Aniline–phenol recognition: from solution through supramolecular synthons to cocrystals

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S1. Crystallization details

3,4,5-trichlorophenol: 4-chloroaniline (11): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated thrice. Solutions of resulting powder were kept for crystallizations. Diffraction quality crystals were obtained from a 1:1 solvent mixture of n-hexane and MeOH after 3-4 days by solvent evaporation.

3,4,5-trichlorophenol: 3-chloroaniline (12): The phenol was taken in a mortar and a few drops of 3-chloroaniline were added to it. The mixture was ground and the grinding process was repeated thrice. Solutions of resulting powder were kept for crystallizations. Diffraction quality crystals were obtained from CHCl₃ after 3-4 days by solvent evaporation.

3,4,5-trichlorophenol: 2,5-dichloroaniline (13): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated thrice. Solutions of resulting powder were kept for crystallizations. Diffraction quality crystals were obtained from CHCl₃ after 3-4 days by solvent evaporation.

3,4,5-trichlorophenol: 3,5-dichloroaniline (14): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated thrice. Solutions of resulting powder were kept for crystallizations. Diffraction quality crystals were obtained from acetone after 3-4 days by solvent evaporation.

3,4,5-trichlorophenol: 3,4-dichloroaniline (15): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated thrice. Solutions of resulting powder were kept for crystallizations. Diffraction quality crystals were obtained from CH₂Cl₂ after 3-4 days by solvent evaporation.

3,4,5-trichlorophenol: 4-bromoaniline (16): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated thrice. Solutions of resulting powder were kept for crystallizations. Diffraction quality crystals were obtained from acetone after 3-4 days by solvent evaporation.

3,4,5-trichlorophenol: 4-iodoaniline (17): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated for thrice. Solutions of resulting powder were kept for crystallizations. Diffraction quality crystals were
obtained from a 1:1 solvent mixture of n-hexane and MeOH after 3-4 days by solvent evaporation.

3,4,5-trichlorophenol: 3-chloro-4-iodoaniline (18): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated thrice. Solutions of resulting powder were kept for crystallizations. Diffraction quality crystals were obtained from MeOH after 3-4 days by solvent evaporation.

2,3,4-trichlorophenol: 4-chloroaniline (19): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated thrice. The resulting powder was put for sublimation. Needle like crystals were obtained after two days.

2,3,4-trichlorophenol: 3-chloroaniline (20): The phenol was taken in a mortar and a few drops of 3-chloroaniline were added to it. The mixture was ground and the grinding process was repeated thrice. The resulting powder was put for sublimation. Needle like crystals were obtained after two days.

2,3,4-trichlorophenol: 3,5-dichloroaniline (21): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated thrice. The resulting powder was dissolved in different solvents. Nice crystals were obtained from EtOH after 3-4 days by solvent evaporation.

2,3,4-trichlorophenol: 3,4-dichloroaniline (22): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated thrice. The resulting powder was put for sublimation. Needle like crystals were obtained after one day.

4-hydroxybenzoic acid: 3-aminobenzamide (23): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated thrice. Solutions of resulting powder were kept for crystallizations. Diffraction quality crystals were obtained from MeOH after 3-4 days by solvent evaporation.

3-hydroxybenzoic acid: 3-aminobenzamide (24): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated thrice. Solutions of resulting powder were kept for crystallizations. Diffraction quality crystals were obtained from EtOH after 3-4 days by solvent evaporation.

3,5-dihydroxybenzoic acid: 4-aminobenzamide (25): The two compounds were taken together in a mortar in 1:1 ratio and ground with a few drops of MeOH. The grinding process was repeated
thrice. Solutions of resulting powder were kept for crystallizations. Diffraction quality crystals were obtained from EtOH after 3-4 days by solvent evaporation.

