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# Influence of Secondary Interactions on Structural Diversity between a Pair of Halogen-Bonded Co-Crystals Containing Isosteric Donors

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**Abstract:** The formation of a pair of co-crystals based upon isosteric halogen-bond donors, namely 1,4-diiodoperchlorobenzene and iodoperchlorobenzene, along with the acceptor 4,4-bipyridine is reported. As expected, the components in each co-crystal engage in halogen bonding interactions resulting in a one-dimensional chain-like structure. In particular, the co-crystal containing 1,4-diiodoperchlorobenzene is primarily held together by I…N halogen bonds while the solid based upon iodoperchlorobenzene forms both I…N and Cl…N interactions. Structural diversity is achieved between these co-crystals based upon the type of secondary interactions involving the chlorine atoms on each halogen-bond donor even though they are isosteric in nature.

Keywords: halogen bonding; co-crystal; crystal engineering; organic solid state



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## 1. Introduction

Halogen bonding is an attractive interaction between an electrophilic region on a halogen atom, namely a  $\sigma$ -hole, and a nucleophilic region on a different atom [1–3]. In particular, a  $\sigma$ -hole is a positive electrostatic area found at the tip of a carbon-bound halogen atom that can interact with an electron rich group such as a lone pair [4,5]. The  $\sigma$ -hole is most pronounced on iodine and is enhanced by neighboring electronegative atoms, particularly fluorine [6–9]. Solid state chemists utilize halogen bonding interactions since they are similar in strength and directionality when compared to hydrogen bonds. A continuing challenge in crystal engineering is how small and incremental changes, to either component of the co-crystal, can lead to structural diversity between these solids [10–13]. In these systems, the variations occur due to the type of secondary interactions that ultimately influence the resulting crystal structure, along with chemical and physical properties, even in the presence of the stronger halogen bond [14].

An ongoing focus in our research groups is to develop halogen-bond donors that contain chlorine rather than fluorine as the electron-withdrawing group. In particular, we have investigated the halogen bonding propensity of 1,4-diiodoperchlorobenzene ( $C_6I_2Cl_4$ ) where it has shown to reliably form I···N halogen bonds when coupled with various acceptor molecules [15–19]. To understand the formation of these halogen bonds, a molecular electrostatic potential calculation was performed on  $C_6I_2Cl_4$  and a  $\sigma$ -hole was located on the iodine atoms with a value of 146 kJ/mol which is well within range for a halogenbond donor (Scheme 1) [19]. With a similar goal, we have also reported on the ability of iodoperchlorobenzene ( $C_6ICl_5$ ) to engage in I···N halogen bonds with many of these same acceptors [20]. The *para*-chlorine atom on  $C_6ICl_5$ , in reference to the iodine, forms an unexpected Cl···N halogen bond which generated a one-dimensional chain-like structure when combined with appropriate ditopic acceptors. In a similar calculation, the  $\sigma$ -hole on both the iodine and *para*-chlorine atoms on  $C_6ICl_5$  supported halogen bond formation with

values of 157 and 78 kJ/mol, respectively (Scheme 1) [20]. Curiously, these co-crystals are all isostructural to related solids containing  $C_6I_2Cl_4$  as the halogen-bond donor.



**Scheme 1.** Rendering of the components of these co-crystals: (**a**) halogen-bond donors  $C_6I_2Cl_4$  and  $C_6ICl_5$  along with (**b**) the halogen-bond acceptor 4,4-BP. The electrostatic potential values for the  $\sigma$ -hole on selected atoms on the halogen-bond donors are shown as previously reported [19,20]. All indicated values are in kJ/mol.

Using this as inspiration, we report here the formation and structure of a pair of halogen-bonded co-crystals based upon 4,4-bipyridine (4,4-BP) along with two isosteric donors, namely  $C_6I_2Cl_4$  and  $C_6ICl_5$  (Scheme 1). As expected, the resulting co-crystals ( $C_6I_2Cl_4$ )·(4,4-BP) and ( $C_6ICl_5$ )·(4,4-BP) are primarily held together by the combination of I···N and Cl···N halogen bonds which generate a one-dimensional chain structure for each solid. Even though these co-crystals contain isosteric donors, which have previously yielded isostructural solids, the resulting materials have drastically different crystal structures. This structural diversity is based upon the type of secondary non-covalent interactions observed between the components involving chlorine atoms on a particular halogen-bond donor.

