to one of the carboxylate O atoms.



**Figure S2.3.1** The  $R_4^3(10)$  hydrogen-bonded ring (shown for molecular complex **8**) formed through moderate strength N-H···O hydrogen bonds between the hydrogen atoms of NH<sub>3</sub><sup>+</sup> and carboxylate group oxygen atoms. The interactions are identical across the three complexes **6**, **8** and **10**.

The halogen atom of the 4-X-2-MA cation forms a short X···O contact to the O atom of one of the nitro groups (I···O = 3.204(2), Br···O = 3.160(3), CI···O = 3.170(3) Å, compared to the sum of the van der Waals radii of the two atoms of 3.50, 3.37 and 3.27 Å, respectively). In addition, there are  $O_{nitro}$ ···O<sub>nitro</sub> interactions between adjacent 3,5-DNBA anions and O··· $\pi$  interactions involving nitro and carboxylate group O atoms. Overall, the hydrogen-bonding interactions of the tetrahedral anilinium group lead to a non-layered structure similar to the ionic 4-IA 3,5-DNBA molecular complex, **2**, with alternating sections of 4-X-2-MA and 3,5-DNBA molecules (Figure S2.3.2).



Figure S2.3.2 Non-layered crystal packing in molecular complexes 6, 8 and 10. 4-X-2-MA and 3,5-DNBA molecules are shown in blue and yellow, respectively.

#### S2.4. 4-halo-2-methylaniline 3,5-dinitrobenzoic acid complexes

Molecular complexes **7** and **9** both crystallise in the triclinic space group  $P^1$ , with the neutral molecular components in a 1:1 ratio. The asymmetric unit contains one molecule of each of the neutral molecules. Similarly to the pair of neutral 4-XA 3,5-DNBA molecular complexes, the overall crystal packing in **7** and **9** is similar, but the complexes are not isostructural.

Two molecules of 3,5-DNBA form a hydrogen-bonded homodimer through moderate-strength

O-H…O hydrogen bonds, leading to  $R_2^2$ (8) rings (Figure S2.4.1). Alternating rows of the haloaniline molecules and 3,5-DNBA dimers interact to form planar two-dimensional sheets. However, the intermolecular interactions and molecular orientations within the sheets differ between the two complexes (Figure S2.4.1). In **9**, rotation of the aniline molecule has the effect of pushing the 3,5-DNBA dimer units apart. In **7** (Figure S2.4.1(a)), the 3,5-DNBA dimers interact with one another through weak C-H…O hydrogen bonds (C…O = 3.614(2) Å) to form a hydrogen-bonded chain. The same chain is observed in the neutral 4-IA 3,5-DNBA complex **3**. The methyl group is again only involved in one weak hydrogen bond to a nitro group O atom (Figure S2.4.1(a)), and the iodine atom is not involved in any interactions within the sheets.

In **9** (Figure S2.4.1(b)), there are no interactions between the 3,5-DNBA dimers. Weak N-H···O hydrogen bonds form between only one of the amine group H atoms, H1B, and the nitro group oxygen atom O3 (Figure S2.4.1(b)). Here, the methyl group is not involved in any interactions within the sheet, but there are interactions between the halogen and a nitro group O atom (Br···O = 3.120(2) Å, compared to the sum of the van der Waals radii of 3.37 Å) (Figure S2.4.1(b)).



**Figure S2.4.1** Two-dimensional sheets formed in molecular complex **7** (a), showing the 3,5-DNBA dimers interacting with 4-I-2-MA molecules and adjacent 3,5-DNBA dimers through weak N-H…O and C-H…O hydrogen bonds, and (b) molecular complex **9**, showing the bonded 3,5-DNBA dimers interacting with 4-Br-2-MA molecules through weak N-H…O and C-H…O hydrogen bonds and short C-Br…O halogen bonds.

Similarly to the neutral 4-XA 3,5-DNBA complexes, the interactions within the sheets are all weak or close to weak, again highlighting the poor hydrogen-bond donating ability of the N-H donor groups and providing an explanation as to why the neutral complex is the least stable form. In general, the hydrogen bonds in **7** are stronger than in **9**.

The planar sheets stack to form a layered structure, with alternately stacked 4-X-2-MA (donor) and 3,5-DNBA (acceptor) molecules forming mixed-stack columns. In 4-I-2-MA 3,5-DNBA, there are aromatic donor···acceptor interactions between pairs of 4-I-2-MA and 3,5-DNBA, and there are  $\pi$ ··· $\pi$  interactions between offset 3,5-DNBA molecules in adjacent layers. In 4-Br-2-MA 3,5-DNBA, there are aromatic donor···acceptor interactions continuously along the stack, but there are no offset  $\pi$ ··· $\pi$  interactions between 3,5-DNBA molecules. There are very similar intermolecular separations of ~3.23 and~3.30 Å between stacked 4-X-2A and 3,5-DNBA molecules in **7** and **9**, respectively. The colour in both molecular complexes may be attributed to  $\pi$ ··· $\pi$ \* charge-transfer between the neutral aromatic donor and acceptor molecules in the mixed stacks.

# **S3.** Optical properties



**Figure S3.1** (a) Photographs of single crystals of molecular complexes **3** (left) and **5** (right). (b) Single-crystal UV-visible absorption spectrum for molecular complex **3** collected at room temperature.



**Figure S3.2** (a) Photographs of single crystals of molecular complexes **7** (left) and **9** (right). (b) Single-crystal UV-visible absorption spectrum for molecular complex **7** collected at room temperature.

