Supporting Information

for

Hierarchy and cooperativity between π-type halogen bonds and aromatic carboxylic acid dimers in co-crystal formation

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1. Materials and Synthesis of the Co-crystals

Materials

The solvent toluene (reagent grade), benzoic acid (**benz**), and cinnamic acid (**cinn**) were all purchased from Sigma-Aldrich (St. Louis, MO) and were used as received without any further purification. The halogen-bond donor 1,4-diiodoperchlorobenzene (**$C_6I_2Cl_4$**) was synthesized by a previously reported method.[1] All crystallization experiments were performed in 20 mL scintillation vials.

Synthesis of the Co-crystals

*Synthesis of ($C_6I_2Cl_4$)·2(**benz**)*

The co-crystal (**$C_6I_2Cl_4$**)·2(**benz**) was synthesized by dissolving 50.0 mg of **$C_6I_2Cl_4$** in 1.0 mL of toluene, which was then combined with a separate 1.0 mL toluene solution containing 26.1 mg of **benz** (1:2 molar equivalent). The resulting solution was allowed to slowly evaporate, and within one day, crystals suitable for X-ray diffraction formed.

*Synthesis of ($C_6I_2Cl_4$)·2(**cinn**)*

The co-crystal (**$C_6I_2Cl_4$**)·2(**cinn**) was synthesized by dissolving 50.0 mg of **$C_6I_2Cl_4$** in 1.0 mL of toluene, which was then combined with a separate 1.0 mL toluene solution containing 31.7 mg of **cinn** (1:2 molar equivalent). The resulting solution was allowed to slowly evaporate, and within one day, crystals suitable for X-ray diffraction formed.

2. Electronic Structure Calculations

To obtain the various binding energies, density functional theory calculations were performed using the M06-2X density functional as implemented in the Gaussian 16 program.[2] X-ray diffraction data was used to determine the positions of all atoms, with the exception of hydrogen. The hydrogen coordinates were obtained by performing a molecular mechanics[3] optimization with all non-hydrogen atoms frozen at the X-ray diffraction values. An aug-cc-pVTZ basis set, stored internally in the Gaussian program was used for all atoms. 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 no more than about 10% of the computed value.

3. Single X-ray Diffraction Information and Data Table

Data were collected on a Bruker D8 VENTURE DUO diffractometer equipped with a IµS 3.0 microfocus source operated at 75 W (50 kV, 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 Paratone-N oil. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The selected crystal and a small amount of the oil were collected on a MiTeGen 100-micron MicroLoop and transferred to the instrument. 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. A unit cell collection was then carried out. After it was determined that the unit cell was not present in the CCDC database, a data collection strategy was calculated by *APEX6*.[4] The crystal was measured for size, morphology, and color.

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*.[4] 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*.[4] The program *SHELXT*[5] 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 atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

Table S1. Single-crystal X-ray diffraction data for **($C_6I_2Cl_4$)**·2(**benz**) and **($C_6I_2Cl_4$)**·2(**cinn**) at 290 K.

compound name	**($C_6I_2Cl_4$)**·2(**benz**)	**($C_6I_2Cl_4$)**·2(**cinn**)
chemical formula	$C_{20}H_{12}Cl_4I_2O_4$	$C_{24}H_{16}Cl_4I_2O_4$
formula mass	711.90	763.97
crystal system	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	5.4271(3)	5.3023(2)
b/Å	6.5120(4)	6.6859(3)
c/Å	16.5542(10)	18.7003(9)
α/°	99.824(2)	87.260(2)
β/°	94.165(2)	82.1720(10)
γ/°	99.031(2)	82.178(2)
V/Å^3	566.34(6)	650.36(5)
ρ_{calc} /g cm^{-3}	2.087	1.951
T/K	290	290
Z	1	1
radiation type	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
absorption coefficient, μ/mm^{-1}	3.274	2.858
no. of reflections measured	25254	24563
no. of independent reflections	2832	3246
R_{int}	0.0476	0.0370
R_1 (I > 2σ(I))	0.0212	0.0222
wR(F^2) (I > 2σ(I))	0.0462	0.0501
R_1 (all data)	0.0255	0.0258
wR(F^2) (all data)	0.0482	0.0522
Goodness-of-fit	1.074	1.052
CCDC deposition number	2452473	2452474

4. Powder X-ray Diffraction Data

Powder X-ray diffraction data were collected at room temperature on a Bruker D8 Advance X-ray diffractometer using Cu K_α radiation (λ = 1.54056 Å) between 5° to 40° 2θ.