#### 2. Materials and Methods

### 2.1. Materials

The acceptor 4,4-bipyridine (4,4-BP) and reagent grade toluene were both purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. Both of the donors, 1,4-diiodoperchlorobenzene ( $C_6I_2Cl_4$ ) [21] and iodoperchlorobenzene ( $C_6ICl_5$ ) [22], were synthesized by a previously reported method. All crystallization experiments were performed in 20 mL scintillation vials.

#### 2.2. Formation of $(C_6I_2Cl_4) \cdot (4,4-BP)$

Co-crystals of  $(C_6I_2Cl_4) \cdot (4,4\text{-BP})$  were formed by dissolving 25.0 mg of  $C_6I_2Cl_4$  in 2.0 mL of toluene, which was combined with a separate 2.0 mL toluene solution containing 8.3 mg of 4,4-BP (1:1 molar equivalent). The resulting solution was allowed to slowly evaporate and within two days, crystals suitable for X-ray diffraction were realized.

#### 2.3. Formation of $(C_6ICl_5) \cdot (4, 4-BP)$

In a similar manner, co-crystals of  $(C_6ICl_5) \cdot (4,4-BP)$  were achieved by taking 25.0 mg of  $C_6ICl_5$  and dissolving it in 2.0 mL of toluene. Then, a separate 2.0 mL toluene solution of 10.4 mg of 4,4-BP was combined with the previous solution (1:1 molar equivalent). Again, the combined solution was allowed to slowly evaporate and within three days, single crystals suitable for X-ray diffraction were formed.

#### 2.4. Single-Crystal X-ray Diffraction

X-ray data were collected on a Rigaku XtaLAB Synergy-*i* Kappa diffractometer (Rigaku Americas Corporation, The Woodlands, TX, USA) equipped with a PhotonJet-i X-ray source to generate Cu K $\alpha$  radiation. Suitable single crystals were transferred to a glass slide in type NVH immersion oil. Each co-crystal was then mounted on a MiTeGen 50  $\mu$ m MicroLoop and placed on the diffractometer under a cold nitrogen stream at 100 K. After data collection, the unit cell was redetermined using a subset of all the collected data. The intensity data were corrected for Lorentz, polarization, and background effects using CrysAlisPro (Rigaku Americas Corporation, The Woodlands, TX, USA). A numerical absorption correction

was applied based on a Gaussian integration over a multi-faceted crystal then followed by a semi-empirical correction for adsorption. The program SHELXT [23] was used for the initial structure solution while SHELXL [24] was used for the refinement of each cocrystal. These programs were utilized within the OLEX2 software (OlexSys Ltd, Durham, UK) [25]. Hydrogen atoms bound to carbons were geometrically constrained using the appropriate AFIX commands. Selected crystallographic and refinement parameters for  $(C_6I_2Cl_4) \cdot (4,4-BP)$  and  $(C_6ICl_5) \cdot (4,4-BP)$  are listed in Table 1.

**Table 1.** Crystallographic and refinement parameters for the co-crystals ( $C_6I_2Cl_4$ )·(4,4-BP) and ( $C_6ICl_5$ )·(4,4-BP).

Co-Crystal	(C <sub>6</sub> I <sub>2</sub> Cl <sub>4</sub> ) ⋅ (4,4-BP)	(C <sub>6</sub> ICl <sub>5</sub> ) ⋅ (4,4-BP)
Formula	$C_{16}H_8Cl_4I_2N_2$	C <sub>16</sub> H <sub>8</sub> Cl <sub>5</sub> IN <sub>2</sub>
Formula Mass (g∙mol <sup>-1</sup> )	623.84	532.39
Crystal system	triclinic	monoclinic
Space group	$P\overline{1}$	$P2_1/n$
a (Å)	4.0843(1)	14.3260(3)
b (Å)	9.4089(2)	3.8878(1)
<i>c</i> (Å)	12.8307(2)	17.0394(4)
$\alpha$ (°)	68.543(2)	90
β (°)	84.458(2)	113.747(3)
$\gamma$ (°)	87.780(2)	90
Z	1	2
V (Å <sup>3</sup> )	456.747(18)	868.68(4)
$\rho_{\rm calcd} ~({\rm g} \cdot {\rm cm}^{-3})$	2.268	2.035
T (K)	100	100
$\mu$ (mm <sup>-1</sup> )	32.436	21.570
F(000)	292.0	512.0
Radiation source	Cu Ka	Cu Kα
Reflections collected	8062	6948
Independent reflections	1800	1617
Data/restraints/parameters	1800/0/110	1617/204/151
R <sub>int</sub>	0.0588	0.0573
$R_1 \ (I \ge 2\sigma(I))$	0.0320	0.0673
$wR(F^2)$ $(I \ge 2\sigma(I))$	0.0840	0.1877
$R_1$ (all data)	0.0326	0.0686
$wR$ ( $F^2$ ) (all data)	0.0844	0.1895
Goodness-of-net on $F^2$	1.080	1.074
CCDC deposition number	2,204,844	2,204,845