## S4. Thermal analysis

#### S4.1. 4-iodoaniline 3,5-dinitrobenzoic acid

The thermal behaviour of the molecular complexes is complicated, but the observations from HSM and DSC experiments match well. No thermal events were observed in molecular complex **1** prior to 100 °C, whereas the other complexes all appear to undergo solid-to-solid transformations. In the case of **3**, the loss of colour following the phase transformation suggests conversion to an ionic form of the molecular complex, either the known **1** or **2** or an unknown phase.



Figure S4.1.1 Differential-scanning calorimetry thermograms of samples of molecular complexes 1 (a), 2 (b) and 3 (c). Possible phase-transformation events are circled in red.

In each sample, melting occurs at ~120 °C, suggesting that each of the complexes has transformed to the same phase prior to reaching this temperature. PXRD experiments suggest that, at least in some cases, molecular complex **3** transforms to **1** or **2**. However, this is only observed across a limited number of samples, with many of the diffraction patterns showing mixtures of phases which cannot be identified (see Section S6). In order to fully understand the thermal behaviour of the complexes, it would be necessary to collect high-resolution powder data for each of the pure molecular complexes in combination with *in situ* variable-temperature measurements on a larger range of samples. For this, pure samples of the metastable molecular complex **3** would need to be grown and preserved in sufficient quantities.

## S4.2. 4-bromoaniline 3,5-dinitrobenzoic acid

HSM analysis was conducted on samples of the ionic molecular complex **4** and a sample of the phase obtained from transformation of **5**. All crystals of **5** were found to transform too quickly for HSM experiments to be performed. Samples were heated from 30-210 °C at a rate of 5 °C/minute. In the single crystal of **4** there is a very small shift in position at 105 °C, followed by a small jump at 115 °C. At 127 °C, there is a significant jump of the crystal and a simultaneous change in colour from colourless to orange as the sample begins to melt. Between 132-135 °C there is a loss of colour across the sample and recrystallisation of a colourless polycrystalline phase which melts at ~200 °C. The sample of the polycrystalline colourless phase showed similar thermal behaviour. The sample appears to undergo a phase transition, with darkening and large cracks appearing across the sample between 100-112 °C. At 126 °C, the sample begins to melt, forming a pale orange liquid, followed by recrystallisation of a polycrystalline colourless phase between 132-140 °C. This phase melts at ~203 °C. It is possible that the final melt in each experiment corresponds to the melt of recrystallised starting material 3,5-DNBA (204-206 °C).

A sample of pure molecular complex **4** and a sample of the polycrystalline transformed phase were also analysed by DSC with an equivalent temperature ramp. There are a number of endothermic peaks observed in each of the sample traces. In the DSC thermogram of **4** (Figure S4.2.1(a)), the first two endothermic peaks observed have onset temperatures of 102.1 °C (i) and 116.6 °C (ii), which match the temperatures at which the jumps in crystal position are observed in the HSM analysis, and possibly correspond to phase transitions. There is a third significant peak with an onset temperature of 127.1 °C (iii), which is likely to be due to the melting of the complex. There are two further endothermic events, with onset temperatures of 135.6 °C and 141.4 °C (iv and v), followed by decomposition of the sample up to 200 °C.

In the DSC thermogram of the transformed sample (Figure S4.2.1 (b)), there is a small endothermic peak over the approximate range 102-113 °C (i). This is followed by a sharp peak with an onset temperature of 123.2 °C (ii) which is likely to correspond to melting of the complex. There is a further endothermic peak with an onset temperature of 134.9 °C (iii), and an additional event with an onset temperature of 146.83 °C (iv). The DSC thermograms suggest that both samples are in the same phase upon melting.

The HSM and DSC experiments revealed complicated thermal behaviour. Prior to the melting at  $\sim$ 126 °C in HSM, molecular complex **4** appears to undergo two phase transitions at 105 °C and 115 °C, while the transformed sample appears to undergo only a single transition at 112 °C. This difference in thermal behaviour suggests that the spontaneous transformation of molecular complex **5** does not

result in the known ionic complex **4**. However, the melt occurs at approximately 126 °C in both samples, which suggests that, upon heating, both convert to the same phase prior to melting.



**Figure S.4.2.1** Differential-scanning calorimetry thermograms of samples of molecular complex **4** (a) and the colourless polycrystalline phase obtained following transformation of molecular complex **5** (b). The labels **i**-**v** denote the temperatures of the thermal events discussed in the text.

#### S4.3. 4-iodo-2-methylaniline 3,5-dinitrobenzoic acid

Crystals of molecular complex **7** were sufficiently stable for thermal analysis *via* HSM and DSC. For the HSM analysis, a red single crystal of **7** was heated between 30-130 °C at a rate of 5 °C/minute. A colour change from red to colourless was observed over the temperature range 77-84 °C. The transition moves across the crystal in a wave with loss of single-crystallinity, demonstrating that the transformation occurs both spontaneously and upon heating. Following the transformation, the colourless phase starts to melt at ~117 °C, forming a red liquid, and there is immediate recrystallisation of colourless needles. HSM experiments were also carried out on a single crystal of the colourless ionic form **6**, showing the same melting and recrystallisation as transformed **7**.

DSC experiments were also conducted on pure samples of **6** (ionic) and **7** (neutral). Samples were heated between 40-130 °C at a rate of 5 °C/minute. The DSC thermogram obtained for **6** has a sharp endothermic peak corresponding to melting with an onset temperature of 114.01 °C (Figure S4.3.1 (a)). DSC measurements on **7** show a small exothermic event between 43-65 °C, which most

likely corresponds to the phase transformation to the colourless phase; the slight discrepancy between the phase transition temperatures in HSM and DSC may be a crystal-size effect. This is followed by a large, sharp endothermic peak with an onset temperature of 113.98 °C corresponding to melting (Figure S4.3.1 (b)).