Table S1  Additional crystallographic details

| Name         | 11          | 12          | 13          | 14          | 15          |
|--------------|-------------|-------------|-------------|-------------|-------------|
| Molecular weight | 325.00      | 325.00      | 359.44      | 359.44      | 358.44      |
| ρ<sub>calc</sub> (g/cm<sup>3</sup>) | 1.568       | 1.601       | 1.676       | 1.614       | 1.655       |
| F(000)       | 328         | 656         | 720         | 1440        | 358         |
| μ (MoKα) (mm<sup>-1</sup>) | 0.845       | 0.863       | 1.007       | 0.970       | 0.997       |
| Temp. (K)    | 150         | 150         | 150         | 150         | 150         |
| θ Range for data collection (°) | 3.0, 27.5   | 3.1, 27.5   | 3.1, 27.5   | 3.0, 25.2   | 3.1, 27.5   |
| R<sub>1</sub> | 0.0322      | 0.0330      | 0.0256      | 0.0925      | 0.0642      |
| wR<sub>2</sub> | 0.0836      | 0.0846      | 0.0558      | 0.2015      | 0.1496      |
| Goodness-of-fit | 1.09        | 1.09        | 1.06        | 1.21        | 1.04        |
| Reflns collected | 7315        | 13875       | 15205       | 12389       | 7652        |
| Unique reflns | 3144        | 3066        | 6493        | 2662        | 3293        |
| Observed reflns | 2604        | 2703        | 6193        | 2516        | 2949        |
| Name | 16 | 17 | 18 | 19 | 20 |
|------|----|----|----|----|----|
| Molecular weight | 369.45 | 416.45 | 449.89 | 325.00 | 325.00 |
| \( \rho_{\text{calc}} \) (g/cm\(^3\)) | 1.753 | 1.909 | 1.991 | 1.626 | 1.624 |
| F(000) | 364 | 400 | 430 | 656 | 328 |
| \( \mu \) (MoK\(\alpha\)) (mm\(^{-1}\)) | 3.494 | 2.749 | 2.835 | 0.876 | 0.875 |
| Temp. (K) | 150 | 150 | 150 | 150 | 150 |
| \( \theta \) Range for data collection (\(^\circ\)) | 3.0, 27.5 | 3.2, 27.5 | 3.0, 27.5 | 2.2, 27.6 | 2.0, 25.2 |
| \( R_1 \) | 0.0394 | 0.0276 | 0.0475 | 0.0416 | 0.0422 |
| \( wR_2 \) | 0.0978 | 0.0697 | 0.1235 | 0.1436 | 0.1390 |
| Goodness-of-fit | 1.04 | 1.12 | 1.20 | 1.14 | 1.14 |
| Reflns collected | 7199 | 7553 | 7564 | 13867 | 5849 |
| Unique reflns | 3204 | 3313 | 3429 | 3068 | 2397 |
| Observed reflns | 2717 | 3105 | 3038 | 2843 | 2240 |

| Name | 21 | 22 | 23 | 24 | 25 |
|------|----|----|----|----|----|
| Molecular weight | 359.44 | 359.44 | 274.27 | 274.27 | 580.54 |
| \( \rho_{\text{calc}} \) (g/cm\(^3\)) | 1.624 | 1.673 | 1.418 | 1.430 | 1.458 |
| F(000) | 360 | 360 | 1152 | 576 | 304 |
| \( \mu \) (MoK\(\alpha\)) (mm\(^{-1}\)) | 0.975 | 1.005 | 0.106 | 0.106 | 0.112 |
| Temp. (K) | 150 | 150 | 150 | 150 | 150 |
| \( \theta \) Range for data collection (\(^\circ\)) | 3.0, 27.5 | 3.2, 27.5 | 3.3, 27.5 | 1.6, 27.5 | 3.3, 27.5 |
| \( R_1 \) | 0.0371 | 0.0252 | 0.0385 | 0.0476 | 0.0402 |
| \( wR_2 \) | 0.0992 | 0.0665 | 0.1085 | 0.1689 | 0.1083 |
| Goodness-of-fit | 1.09 | 1.07 | 1.10 | 1.14 | 1.03 |
| Reflns collected | 7780 | 7624 | 12832 | 12530 | 6973 |
| Unique reflns | 3366 | 3265 | 2944 | 2914 | 3013 |
| Observed reflns | 3035 | 3023 | 2635 | 2416 | 2472 |
### Table S2  Multi-component crystals: 29

