Supporting Information

for

Exploiting π-type halogen bonds as a means to achieve mixed co-crystals: crystallographic and computational evidence of a Cl···π halogen bond in the organic solid state

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1. Materials and Synthesis of the Co-crystals

Materials

Benzoic acid (**BAc**) and benzamide (**BAm**) as well as the solvent toluene and ethanol were all purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. The halogen-bond donors 1,4-iodoperchlorobenzene (**$C_6I_2Cl_4$**)[1] and iodoperchlorobenzene (**C_6ICl_5**)[2] were synthesized by a previous reported method. All crystallization studies were performed in 20 mL scintillation vials.

Synthesis of the mixed co-crystal with BAc

The mixed co-crystal $(\mathbf{C_6I_2Cl_4})_{.70}\cdot(\mathbf{C_6ICl_5})_{.30}\cdot 2(\mathbf{BAc})$ was synthesized by dissolving 24.1 mg of **$C_6I_2Cl_4$** and 19.4 mg of **C_6ICl_5** both in 1.0 mL of toluene, which was then combined with a separate 1.0 mL toluene solution containing 25.0 mg of **BAc** (0.5:0.5:2 molar equivalent). Then the solutions were combined and then the cap was removed to allow for slow evaporation. After two days and significant loss of solvent single crystals suitable for X-ray diffraction were formed.

Synthesis of the mixed co-crystal with BAm

Similar to before, he mixed co-crystal $(\mathbf{C_6I_2Cl_4})_{.62}\cdot(\mathbf{C_6ICl_5})_{.38}\cdot 2(\mathbf{BAm})$ was synthesized by dissolving 24.1 mg of **$C_6I_2Cl_4$** and 19.4 mg of **C_6ICl_5** both in 1.0 mL of toluene, which was then combined with a separate 1.0 mL toluene and 1.0 mL ethanol solution containing 25.0 mg of **BAm** (0.5:0.5:2 molar equivalent). Then the solutions were combined and then the cap was removed to allow for slow evaporation. After two days single crystals suitable for X-ray diffraction formed.

Synthesis of $(\mathbf{C_6I_2Cl_4})\bullet 2(\mathbf{BAm})$

The binary co-crystals $(\mathbf{C_6I_2Cl_4})\bullet 2(\mathbf{BAm})$ was synthesized by dissolving 48.3 mg of **$C_6I_2Cl_4$** in 2.0 mL of toluene then was combined with a 1.0 mL toluene and 1.0 mL ethanol solution containing 25.0 mg of **BAm** (1:2 molar equivalent). As before, the combined solution was mixed and the cap removed to allow for slow evaporation. Within two days single crystals suitable for X-ray diffraction were realized.

2. Electronic Structure Calculations

To obtain binding energies, density functional theory calculations were performed using the M06-2X density functional as implemented in the Gaussian 16 program.[3] An aug-cc-pVTZ basis set was used on all atoms, with the exception of iodine, using the basis sets stored internally in the Gaussian program. For iodine, the basis set, which included a core potential replacing the inner 28 electrons, was obtained from the EMSL Basis Set Exchange Library.[4] The energies were computed using the counterpoise method as implemented in Gaussian. This procedure computes the energy as the difference between the energy of the pair and the energies of the separated molecules. In the case of the separated fragments, the energies are computed using the entire set of orbitals for the molecular pair. For all calculations, the counterpoise correction was rather modest, comprising about 10% of the computed value.

3. Single X-ray Diffraction Information and Data Tables

Data were collected on a Bruker D8 VENTURE DUO diffractometer equipped with an IμS 3.0 microfocus source operated at 75 W (50kV, 1.5 mA) to generate Mo Kα radiation (λ = 0.71073 Å) and a PHOTON III detector. Crystals were transferred from the vial and placed on a glass slide in type NVH immersion oil by Cargille. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on a MiTeGen 100-micron MicroLoop and transferred to the instrument, where it was placed under a cold nitrogen stream (Oxford 800 series) at 290K. The sample was optically centered with the aid of a video camera to ensure that no translations were observed as the crystal was rotated through all positions.