**Figure S4.3.1** Differential-scanning calorimetry thermograms of molecular complexes **6** (a), showing a large endothermic melt peak with an onset temperature of ~114 °C, and **7** (b), showing a small exothermic event between 43-65 °C (inset), corresponding to the colour change observed in hot-stage microscopy, and a melt with the same onset temperature as **6**.

The HSM and DSC experiments suggest that the red, neutral form of 4-I-2-MA 3,5-DNBA (7) undergoes a transformation to the ionic complex **6** either spontaneously or upon heating. A thermally-induced colour change from red to colourless was observed during HSM analysis over the temperature range 77-84 °C. A small exothermic peak was also observed in the DSC thermogram of **7** at a slightly lower temperature, which was interpreted to correspond to the same phase transition. Following the transformation of **7** to the colourless phase, the sample melted at the same temperature as the pure sample of **6** with onset at ~114 °C.

#### S4.4. 4-bromo-2-methylaniline

It was possible to carry out HSM analysis on a single crystal of molecular complex **9**. An orange single crystal of molecular complex **9** was heated between 30-150 °C at a rate of 5 °C/minute. A colour change from orange to colourless was observed over a broad temperature range of 61-83 °C. As with **7**, the transition moves across the crystal in a wave with loss of single-crystallinity. Following the transformation, the colourless phase starts to melt at ~126 °C, forming an orange liquid, followed by

immediate recrystallisation of colourless needles. The same HSM experiment was also carried out on a single crystal of the colourless, ionic form of the molecular complex (8), in which the crystal began to melt at  $\sim$ 127 °C and again formed an orange liquid followed by recrystallisation of colourless needles from the melt.

Although it was not possible to carry out DSC experiments on the neutral form **9** due to rapid transformation, experiments were conducted on samples of **8** and a transformed sample of **9**. Samples were heated between 40-150 °C at a rate of 5 °C/minute. The DSC thermogram obtained for the ionic form **8** has a sharp endothermic peak corresponding to melting with an onset temperature of 125.13 °C. There is also a small exothermic peak on cooling with an onset temperature of 91.6 °C (Figure S4.4.1 (a)). The DSC thermogram for the transformed sample of **9** matches that of **8** very closely, with a sharp endothermic peak with an onset temperature of 128.55 °C, corresponding to melting, and a small endothermic peak on cooling with an onset temperature of 102.72 °C (Figure S4.4.1 (b)).



**Figure S4.4.1** Differential-scanning calorimetry thermograms of (a) molecular complex **8**, showing a large endothermic melt peak with an onset temperature of 125.13 °C, and (b) a transformed sample of molecular complex **9**, which matches that of **8** very closely.

The HSM and DSC experiments suggest that the orange neutral form of 4-Br-2-MA 3,5-DNBA (9) undergoes a transformation to the ionic form 8. A thermally-induced colour change from orange to colourless was observed during HSM analysis over the temperature range 62-83 °C. Following the transformation, the crystal began to melt at ~126 °C, which matches the melting point of the ionic form 8. Although it was not possible to carry out DSC analysis on the neutral form, experiments were carried on the ionic form and a spontaneously transformed sample of 9, and both were found to melt at approximately the same temperature.

#### S4.5. 4-chloro-2-methylaniline

Despite numerous attempts, it was not possible to obtain a neutral form of 4-Cl-2-MA 3,5-DNBA, with the ionic molecular complex **10** being obtained in all our crystallisation trials. HSM and DSC experiments were carried out on **10**, in each case heating between 40-150 °C at a rate of 5 °C/minute. A sharp endothermic peak was observed in the DSC thermogram with an onset temperature of 126.47 °C (Figure S4.5.1), which corresponds to the melting of the crystal observed at ~127 °C in the HSM experiment.



**Figure S4.5.1** Differential-scanning calorimetry thermogram of molecular complex **10**, showing a large endothermic melt peak with an onset temperature of 126.47 °C.

## **S5.** Powder X-ray diffraction

#### S5.1. 4-iodoaniline 3,5-dinitrobenzoic acid

A selection of the samples of each molecular complex, formed under various crystallisation conditions, was analysed by powder X-ray diffraction (PXRD). The PXRD patterns were compared against each other, against simulated patterns for molecular complexes **1**-**3**, and against simulated patterns of the starting materials 4-IA and 3,5-DNBA. The PolySNAP program was used to determine the similarity of powder patterns and to aid interpretation of the results.

The PXRD patterns of pure samples of **1** and **2** (Figure S5.1.1, green) matched the simulated patterns of the molecular complexes very well, with just a small peak shift due to the different data-collection temperatures (PXRD - ambient, single-crystal XRD - 100 K).

However, the analysis of **3** was more complicated. It was not possible to analyse a pure sample by PXRD due to a mixture of phases being present - in each case prior to grinding the bulk sample consisted partially of red crystals of **3** and partially of a colourless phase. The PXRD patterns of some of the red/colourless mixtures (Table S5.1.1, blue) matched the patterns of one of the known colourless ionic forms **1/2** (Figure S5.1.1 (a) and (b)), although there were peaks that did not match either as well as some preferred-orientation effects. It appears, therefore, that the crystals of **3** in the sample transformed to **1** or **2** in the time between removing the sample from the crystallisation vessel and starting the PXRD experiment.

**Table S5.1.1** Summary of the crystallization conditions used to obtain the samples characterized by powder X-ray diffraction. Pure samples grown evaporatively are shown in green, fully transformed samples of **3** are shown in blue, and mixtures are shown in red.