| O–H···N | N–H···O | N–H···π | O–H···O | N–H···N | Synthon | Others |
|---------|---------|---------|---------|---------|---------|--------|
| CIQP AU | CIQP AU | | | | | |
| EXAMUM | | | | | | |
| EXANAT | | | | | | |
| EXAPID01 | EXAPID01 | | | | | |
| FIDLIO | FIDLIO | | | | II | |
| FIDLOU | FIDLOU | | | | II | |
| FIDLUA | FIDLUA | | | | I | |
| FIDMAH | FIDMAH | FIDMAH | FIDMAH | | | |
| HEBHAK | | | | | | |
| JAKPIV | JAKPIV | | | | III | |
| JAKPOB | JAKPOB | | | | III | |
| JAKPUH | JAKPUH | | | | III | |
| KIBQOC | KIBQOC | | | | N–H···F | |
| KIBQOC01 | KIBQOC01 | | | | O–H···F | |
| OFEPUK | OFEPUK | OFEPUK | | | | |
| OFEQUIZ | OFEQUIZ | OFEQUIZ | | | OH: NH₂ (2:1) | |
| PITYAS | PITYAS | | | | III | |
| PITYEW | PITYEW | | | | III | |
| PITYIA | PITYIA | | | | III | |
| PITYOG | PITYOG | | | | III | |
| PUVNID | PUVNID | | | | | Synthon is interrupted by H₂O |
| PUZZIT | PUZZIT | | | | OH: NH₂ (2:1) | |
Table S3  Single-component crystals: 44

| O–H···N | N–H···O | N–H···π | O–H···O | N–H···N | Synthon          | Others                  |
|---------|---------|---------|---------|---------|------------------|-------------------------|
| AMNPHA  |         |         |         |         |                  | Interrupted by NO₂      |
| AMPHOL01| AMPHOL01|         |         |         | III              |                         |
| AMPHOM02| AMPHOM02| AMPHOM02|         |         |                 |                         |
| AMPHOM03| AMPHOM03| AMPHOM03|         |         |                 |                         |
| EBITALF| EBITALF|         |         |         | III              |                         |
| EBITALF| EBITALF|         |         |         | III              |                         |
| ENALOU  | ENALOU  |         |         |         | II               |                         |
| ENALUA  | ENALUA  |         |         |         | III              |                         |
| ENAMAH  | ENAMAH  | ENAMAH  |         |         |                 |                         |
| ENAMEL  | ENAMEL  |         |         |         | III              |                         |
| ENAMIP  | ENAMIP  | ENAMIP  |         |         |                 |                         |
| ENAMOV  | ENAMOV  |         |         |         | II               |                         |
| ENAMUB  | ENAMUB  |         |         |         | III              |                         |
| ENANAI  | ENANAI  |         |         |         | III              |                         |
| ENANEM  | ENANEM  | ENANEM  |         |         |                 |                         |
| ENANIQ  | ENANIQ  | ENANIQ  |         |         |                 |                         |
| ENANOW  | ENANOW  | II   |
|---------|---------|------|
| ENANUL  | ENANUL  | II   |
| ENAPAK  | ENAPAK  |      |
| FUHTAE  | FUHTAE  | I    |
| FUHTAE01| FUHTAE01| I    |
| GEBVAK  | GEBVAK  | GEBVAK|
| GEBVAK01| GEBVAK01|      |
| GIVRIM  | GIVRIM  |      |
| HIWMUW  | HIWMUW  | HIMUW|
| HIWNAD  | HIWNAD  | HIWNAD|
| HIWNEH  |         | N–H···O=C|
| MAMPOL  | MAMPOL  | MAMPOL|
| MAMPOL02| MAMPOL02| MAMPOL02|
| MASZIQ  | MASZIQ  | MASZIQ|
| MASZOW  | MASZOW  | II   |
| MASZUC  | MASZUC  | MASZUC|
| MATBAL  | MATBAL  | II   |
| MATBEP  | MATBEP  | MATBEP|
| MATBIT  | MATBIT  | MATBIT|
| MATBOZ  | MATBOZ  | MATBOZ|
| MATBUF  | MATBUF  | II   |
| MATCAM  | MATCAM  | II   |
| MATCEQ  | MATCEQ  | II   |
| NODTIJ  | NODTIJ  |      |
| PEJCAJ  | PEJCAJ  |      |
| PEJCAJ01| PEJCAJ01|      |