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using the *APEX6*[5]. A numerical absorption correction was applied based on a Gaussian integration over a multifaceted crystal and followed by a semi-empirical correction for adsorption applied using *SADABS*[5]. The program *SHELXT*[6] was used for the initial structure solution, and *SHELXL*[6] was used for refinement of the structure. Both programs were utilized within the OLEX2 software[7]. Hydrogen atoms bound to carbon, oxygen, and nitrogen atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. For structures $(\mathbf{C_6I_2Cl_4})_{.70}\cdot(\mathbf{C_6ICl_5})_{.30}\cdot2(\mathbf{BAc})$ and $(\mathbf{C_6I_2Cl_4})_{.62}\cdot(\mathbf{C_6ICl_5})_{.38}\cdot2(\mathbf{BAm})$, the 1,4-diiodoperchlorobenzene molecule is partially substituted by iodoperchlorobenzene. To help maintain a reasonable ADP value for Cl3 in both structures, an EADP constraint between I1 and Cl3 was applied.

Table S1. X-ray data for the reported mixed and binary co-crystals.

co-crystal	$(\mathbf{C_6I_2Cl_4})_{.70}\cdot(\mathbf{C_6ICl_5})_{.30}\cdot2(\mathbf{BAc})$	$(\mathbf{C_6I_2Cl_4})_{.62}\cdot(\mathbf{C_6ICl_5})_{.38}\cdot2(\mathbf{BAm})$	$(\mathbf{C_6I_2Cl_4})\bullet2(\mathbf{BAm})$
chemical formula	$C_{20}H_{12}Cl_{4.3}I_{1.7}O_4$	$C_{20}H_{14}Cl_{4.37}I_{1.63}N_2O_2$	$C_{20}H_{14}Cl_4I_2N_2O_2$
formula mass	684.46	676.09	709.93
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	5.3509(2)	5.0831(10)	5.0898(2)
b/Å	6.4894(3)	6.9377(11)	6.9260(3)
c/Å	16.2659(6)	16.190(5)	16.2552(6)
α/°	100.729(1)	100.350(9)	99.932(1)
β/°	94.129(1)	93.108(14)	93.092(1)
γ/°	98.966(1)	96.628(7)	96.812(1)
V/Å^3	545.19(4)	556.2(2)	558.83(4)
ρ_{calc} /g cm^{-3}	2.085	2.018	2.110
T/K	100	100	100
Z	1	1	1
radiation type	Mo Kα	Mo Kα	Mo Kα
absorption coefficient, μ/mm^{-1}	3.013	2.860	3.313
no. of reflections measured	33268	37712	33349
no. of independent reflections	2705	2755	2776
R_{int}	0.0285	0.0360	0.0367
R_1 (I > 2σ(I))	0.0121	0.0144	0.0133
wR(F^2) (I > 2σ(I))	0.0289	0.0333	0.0309
R_1 (all data)	0.0124	0.0149	0.0137
wR(F^2) (all data)	0.0290	0.0335	0.0312
Goodness-of-fit	1.144	1.096	1.079
CCDC deposition number	2522595	2522597	2522596

4. Additional Figures

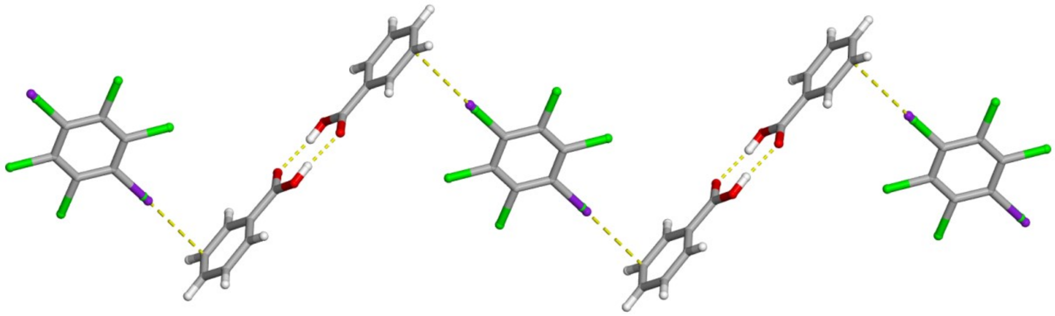

Figure S1: X-ray structure of $(\mathbf{C_6I_2Cl_4})_{.70}$·$(\mathbf{C_6ICl_5})_{.30}$·2(**BAc**) illustrating the various π-type halogen bonds and the acid dimer that generates the wave-like one-dimensional chain structure. The π-type halogen bonds as well as the carboxylic acid dimer hydrogen bonds are shown with yellow dashed lines. The observed crystallographic disorder is indicated by green (chlorine) and purple (iodine) on the same atom.