Crystallisation conditions						
Sample Solvent		Temperature (°C)	PXRD Pattern Match			
1	Acetonitrile	4	Molecular complex 1			
2	Acetonitrile	RT	Molecular complex 1			
3	Ethanol	RT	Molecular complex 1			
4	Ethyl acetate	4	Molecular complex 1			
5	2-propanol	RT	Molecular complex 1			
6	Ethanol	40	Molecular complex 1			
7	Ethanol	4	Molecular complex 1			
8	Ethanol	30	Molecular complex 2			
9	Ethanol	30	Molecular complex 2			
10	Methanol	4	Methanol solvate			
11	Methanol	RT	Methanol solvate			
12	Acetonitrile	40	Mixture			
13	Ethanol	40	Mixture			
14	Ethanol	50	Mixture			
15	Ethyl acetate	40	Mixture			
16	Ethyl acetate	60	Mixture			



**Figure S5.1.1** Powder X-ray diffraction patterns collected on some of the samples containing mixtures of red and colourless phases. The sample numbers refer to Table S.6.1. (a) Pure molecular complex **1** (Sample 1) shown in green and transformed sample (Sample 6) shown in blue. (b) Pure molecular complex **2** (Sample 7) shown in green and transformed sample (Sample 8) shown in blue. (c) Example diffraction pattern obtained for a mixed-phase sample (Sample 13).

However, the diffraction patterns of the majority of the mixtures (Table S5.1.1, red) were much more complicated and did not match either of **1** or **2**. The diffraction patterns of these

samples were also poorer quality in terms of crystallinity, possibly due to the crystallites going through a phase transition (Figure S5.1.1 (c)). In addition to the preferred-orientation effects, this made the analysis of the patterns very difficult. It is probable that the peaks correspond to a mixture of **3** and a colourless phase (either **1** or **2** or an unknown form), but higher-quality diffraction patterns would need to be obtained to confirm this.

#### S5.2 4-bromoaniline 3,5-dinitrobenzoic acid

PXRD analysis was conducted on pure and transformed samples of molecular complex **4**. The PXRD patterns were compared against each other, against simulated patterns of molecular complexes **4** and **5**, and against the simulated patterns of the starting materials 4-BrA and 3,5-DNBA.

In the 4-IA 3,5-DNBA series of molecular complexes, some of the samples of the neutral molecular complex were observed to transform to one of the known ionic forms. It was possible, therefore, that a similar transformation was occurring in the 4-BrA 3,5-DNBA molecular complexes. However, the PXRD patterns of the transformed samples did not match the patterns of the ionic complex **4** (Figure S5.2.1), nor the simulated patterns for either of the structurally characterised complexes, nor the PXRD patterns of either of the starting materials. It is thus possible that the transformation is to an unknown ionic form of the complex.



**Figure S5.2.1** Powder X-ray diffraction patterns collected on a sample of molecular complex **4** (black) and the polycrystalline colourless phase obtained following transformation of **5** (red).

The results of the PXRD experiments are consistent with the thermal analysis, showing that the transformed sample does not match **4**. However, given the colourless nature of the sample, it is likely that the transformation is to an unknown ionic form. In order to fully understand the thermal behaviour of the complexes, it would be necessary to collect high-resolution powder data for each of

the pure molecular complexes in combination with *in situ* variable temperature measurements. For this, pure samples of molecular complex **5** would need to be grown and preserved in sufficient quantities. Furthermore, a broader range of crystallisation trials would need to be conducted to investigate the possibility of additional ionic forms of the molecular complex.

#### S5.3. 4-iodo-2-methylaniline

PXRD was carried out on samples of the ionic molecular complex **6** and on samples of the neutral molecular complex **7** that remained sufficiently stable for analysis, as well as samples of **7** that had spontaneously transformed to the polycrystalline colourless phase. In addition, samples of molecular complex **7** were heated to 80 °C, just above the phase transition temperature, in order to convert the sample to the colourless form and to investigate the phase transformation associated with the thermally-induced colour change. The PXRD patterns of the samples of molecular complex **7** transformed spontaneously and through heating match the diffraction pattern of the ionic molecular complex **6** very well (Figure S5.3.1). This confirms that **7** transforms to the known ionic form **6**.

The diffraction patterns of the spontaneously- and thermally-transformed samples of **7** match the diffraction patterns of **6**. The phase transformation is therefore associated with a proton transfer from the carboxylic acid group of 3,5-DNBA to the amine group of 4-I-2-MA, resulting in a significant structural rearrangement and colour change. The transformation does not occur in a single-crystal-to-single-crystal manner due to the large structural differences between the neutral and ionic forms of the molecular complex.





#### S5.4. 4-bromo-2-methylaniline

PXRD was carried out on samples of the ionic molecular complex **8** and samples of **9** that had spontaneously transformed to the colourless phase to investigate the phase transformation. It was not possible to carry out PXRD on the neutral complex **9** due to its metastability. The peak positions in the PXRD patterns of the transformed samples and the ionic molecular complex **8** match very well (Figure S5.4.1), suggesting that **9** spontaneously transforms to **8**.

The diffraction patterns of spontaneously-transformed samples of **9** match the diffraction patterns of **8**, indicating that the phase transformation is associated with a proton transfer from the carboxylic acid group of 3,5-DNBA to the amine group of 4-Br-2-MA, resulting in a significant structural rearrangement and colour change. As for the 4-I-2-MA complex, the transformation does not occur in a single-crystal-to-single-crystal manner due to the large structural differences between the neutral and ionic forms of the molecular complex.