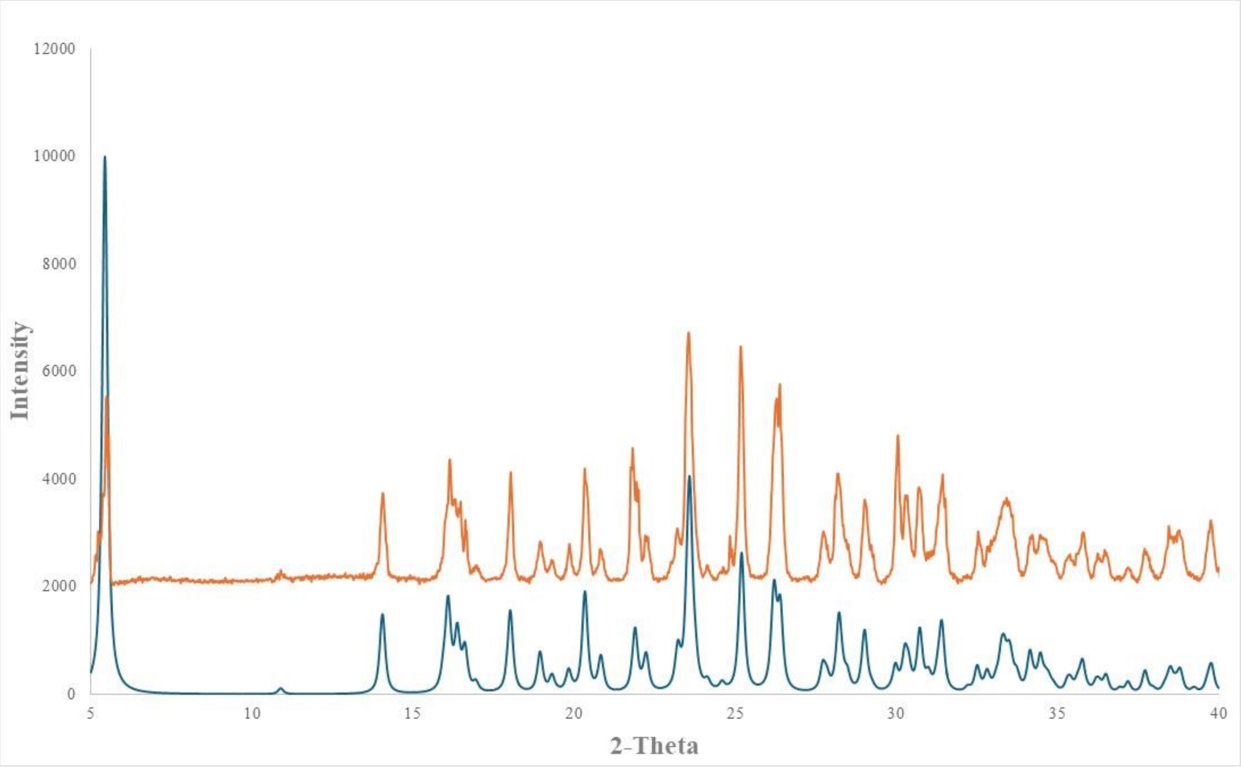


Figure S1. Powder X-ray diffraction data for the bulk sample that contains **($C_6I_2Cl_4$)**·2(**benz**) (orange) along with the theoretical pattern for (**$C_6I_2Cl_4$**)·2(**benz**) (blue).