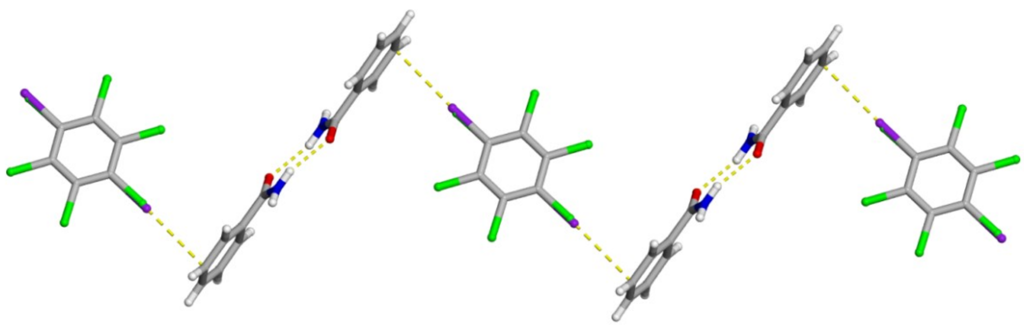

Figure S2: X-ray structure of $(\mathbf{C_6I_2Cl_4})_{.62}$·$(\mathbf{C_6ICl_5})_{.38}$·2(**BAm**) illustrating the various π-type halogen bonds and the amide dimer that generates the wave-like one-dimensional chain structure. The π-type halogen bonds as well as the amide dimer hydrogen bonds are shown with yellow dashed lines. The observed crystallographic disorder is indicated by green (chlorine) and purple (iodine) on the same atom.

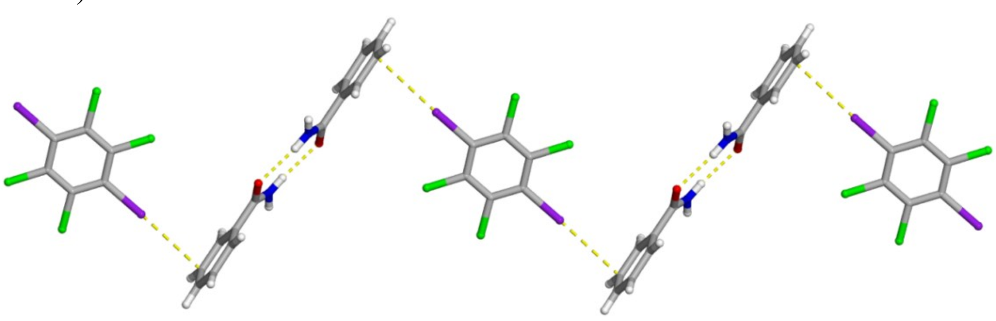

Figure S3: X-ray structure of $(\mathbf{C_6I_2Cl_4})$·2(**BAm**) illustrating the I···π halogen bond and the amide dimer that generates the wave-like one-dimensional chain structure. The I···π halogen bond as well as the amide dimer hydrogen bonds are shown with yellow dashed lines.