Figure **S5.4.1** Powder diffraction patterns collected on a sample of molecular complex **8** (black) and a transformed sample of **9** (red).

#### **S6.** Computational Modelling

#### S6.1. Method

Density-functional theory (DFT) calculations were carried out on the X-ray structures of **1-10** using the plane-wave pseudopotential formalism implemented in the Vienna *Ab initio* Simulation Package (VASP) code.[2]

Calculations were performed using two exchange-correlation functionals, *viz.* PBEsol[3] and PBEsol with the DFT-D3 dispersion correction[4] (i.e. PBEsol + D3). Projector augmented-wave (PAW) pseudopotentials[5,6] were employed treating the H 1s, C, O and N 2s/2p, Cl 3s/3p, Br 4s/4p and I 5s/5p electrons as valence. A plane-wave basis-set cutoff of 850 eV was used in all calculations, with the Brillouin-zone sampling performed using  $\Gamma$ -centred Monkhorst-Pack *k*-point meshes[7] with the subdivisions listed in Table S6.1.1. These settings were found to be sufficient to converge the absolute total energy and external pressure to < 1 meV atom<sup>-1</sup> and < 1 kbar (0.1 GPa), respectively. Each structure was fully optimised until the magnitude of the forces on the ions fell below 10<sup>-2</sup> eV Å<sup>-1</sup>, and a tolerance of 10<sup>-8</sup> eV on the total energy was applied during the electronic minimisation.

To investigate the electronic structures of the crystalline systems, single-point calculations with the PBE0 hybrid functional[8] were performed on the structures optimised with PBEsol + D3 to obtain more accurate orbital energies and to evaluate the dielectric properties using the linear-optics routines in VASP.[9] For these calculations, the number of electronic bands was increased to around 3  $\times$  the default, in order to provide a large number of empty bands for the sum over electronic transitions.

Con	npound and Formula	# Atoms	k-Points
1	[(3,5-DNBA <sup>-</sup> )(4-IAH <sup>+</sup> )] <sub>8</sub>	264	$2 \times 1 \times 1$
2	[(3,5-DNBA <sup>-</sup> )(4-IAH <sup>+</sup> )] <sub>4</sub>	132	$2 \times 1 \times 1$
3	[(3,5-DNBAH)(4-IA)] <sub>2</sub>	66	3×3×1
4	[(3,5-DNBA <sup>-</sup> )(4-BrAH <sup>+</sup> )] <sub>8</sub>	264	$_3 \times _1 \times _1$
5	[(3,5-DNBA)(4-BrA)] <sub>4</sub>	132	3×1×1
6	[(3,5-DNBA <sup>-</sup> )(4-I,2-MeAH <sup>+</sup> )] <sub>2</sub>	72	$1 \times 3 \times 1$
7	[(3,5-DNBA)(4-1,2-MeA)] <sub>2</sub>	72	$2 \times 2 \times 1$
8	[(3,5-DNBA⁻)(4-Br,2-MeAH⁺)]₂	72	$1 \times 2 \times 1$
9	[(3,5-DNBA)(4-Br,2-MeA)] <sub>2</sub>	72	2×2×1
10	[(3,5-DNBA <sup>-</sup> )(4-Cl,2-MeAH <sup>+</sup> )] <sub>2</sub>	72	$1 \times 2 \times 1$

Table S6.1.1 *k*-point sampling used in the solid-state calculations on 1-10.

To provide a reference with which to compute the formation energies of the ten compounds, we also carried out a set of calculations on the neutral molecular components in the gas phase, *viz.* 3,5-dinitrobenzoic acid (3,5-DNBA), 4-bromoaniline (4-BrA), 4-iodoaniline (4-IA), 4-chloro,2-methylaniline (4-Cl,2-MeA), 4-bromo,2-methylaniline (4-Br,2-MeA) and 4-iodo,2-methylaniline (4-I,2-MeA). Initial models of the species were extracted from the crystal structures, placed in a cubic box with an (initial) vacuum gap of ~10 Å between the closest atoms in periodic images, and then optimised with the same cutoff and convergence thresholds as used in the solid-state calculations and a  $\Gamma$ -point sampling of the electronic Brillouin zone.

## S6.2. Optimised Structures

The optimised lattice parameters of **1-10** obtained with PBEsol and PBEsol + D3 are compared to those of the experimental structures in Tables S6.2.1 and S6.2.2, respectively.

The average absolute deviation in the lattice lengths, cell angles and volume from the experimental structures across all ten compounds was found to be 1.92, 0.76 and 4.84 %, respectively, with PBEsol, and 1.95, 0.53 and 5.32 % with PBEsol + D3.

It is worth noting, however, that standard optimisation procedures yield athermal structures at 0 K (i.e. the lattice parameters and atomic positions are adjusted without accounting for thermal effects, principally vibrational motion). Therefore, assuming positive thermal expansion, we would expect the calculations to underestimate the cell volume. Bearing this in mind, while the average deviations from the experimental structures are similar for PBEsol and PBEsol + D3, the former consistently predicts a volume increase, whereas the latter predicts a volume contraction. This suggests the D3 correction provides a better overall description of the intermolecular interactions.

We also verified that each structure retained its original identity as a salt or cocrystal after optimisation with either functional.

#### S6.3. Energetics

The total energies obtained after optimisation were used to calculate formation energies with respect to the neutral acid and aniline components in the gas phase (Table S6.3.1).