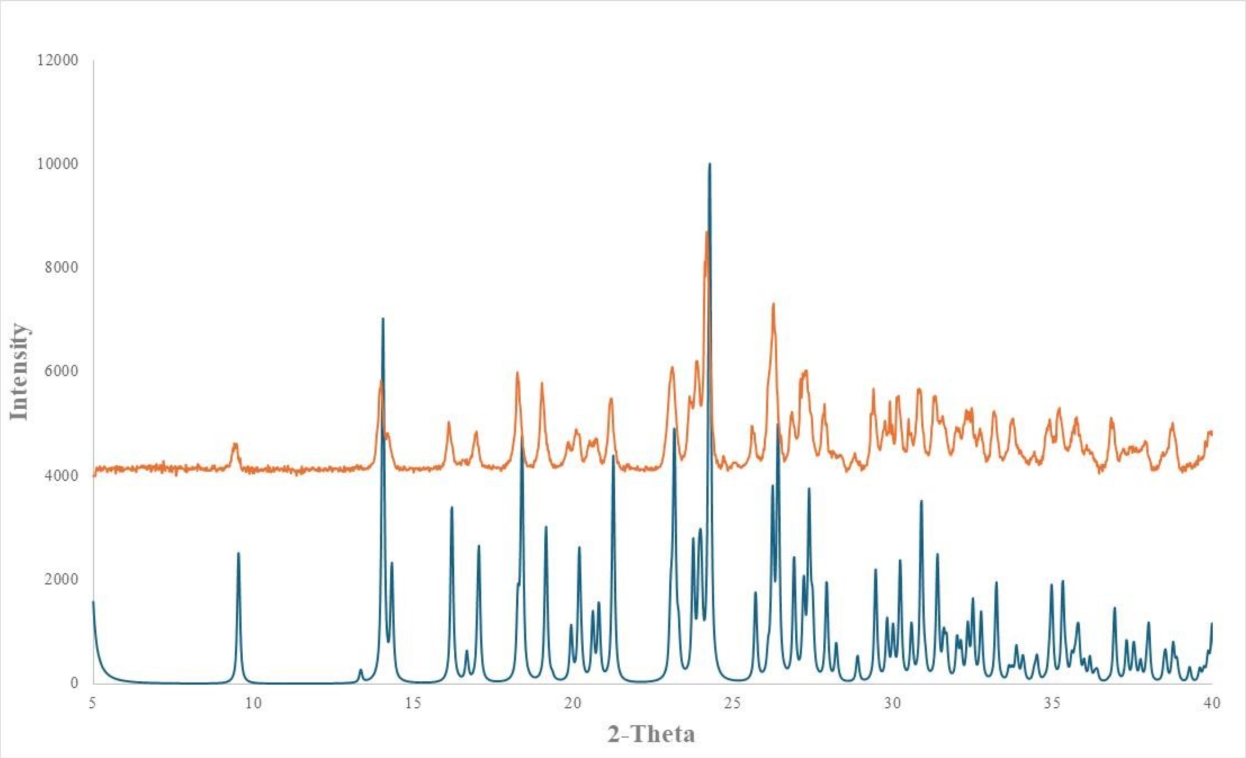


Figure S2. Powder X-ray diffraction data for the bulk sample that contains **($C_6I_2Cl_4$)**·2(**cinn**) (orange) along with the theoretical pattern for (**$C_6I_2Cl_4$**)·2(**cinn**) (blue).

5. Density Functional Theory Calculation Figures

complexation energy = -25.77 kcal/mole (raw)
complexation energy = -25.40 kcal/mole (corrected)