Interrupted by NO₂

Not Infinite
|       |       |       |       |
|-------|-------|-------|-------|
| PITZAT | PITZAT |       | III   |
| QEPGAU | QEPGAU | QEPGAU |       |
| SADJAK | SADJAK | SADJAK |       |
| UHEVOT | UHEVOT |       |       |
| WURNAZ | WURNAZ |       |       |
| YEJPUA | YEJPUA |       | I     |
Figure S1  Diagrams of multi-component crystals with $\cdots$O–H$\cdots$N–H$\cdots$ hydrogen bonding

FIDLIO

FIDLOU

FIDLUA

JAKPIV
| Table S4 | Hydrogen-bonding parameters for cocrystals 11-25 |
|---------|-----------------------------------------------|
| D–H···A | Symmetry code | D–H (Å) | H···A (Å) | D–H···A (°) |
| 11      | N1–H1A···O1  | -x,3-y,1-z | 0.829(19) | 2.36(2) | 147.7(19) |
|         | O1–H10···N1  | 0.79(2)    | 1.98(2)  | 171(3)  |
| 12      | N1–H1B···O1  | -x,1-y,2-z | 0.85(3)   | 2.24(2) | 150(2)    |
|         | O1–H10···N1  | 0.81(3)    | 1.96(3)  | 174(3)  |
| 13      | N1–H1A···O1  | 1-x,1/2+y,-z | 0.87(2)  | 2.17(2) | 162(2)    |
|         | N1–H1B···Cl10 | 0.84(3)   | 2.61(3)  | 109(2)  |
|         | O1–H10···N2  | 0.73 (3)  | 2.12 (3) | 163(3)  |
|         | N2–H2A···Cl7  | 0.81(3)   | 2.62(2)  | 110(2)  |
|         | N2–H2B···O2  | 0.82 (3)  | 2.44 (3) | 161(3)  |
|         | O2–H2O···N1  | 0.75 (3)  | 2.03 (3) | 165(3)  |
|         | C6–H6···Cl7  | 0.93       | 2.79     | 160.00  |
|         | C8–H8···Cl9  | 0.93       | 2.79     | 157.00  |
| 14      | N1–H1B···O1  | x,1-y,1-z  | 0.89 (3)  | 2.18 (4) | 145 (5)   |
|         | O1–H10···N1  | -x,y,1/2-z | 0.85 (7)  | 1.96 (6) | 169 (5)   |
| 15      | N1–H1A···O1  | 1+x,-1+y,1+z | 0.92 (7) | 2.31 (7) | 142 (6)   |
|         | O1–H7···N1   | 0.81 (6)   | 1.97 (6) | 171 (6)  |
| 16      | O1–H10···N1  | -x,1-y,2-z | 0.82 (4)  | 1.96 (4) | 173 (4)   |
|         | N1–H2B···O1  | 1+x,-1+y,1+z | 0.85 (5) | 2.34 (4) | 148 (4)   |
| 17      | N1–H1A···O1  | 1-x,2-y,-z  | 0.83 (4)  | 2.33 (4) | 151 (4)   |
|         | O1–H10···N1  | x,1+y,z    | 0.8200    | 1.9600   | 169.00    |
| 18      | N1–H1A···O1  | -x,2-y,-z  | 0.93 (7)  | 2.27 (7) | 148 (6)   |
|         | O1–H10···N1  | 0.8200      | 1.9800    | 169.00   |
| 19      | N1–H1A···O1  | -x,2-y,-z  | 0.90 (7)  | 2.29 (7) | 149 (6)   |
|         | O1–H10···N1  | 0.8200      | 1.9800    | 169.00   |
| 20      | N1–H1A···O1  | x,1+y,z    | 0.80 (3)  | 2.28 (3) | 154 (3)   |
|         | O1–H10···N1  | -x,-1+y,1-z | 0.92 (3) | 1.81 (3) | 166 (3)   |
| 21      | N1–H1B···O1  | -x,-y,1-z  | 0.85 (3)  | 2.19 (3) | 163 (3)   |
|         | O1–H10···N1  | 0.8200      | 1.9300    | 163.00   |
| 22      | N1–H1A···O1  | 1+x,1+y,z  | 0.845(19) | 2.242(19)| 156.5(19) |