The formation energies range from approx. -110 to -130 kJ mol<sup>-1</sup> (-1.15 to -1.45 eV) per formula unit (F.U.) with PBEsol, and from -245 to -270 kJ mol<sup>-1</sup> (-2.56 to -2.81 eV) per F.U. with PBEsol + D3. Similar total energies were obtained for the gas-phase molecules with and without the dispersion correction, with a maximum difference of ~20 kJ mol<sup>-1</sup> (~0.2 eV), so this difference can be ascribed to the better description of the weak intermolecular interactions in the solid state afforded by PBEsol + D3. This is consistent with the differences in the optimised structures obtained with the two functionals.

	[kJ mol <sup>-1</sup> per F.U.]				
	PBE	sol	PBEsol-D3		
Compound	E <sub>F</sub>	$\Delta_{E_{\text{Cocrystal}}}$	E <sub>F</sub>	$\Delta_{E_{\text{Cocrystal}}}$	
1	-129.38	-16.76	-262.48	-11.86	
2	-139.55	-26.93	-264.01	-13.38	
3	-112.62	-	-250.63	-	
4	-128.50	-13.07	-258.28	-11.33	
5	-115.43	-	-246.95	-	
6	-131.02	-8.65	-270.69	-10.26	
7	-122.37	-	-260.43	-	
8	-130.62	-14.24	-267.29	-8.51	
9	-116.37	-	-258.78	-	
10	-130.56	-	-262.65	-	

**Table S6.3.1** Formation energies of **1-10**, referenced to the energies of the neutral gas-phase components, calculated using PBEsol and PBEsol + D3. For each set of compounds, the energies of the ionic forms with respect to the H-bonded cocrystal (if formed) are also given.

Compound	a [Å]	b [Å]	<i>c</i> [Å]	α [°]	β [°]	γ [°]	<i>V</i> [ų]
1	6.807 (+0.72)	12.380 (+2.37)	36.835 (+1.02)	90	90	90	3104 (+4.16)
2	6.307 (+4.18)	10.445 (-0.80)	24.485 (+0.17)	90	90	90	1613 (+3.52)
3	7.385 (+1.49)	7.567 (+2.44)	14.402 (+0.79)	97.88 (-1.48)	104.01 (+0.28)	92.40 (+2.36)	767 (+4.65)
4	6.814 (+0.30)	12.179 (+1.85)	36.367 (+1.38)	90	90	90	3018 (+3.57)
5	7.414 (+1.11)	14.290 (+2.53)	16.164 (+3.54)	64.22 (-1.41)	82.01 (-0.91)	83.68 (+0.42)	1537 (+6.83)
6	10.998 (+2.25)	5.837 (+0.81)	13.770 (+3.05)	90	110.01 (+1.99)	90	831 (+4.86)
7	8.312 (-2.60)	8.905 (+1.55)	12.604 (+6.08)	113.62 (+2.33)	97.52 (-3.76)	94.91 (-0.39)	845 (+6.15)
8	10.705 (+2.85)	5.876 (+0.72)	13.645 (+2.84)	90	109.01 (+1.84)	90	811 (+5.35)
9	7.250 (+0.97)	7.415 (+2.39)	14.723 (-0.04)	88.96 (+2.19)	88.23 (+0.18)	88.52 (-1.56)	792 (+3.47)
10	10.565 (+2.99)	5.898 (+0.75)	13.690 (+3.07)	90	108.84 (+1.78)	90	807 (+5.81)

**Table S6.2.1** Optimised lattice parameters of **1-10** obtained with the PBEsol functional. The numbers in parentheses give the % deviation with respect to the experimentally-measured X-ray structures.

Table S6.2.2 Optimised lattice parameters of 1-10 obtained with the PBEsol functional with the DFT-D3 dispersion correction. The numbers in parentheses give the % deviation with respect to the experimentally-measured X-ray structures.

Compound	a [Å]	b [Å]	<i>c</i> [Å]	α [°]	β [°]	γ [°]	V [ų]
1	6.586 (-2.56)	12.015 (-0.65)	36.041 (-1.16)	90	90	90	2852 (-4.31)
2	6.036 (-0.30)	10.287 (-2.29)	24.101 (-1.40)	90	90	90	1496 (-3.95)
3	6.910 (-5.03)	7.309 (-1.05)	14.090 (-1.39)	99.34 (-0.01)	104.10 (+0.37)	89.43 (-0.94)	678 (-7.50)
4	6.587 (-3.05)	11.860 (-0.82)	35.390 (-1.35)	90	90	90	2764 (-5.14)
5	7.094 (-3.26)	13.457 (-3.45)	15.630 (+0.12)	65.51 (+0.57)	83.15 (+0.47)	86.50 (+3.80)	1358 (-5.65)
6	10.472 (-2.64)	5.769 (-0.36)	13.074 (-2.16)	90	106.62 (-1.15)	90	757 (-4.45)
7	8.023 (-5.99)	8.744 (-0.29)	11.964 (+0.69)	112.18 (+1.03)	101.18 (-0.14)	93.85 (-1.50)	752 (-5.54)
8	10.152 (-2.46)	5.819 (-0.25)	12.960 (-2.31)	90	105.63 (-1.31)	90	737 (-4.28)
9	7.023 (-2.19)	6.943 (-4.12)	14.445 (-1.93)	89.24 (+2.51)	87.96 (-0.13)	90.70 (+0.86)	705 (-7.90)
10	9.992 (-2.60)	5.829 (-0.42)	13.001 (-2.11)	90	105.70 (-1.15)	90	729 (-4.46)

The 4-iodoaniline system forms two salt polymorphs (1 and 2). The PBEsol formation energies predict 2 to be 10.2 kJ mol<sup>-1</sup> per F.U. more stable than 1, which is on the same order as the energy differences between the salt and cocrystal forms of the other systems obtained with the same functional. On the other hand, the PBEsol + D3 formation energies predict 2 to be a much smaller 1.53 kJ mol<sup>-1</sup> per F.U. lower in energy than 1. Experimentally, both 1 and 2 can be isolated, with 1 occurring more frequently. This implies that 1 and 2 are close in energy, and, disregarding kinetics and/or solvent effects during crystallisation, we would anticipate 1 to be lower in energy than 2. While neither set of results reproduces the latter, 1.53 kJ mol<sup>-1</sup> is close to the limit of the accuracy in these calculations and could easily be modulated by factors such as crystallisation conditions and energetic barriers to polymorph conversion. We therefore take the smaller energy difference predicted with the dispersion-corrected functional as a further indication that PBEsol + D3 gives better results for these systems.