5. Density Functional Theory Calculation Figures

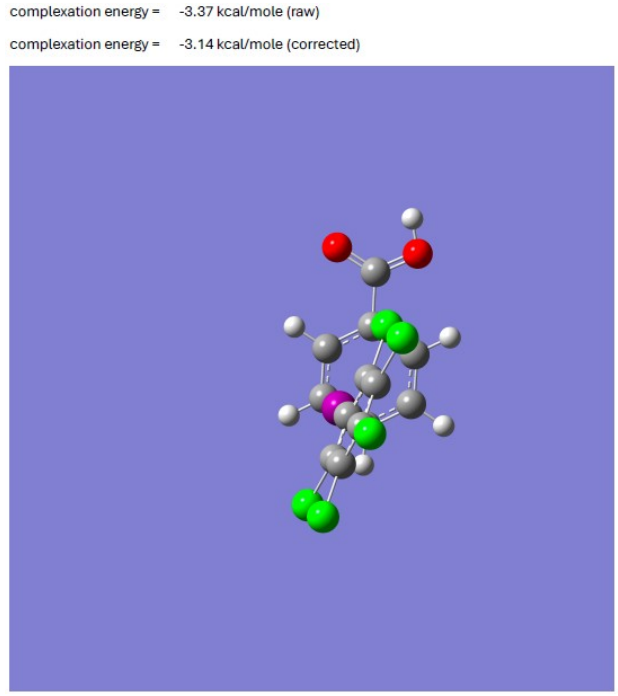

Figure S4: View of the orientation and binding energy for the observed I···π halogen bond within the mixed co-crystal **($C_6I_2Cl_4$)**$_{.70}$·**(C_6ICl_5)**$_{.30}$·2(**BAc**). Color scheme of the atoms: carbon is grey, hydrogen is white, oxygen is red, chlorine is green, and iodine is purple.

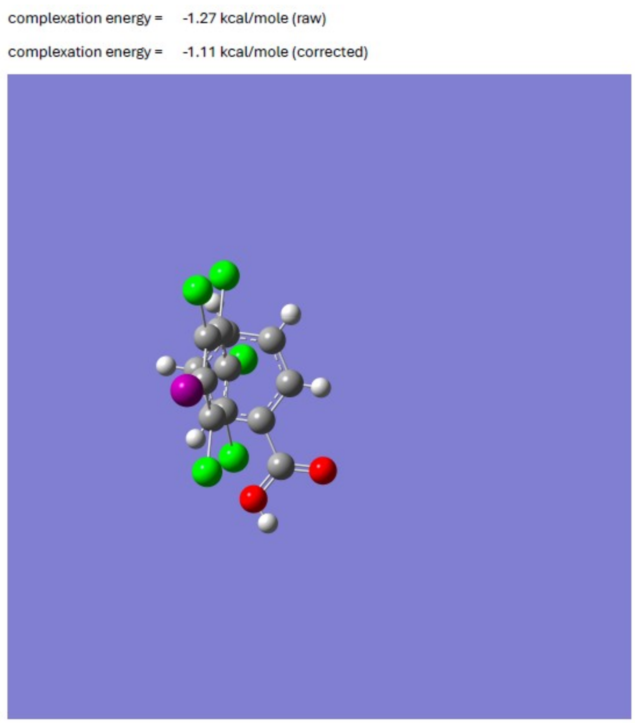

Figure S5: View of the orientation and binding energy for the observed Cl···π halogen bond within the mixed co-crystal **($C_6I_2Cl_4$)**$_{.70}$·**(C_6ICl_5)**$_{.30}$·2(**BAc**). Color scheme of the atoms: carbon is grey, hydrogen is white, oxygen is red, chlorine is green, and iodine is purple.

complexation energy = -3.41 kcal/mole (raw)

complexation energy = -3.18 kcal/mole (corrected)

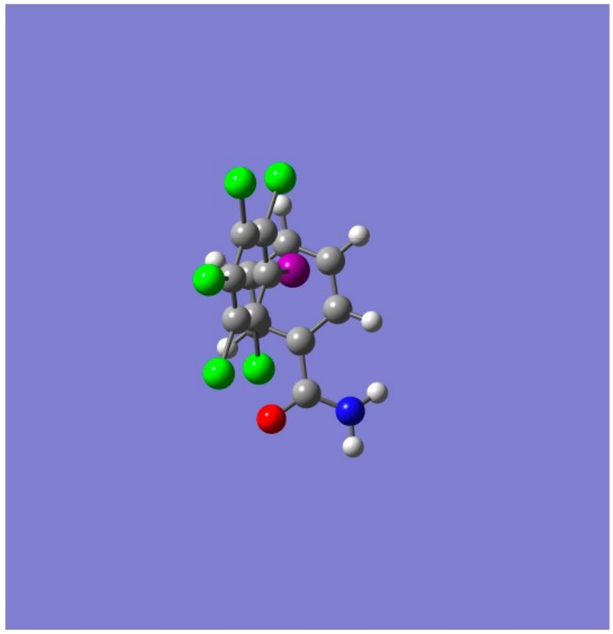

Figure S6: View of the orientation and binding energy for the observed I···π halogen bond within the mixed co-crystal $(\mathbf{C_6I_2Cl_4})_{.62}\cdot(\mathbf{C_6ICl_5})_{.38}\cdot 2(\mathbf{BAm})$. Color scheme of the atoms: carbon is grey, hydrogen is white, oxygen is red, nitrogen is blue, chlorine is green, and iodine is purple.