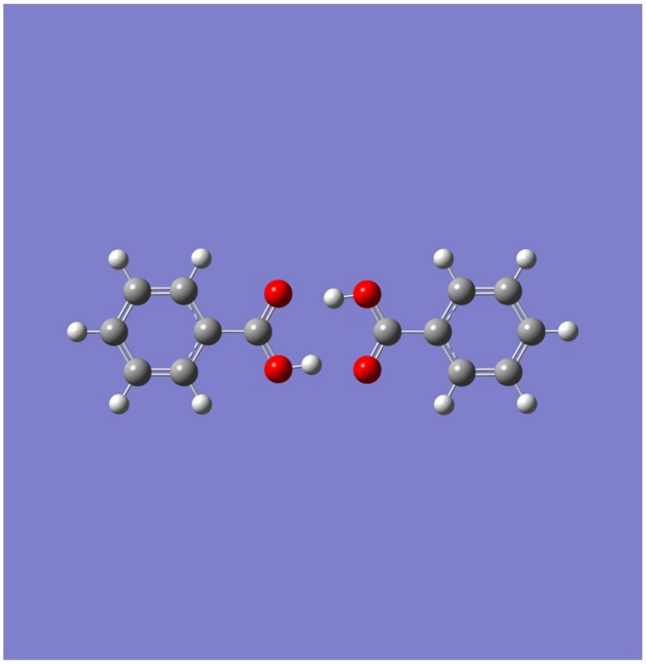


Figure S3. View of the orientation and binding energies of the observed carboxylic acid dimer of benzoic acid **(benz)** within the co-crystal (**$C_6I_2Cl_4$**)·2(**benz**).

complexation energy = -22.53 kcal/mole (raw)
complexation energy = -22.21 kcal/mole (corrected)

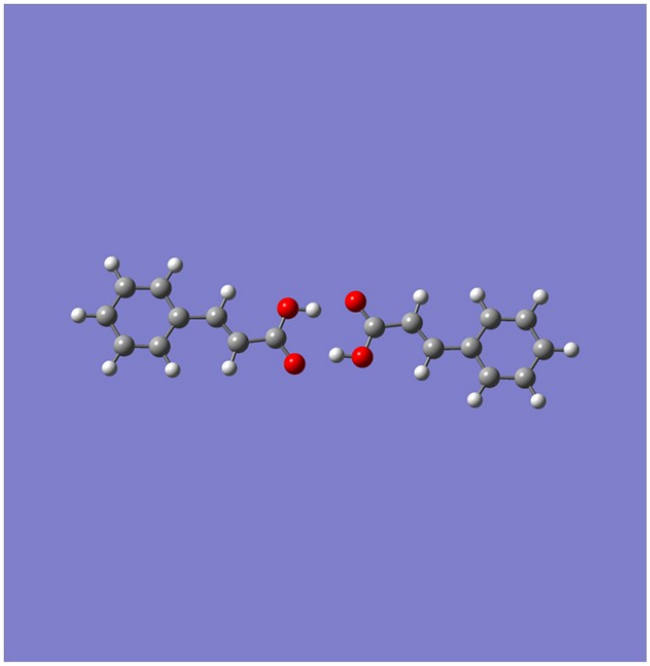
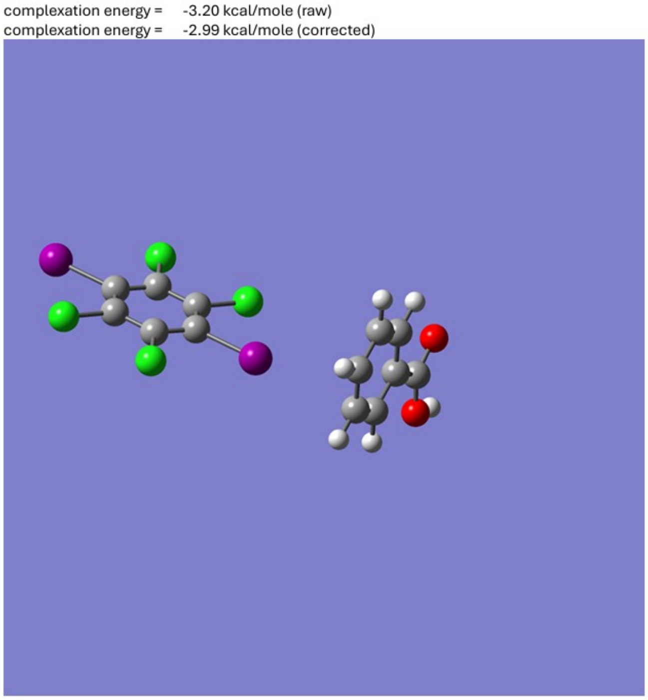
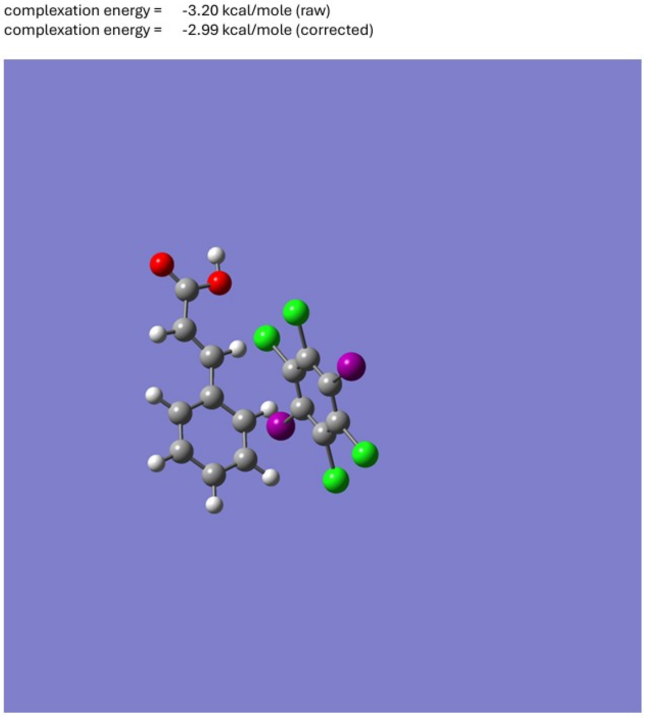