The relative formation energies consistently place the salt forms of each acid/amine system at lower energies than the H-bonded cocrystals, with the differences ranging from 8.51 to 13.4 kJ mol<sup>-1</sup> per F.U. with PBEsol + D3. These energies are around the threshold where one might expect both polymorphs to be accessible depending on crystallisation conditions. The fact that the cocrystal-to-salt transition invariably lowers the energy is consistent with the phase transitions being irreversible, and with the cocrystal forms being kinetic products. However, these calculations do not predict the barriers to the forward and reverse phase transitions, and the relatively-small energy differences could be taken to suggest that high activation barriers to the reverse salt-to-cocrystal transformations may play a role in the irreversibility.

Another trend apparent in the PBEsol + D3 calculations is that the formation energies of comparable 4-haloaniline (X = Br, I) and 4-halo,2-methylaniline (X = Cl, Br, I) species fall into the order of I < Br < Cl, which suggests that, for a given form (salt/cocrystal), the thermodynamic stability would fall into the order I > Br > Cl. The two 4-iodoaniline salts are calculated to be 4.20 (1) and 5.73 (2) kJ mol<sup>-1</sup> per F.U. more stable than the 4-bromoaniline salt 4, while the 4-iodoaniline cocrystal 3 is 3.68 kJ mol<sup>-1</sup> per F.U. more stable than the 4-bromoaniline analogue 5. Among the 4-halo,2-methylaniline systems, the iodoaniline salt 6 is calculated to be 3.40 kJ mol<sup>-1</sup> per F.U. more stable than the bromoaniline salt 8, which is itself 4.64 kJ mol<sup>-1</sup> per F.U. more stable than the chloroaniline salt 10. The 4-iodo,2-methylaniline cocrystal 7 was calculated to be 1.65 kJ mol<sup>-1</sup> per F.U. more stable than the 4-bromo,2-methylaniline equivalent 9.

We also find that the 4-halo,2-methylaniline compounds (X = Br, I) have lower formation energies than the 4-haloaniline equivalents. The formation energy of the 4-iodo,2-methylaniline salt **6** is 8.21 and 6.68 kJ mol<sup>-1</sup> per F.U. lower than the 4-iodoaniline salts **1** and **2**, respectively, while that of the 4-bromo,2-methylaniline salt **8** is 9.01 kJ mol<sup>-1</sup> per F.U. more stable than the corresponding 4bromoanline salt **4**. Similarly, the 4-iodo,2-methylaniline and 4-bromo,2-methylaniline cocrystals **7** and **9** are 9.80 and 11.8 kJ mol<sup>-1</sup> per F.U. lower than those of the 4-iodoaniline and 4-bromoaniline cocrystals **3** and **5**, respectively.

Another interesting question is why no H-bonded cocrystal with 4-chloro,2-methylaniline was isolated. The energetics calculations do not suggest that this species would be unstable; indeed, for the iodoaniline and bromoaniline compounds the energy difference between the salt and cocrystals are smaller for X = Br than for X = I, which suggests that the X = CI cocrystal may be even more energetically accessible. We therefore tentatively suggest that the chloroaniline corrystal may be kinetically, rather than thermodynamically, inaccessible, under the crystallisation conditions investigated in this study.

### **S6.4. Optical Properties**

Table S6.4.1 compares the direct and indirect energy gaps between the highest-occupied and lowest-unoccupied crystal orbitals (HOCOs/LUCOs) of the ten structures, obtained with the PBE0 hybrid functional, along with the coordinates of the *k*-point at which the direct gap occurs. The values reveal a clear trend, namely that the cocrystals consistently have a smaller gap than the corresponding salts. Across all five compositions, the four cocrystals have HOCO-LUCO gaps ranging from approx. 2.0-2.5 eV, whereas the gaps of the six salts span a range of 3.4-4.0 eV. Direct electronic transitions are expected to be more intense than indirect ones, and, since the direct and indirect gaps of all ten crystals are within ~170 meV of each other, we focus our analysis on the direct gaps.

**Table S6.4.1** Direct and indirect energy gaps between the highest-occupied and lowest-unoccupied crystal orbitals (HOCOs/LUCOs;  $E_{g,dir}/E_{g,indir}$ ) in **1-10**, computed with the PBEO hybrid functional.