complexation energy = -1.52 kcal/mole (raw)

complexation energy = -1.35 kcal/mole (corrected)

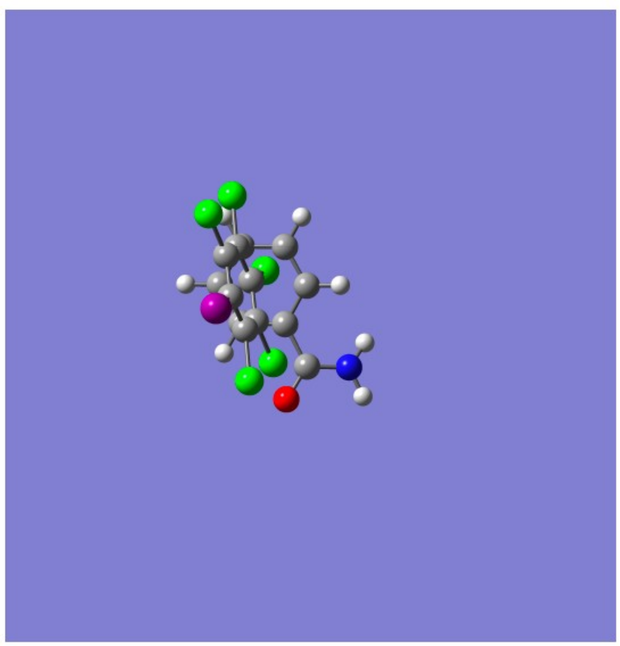

Figure S7: View of the orientation and binding energy for the observed Cl···π halogen bond within the mixed co-crystal $(\mathbf{C_6I_2Cl_4})_{.62}\cdot(\mathbf{C_6ICl_5})_{.38}\cdot 2(\mathbf{BAm})$. Color scheme of the atoms: carbon is grey, hydrogen is white, oxygen is red, nitrogen is blue, chlorine is green, and iodine is purple.

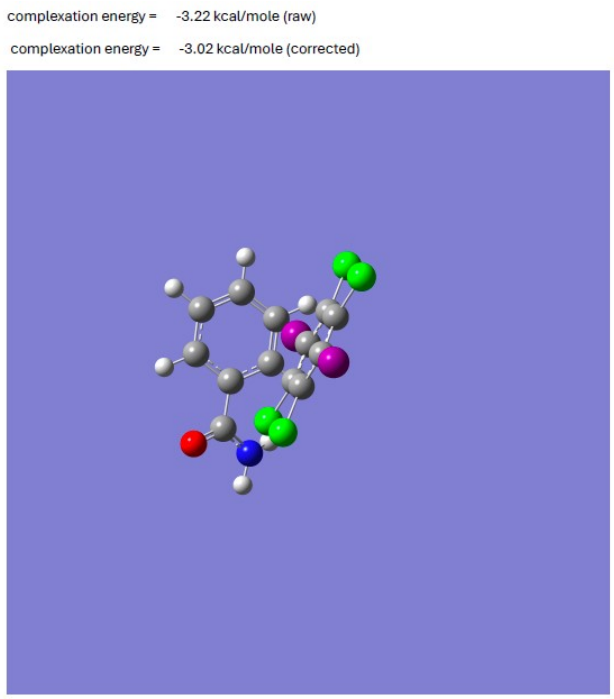

Figure S8: View of the orientation and binding energy for the observed I···π halogen bond within the mixed co-crystal ($\mathbf{C_6I_2Cl_4}$)·2(**BAm**). Color scheme of the atoms: carbon is grey, hydrogen is white, oxygen is red, nitrogen is blue, chlorine is green, and iodine is purple.