Figure S4. View of the orientation and binding energies of the observed carboxylic acid dimer of cinnamic acid (**cinn)** within the co-crystal (**$C_6I_2Cl_4$**)·2(**cinn**).



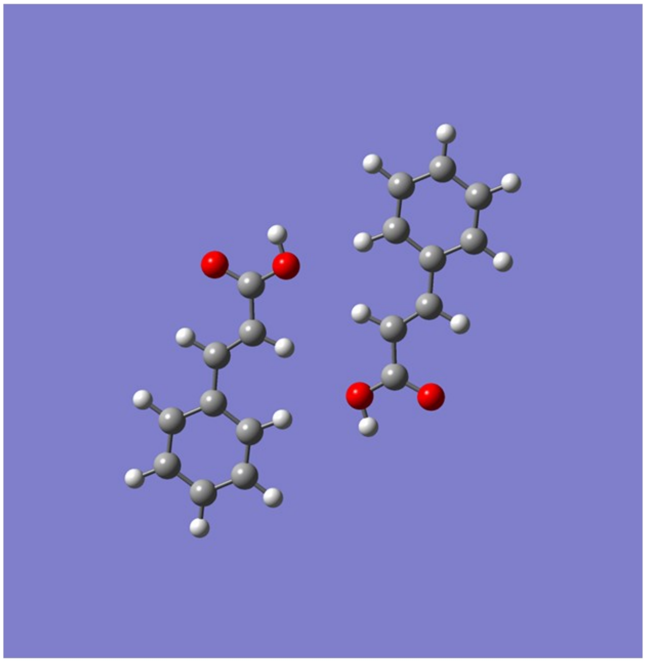
complexation energy = -3.20 kcal/mole (raw)
complexation energy = -2.99 kcal/mole (corrected)

Figure S5. View of the orientation and binding energies of the observed π-type halogen bonds within the co-crystal (**$C_6I_2Cl_4$**)·2(**benz**).



complexation energy = -3.20 kcal/mole (raw)
complexation energy = -2.99 kcal/mole (corrected)

Figure S6. View of the orientation and binding energies of the observed π-type halogen bonds within the co-crystal (**$C_6I_2Cl_4$**)·2(**cinn**).



complexation energy = -1.35 kcal/mole (raw)
complexation energy = -1.01 kcal/mole (corrected)

Figure S7. View of the orientation and binding energies of the observed C-H···O hydrogen bonds between neighboring cinnamic acids (**cinn**) within the co-crystal (**$C_6I_2Cl_4$**)·2(**cinn**).

References

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6. G. M. Sheldrick, *Acta Crystallogr.*, 2015, C**71**, 3.

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