Compound	$E_{g,dir}$ [eV]	<sup>E</sup> <sub>g,indir</sub> [eV]
1	3.00	3.17
2	3.44	3.43
3	2.35	2.30
4	3.38	3.48
5	2.50	2.53
6	3.55	3.56
7	2.01	2.02
8	3.86	3.89
9	2.48	2.48
10	3.95	3.97

The trends in the HOCO-LUCO gaps are clearly reflected in the simulated absorption spectra (Figure S6.4.1). The absorption coefficients of the six salts tail off between ~300-400 nm, whereas the spectra of the four cocrystals display multiple features in the visible range of 300-800 nm. While the spectra of the two classes of structure are remarkably similar in form across the five haloanilines, there are subtle differences in the visible absorption profiles of the cocrystals, with the absorption of the iodoaniline compounds extending to longer wavelengths than the bromo analogues. This is particularly clear when comparing the spectra of the 4-iodo,2-methylaniline and 4-bromo,2-methylaniline cocrystals (7/9, Figures S6.4.1 c/d). Stronger visible absorption would red shift the reflected colour and this thus explains the deeper red colour of the iodoaniline crystals.

We note that we do not expect the independent-particle approach to simulating absorption spectra employed here to reproduce the experimental absorption profiles with quantitative accuracy,[10] but we would expect the calculations to capture the key qualitative differences between compounds, as appears to be the case with reference to the experimental observations.

Comparing the spectrum of orbital energy levels in **1-10** (Figures S6.5.1-S6.5.5) suggests that the primary origin of the reduced HOCO-LUCO gap in the cocrystals is due to a higher-energy HOCO, although in some compounds the LUCO is also lowered in energy. We therefore modelled and compared orbital-density plots of the ten systems (Figure S6.4.2, Figures S6.5.6-S6.5.9).



Figure S6.4.1 Simulated absorption spectra of 1-3 (a), 4/5 (b), 6/7 (c), 8/9 (d) and 10 (e).

As with the energy levels, the orbitals show a consistent pattern. In all ten systems, the frontier orbitals consist of  $\pi$ -type orbitals on the haloaniline (HOCO) and benzoic acid (LUCO) molecules. In the cocrystal structures, there is little interaction evident between molecules in either crystal orbital, whereas in the salt structures pairs of molecules are aligned to allow for overlap of the  $\pi$  systems on adjacent molecules. The plots do not show the phase of the wavefunctions, so we cannot discern whether the interactions are in-phase or antiphase, and thus whether they would lower or raise the energies of the component molecular orbitals.

The orbital-density plots also show that the aniline-based HOCOs include a significant contribution from the halogen lone pairs. This offers a natural explanation for the colour of the iodoaniline compounds being red shifted compared to the bromoaniline analogues, since I would be

expected to have a higher-energy lone pair than Br, and therefore to raise the energy of the lowestunoccupied molecular orbital (LUMO).



HOCO

LUCO

**Figure S6.4.2** Orbital-density plots showing the highest-occupied and lowest-unoccupied crystal orbitals (HOCOs/LUCOs) giving rise to the direct bandgap of **1-3**. These images were generated using the VESTA software.[11] Orbital-density plots for **4-10** can be found in Figures S6.5.6-S6.5.9.

#### S6.5. Appendices



**Figure S6.5.1** Simulated absorption spectra and direct bandgaps of **1-3** obtained with the PBE0 hybrid functional. The left-hand plot compares the normalised wavelength-dependent absorption coefficient  $\alpha$  of the three complexes. The right-hand plot shows spectra of the crystal-orbital energies relative to the average C 1s core level at the k-point where the direct gap occurs (see Table S6.4.1).



**Figure S6.5.2** Simulated absorption spectra and direct bandgaps of **4** and **5** obtained with the PBEO hybrid functional. The left-hand plot compares the normalised wavelength-dependent absorption coefficient  $\alpha$  of the three complexes. The right-hand plot shows spectra of the crystal-orbital energies relative to the average C 1s core level at the k-point where the direct gap occurs (see Table S6.4.1).



**Figure S6.5.3** Simulated absorption spectra and direct bandgaps of **6** and **7** obtained with the PBEO hybrid functional. The left-hand plot compares the normalised wavelength-dependent absorption coefficient  $\alpha$  of the three complexes. The right-hand plot shows spectra of the crystal-orbital energies relative to the average C 1s core level at the k-point where the direct gap occurs (see Table S6.4.1).



**Figure S6.5.4** Simulated absorption spectra and direct bandgaps of **8** and **9** obtained with the PBE0 hybrid functional. The left-hand plot compares the normalised wavelength-dependent absorption coefficient  $\alpha$  of the three complexes. The right-hand plot shows spectra of the crystal-orbital energies relative to the average C 1s core level at the k-point where the direct gap occurs (see Table S6.4.1).



**Figure S6.5.5** Simulated absorption spectrum and direct bandgap of **10** obtained with the PBE0 hybrid functional. The left-hand plot shows the normalised wavelength-dependent absorption coefficient  $\alpha$ . The right-hand plot shows spectrum of the crystal-orbital energies relative to the average C 1s core level at the k-point where the direct gap occurs (see Table S6.4.1).



**Figure S6.5.6** Orbital density plots showing the highest-occupied and lowest-unoccupied crystal orbitals (HOCOs/LUCOs) giving rise to the direct bandgap of **4** and **5**. These images were generated using the VESTA software.[11]



**Figure S6.5.7** Orbital density plots showing the highest-occupied and lowest-unoccupied crystal orbitals (HOCOs/LUCOs) giving rise to the direct bandgap of **6** and **7**. These images were generated using the VESTA software.[11]



**Figure S6.5.8** Orbital density plots showing the highest-occupied and lowest-unoccupied crystal orbitals (HOCOs/LUCOs) giving rise to the direct bandgap of **8** and **9**. These images were generated using the VESTA software.[11]



**Figure S6.5.9** Orbital density plots showing the highest-occupied and lowest-unoccupied crystal orbitals (HOCO/LUCO) giving rise to the direct bandgap of **10**. These images were generated using the VESTA software.[11]

## **S7.** References

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