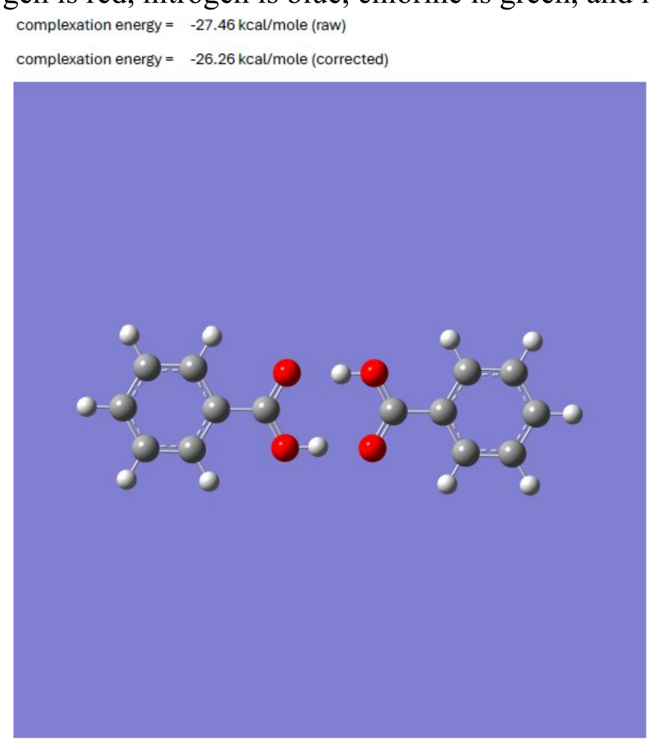

Figure S9: View of the orientation and binding energy for the observed carboxylic acid dimer of benzoic acid **(BAc)** within the mixed co-crystal $(\mathbf{C_6I_2Cl_4})_{.70}$·$(\mathbf{C_6ICl_5})_{.30}$·2(**BAc**). Color scheme of the atoms: carbon is grey, hydrogen is white, and oxygen is red.

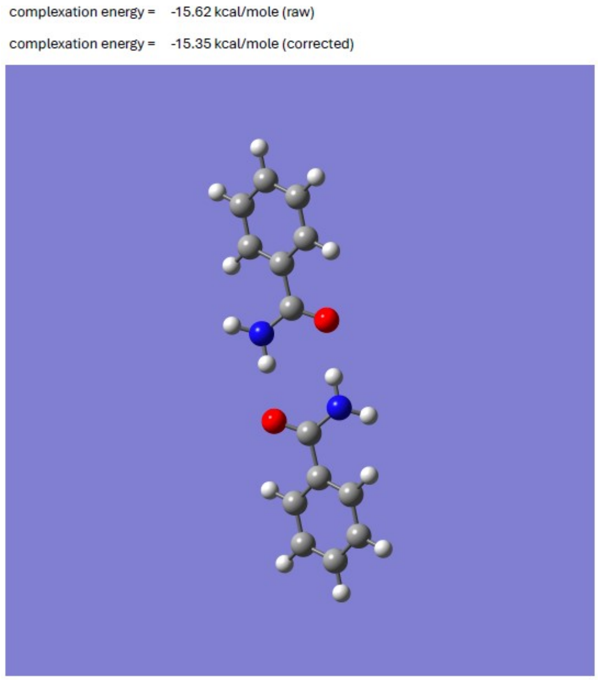

Figure S10: View of the orientation and binding energy for the observed amide dimer of benzamide (**BAm)** within the mixed co-crystal **($C_6I_2Cl_4$)**$_{.62}$·**(C_6ICl_5)**$_{.38}$·2(**BAm**). Color scheme of the atoms: carbon is grey, hydrogen is white, oxygen is red, and nitrogen is blue.