|         | O1–H10···N1  | 1-x,-y,1-z | 0.83(2)   | 1.89(2)  | 171(2)    |
| 23      | N1–H1B···O1  | 1-x,1+y,1/2-z | 0.92 (2) | 2.16 (2) | 156.17 (16)|
|         | O1–H10···N1  | x,2-y,1/2-z | 0.92 (2) | 1.88 (2) | 166.7 (19)|
|         | N2–H2A···O2  | 1/2-x,1/2+y,1/2-z | 0.880 (18)| 2.153 (18)| 159.9 (15)|
|         | N2–H2B···O2  | x,1+y,z    | 0.92 (2) | 2.091 (19)| 166.8 (16)|
|         | O3–H3O···O4  | x,-1+y,z   | 0.91 (2) | 1.69 (2) | 170.7 (19)|
|         | C6–H6···O4  | 1-x,y,1/2-z | 0.9300 | 2.5200 | 152.00 |
|         | C10–H10···O2 | 1/2-x,1/2+y,1/2-z | 0.9300 | 2.5700 | 159.00 |
|         | C14–H14···O4 | 0.9300      | 2.4200   | 100.00  |
|   | Bond                  | Symmetry | d (Å)  | D (Å)  | θ (°)  |
|---|----------------------|----------|--------|--------|--------|
| 24 | N1–H1A···O4          | x,-1+y,z | 0.90 (3)| 2.43 (3)| 130 (2) |
|   | N1–H1B···O3          | -x,-1/2+y,1/2-z | 0.84 (3)| 2.07 (3)| 169 (2) |
|   | O1–H1O···N2          |          | 0.85 (3)| 1.97 (3)| 167 (2) |
|   | N2–H2B···O1          | 1-x,-1-y,1-z | 0.87 (3)| 2.16 (3)| 161 (2) |
|   | O2–H2O···O4          | -x,1/2+y,1/2-z | 0.8200| 1.8200| 170.00 |
|   | C3–H3···O2           | -x,1-y,1-z | 0.9300| 2.6000| 137.00 |
| 25 | N1–H1A···O1          |          | 0.90 (2)| 2.40 (2)| 142.0 (16) |
|   | O1–H1O···N1          | -1-x,-y,1-z | 0.86 (2)| 1.96 (2)| 172 (2) |
|   | N2–H2A···O4          | -1-x,1-y,1-z | 0.88 (2)| 2.30 (2)| 162.5 (18) |
|   | N2–H2B···O5          | -3-x,1-y,-z | 0.898 (19)| 2.002 (19)| 176.4 (18) |
|   | O2–H2O···O5          | 1+x,y,1+z | 0.93 (2)| 1.74 (2)| 167 (2) |
|   | O4–H4O···O3          | 1-x,1-y,1-z | 1.27 (4)| 1.35 (4)| 175 (3) |
|   | C3–H3···O3           |          | 0.9300| 2.4100| 100.00 |
|   | C10–H10···O5         |          | 0.9300| 2.4700| 100.00 |
|   | C13–H13···O3         | -1+x,y,z | 0.9300| 2.5600| 126.00 |
Figure S2  ORTEP diagrams for cocrystals 11-25
Figure S3  Packing diagram of 1,2,3-trichlorobenzene (TCBENZ)

S3. NMR signal intensities as a function of gradient power

Figure S4  Representative spectra were obtained using the bipolar pulse pair gradient stimulated echo pulse program. Shown here are the spectra for sample A of 14. See text for details.
S4. 2-D DOSY plots

**Figure S5** 2-D DOSY plots of A, E, and F of 14 and A₁, E₁ and F₁ of 26.
S5. $^{15}$N NMR spectra for solutions A, E and F

**Figure S6** One-dimensional $^{15}$N spectra of samples A (black), E (green) and F (magenta). Also shown is the reference spectrum of $^{15}$N enriched urea (red). The aniline N resonates at 58.7ppm. See text for details.