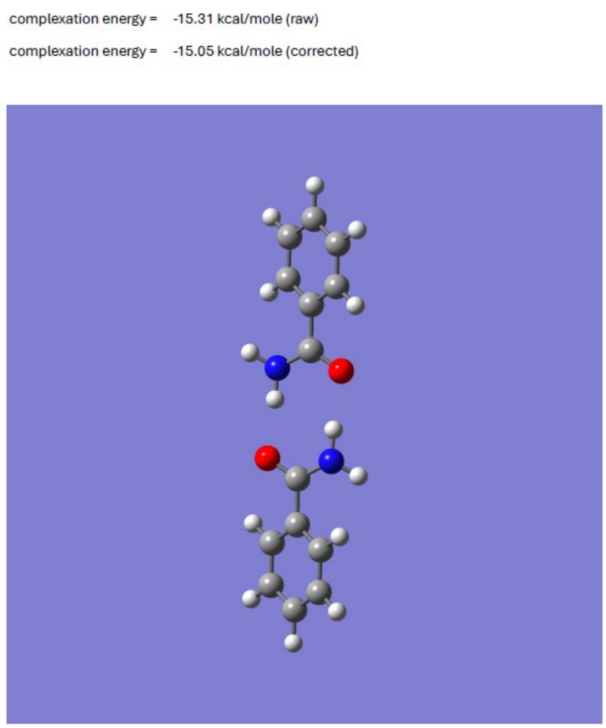

Figure S11: View of the orientation and binding energy for the observed amide dimer of benzamide (**BAm)** within the co-crystal (**$C_6I_2Cl_4$**)·2(**BAm**). Color scheme of the atoms: carbon is grey, hydrogen is white, oxygen is red, and nitrogen is blue.

complexation energy = -9.16 kcal/mole (raw)

complexation energy = -8.79 kcal/mole (corrected)

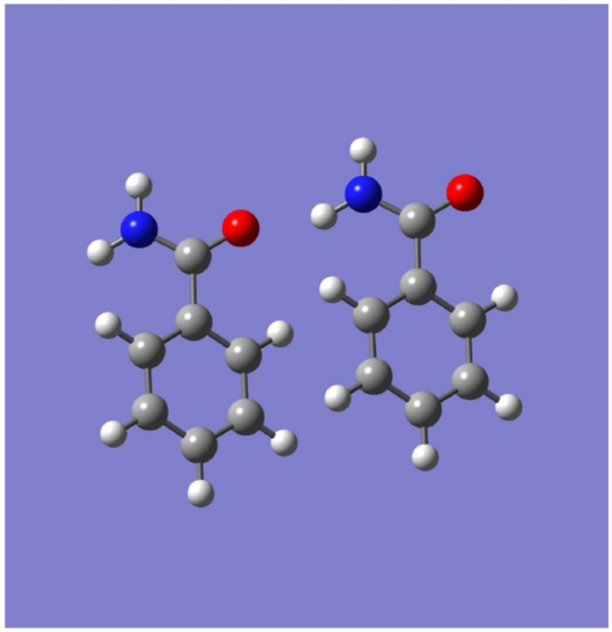

Figure S12: View of the orientation and binding energy for the observed amide chain of benzamide (**BAm)** within the mixed co-crystal (**$C_6I_2Cl_4$**)$_{.62}$·(**C_6ICl_5**)$_{.38}$·2(**BAm**). Color scheme of the atoms: carbon is grey, hydrogen is white, oxygen is red, and nitrogen is blue.

complexation energy = -9.01 kcal/mole (raw)

complexation energy = -8.65 kcal/mole (corrected)

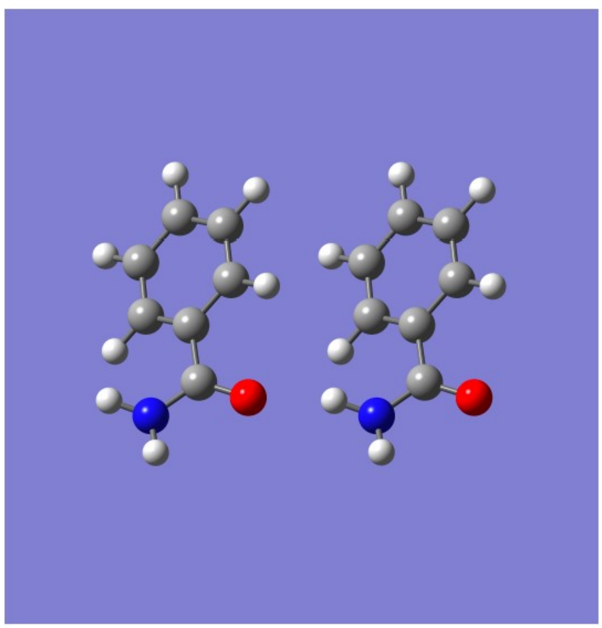

Figure S13: View of the orientation and binding energy for the observed amide chain of benzamide (**BAm)** within the mixed co-crystal (**$C_6I_2Cl_4$**)·2(**BAm**). Color scheme of the atoms: carbon is grey, hydrogen is white, oxygen is red, and nitrogen is blue.

References

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