#### 2.5. Computational Methods

To determine the different I···N and Cl···N halogen-bonding energies, a series of Density Functional Theory (DFT) calculations were performed using the M06-2X density functional in the Gaussian 16 program [26]. The aug-cc-pVTZ basis set, stored in the Gaussian program, was used on all atoms except for iodine. In the case of iodine, the basis set, which included a core potential that replaces the inner 28 electrons, was obtained from the EMSL Basis Set Exchange Library [27]. This approach computes the binding energy as the difference between the energy of the co-crystal and the energies of the separated molecules. These DFT calculations used a single point energy computation with convergence for the energy change of less than  $1.00 \times 10^{-6}$  Hartrees. All of these binding energies were computed using the counterpoise method. The application of the counterpoise correction always decreases the binding energies by typically five to ten percent. In addition, these calculations were also carried out using non-augmented basis functions. When removing the diffuse functions, a change of one to two percent in the dissociation energy results.

# 3. Results

## 3.1. X-ray Crystal Structure of $(C_6I_2Cl_4) \cdot (4,4-BP)$

The components of  $(C_6I_2Cl_4)\cdot(4,4$ -BP) crystallize in the centrosymmetric triclinic space group Pī (Table 1). Within the asymmetric unit is half a molecule of both  $C_6I_2Cl_4$  and 4,4-BP where inverse symmetry generates the remainder of each fragment. As expected,  $C_6I_2Cl_4$ forms a series of I···N halogen bonds [I···N 2.904(6) Å; C–I···N 171.3(2)°] with 4,4-BP which generates a one-dimensional chain-like structure (Figure 1). Due to symmetry, the aromatic rings within 4,4-BP are coplanar. In contrast, the aromatic rings between the donor and acceptor within ( $C_6I_2Cl_4$ )·(4,4-BP) are twisted with an angle of 56.61° (Figures 1 and 2). As seen with other symmetric ditopic halogen-bond acceptors, molecules of  $C_6I_2Cl_4$  engage in infinite homogeneous face-to-face  $\pi$ – $\pi$  stacking (Figure 2). The parallel and slipped orientation of the aromatic ring on  $C_6I_2Cl_4$  runs along the crystallographic *a* axis with a centroid-to-centroid distance of 4.0843(1) Å equal to that axis. Similar  $\pi$ – $\pi$  stacking patterns were observed for  $C_6I_2Cl_4$  in both single- and mutil-component crystals that have been previously reported by our groups [16,19].



**Figure 1.** X-ray structure of  $(C_6I_2Cl_4) \cdot (4,4-BP)$  illustrating the I···N halogen bonds which generate the one-dimensional chain-like structure.



**Figure 2.** X-ray structure of ( $C_6I_2Cl_4$ )·(4,4-BP) illustrating the infinite homogeneous face-to-face  $\pi$ - $\pi$  stacking arrangement of the aromatic rings.

These halogen-bonded chains interact with their nearest neighbors by Type I Cl···Cl interactions [28,29] [Cl···Cl 3.240(2) Å; C–Cl···Cl 165.8(2)°;  $|\theta_1 - \theta_2| = 0°$ ] which results in a two-dimensional sheet (Figure 3). Type I interactions are not considered halogen bonds but instead they are symmetric close contacts between halogen atoms where the difference in bond angles will be equal to zero. In particular, half of the chlorine atoms on C<sub>6</sub>I<sub>2</sub>Cl<sub>4</sub> are found to interact in this type of secondary interactions. Lastly, the remaining chlorine atoms are found to engage in an offset Cl··· $\pi$  interactions with 4,4-BP (Cl··· $\pi$  4.092 Å) measured from the chlorine atom to the centroid of the 4-pyridyl ring. The closest distance for this Cl··· $\pi$  interactions is found between a chlorine and carbon atom with a distance of 3.212(5) Å along with an angle of 170.7(2)°.

#### 3.2. X-ray Crystal Structure of $(C_6ICl_5) \cdot (4,4-BP)$

The components of  $(C_6ICl_5) \cdot (4,4-BP)$  crystallize in the centrosymmetric monoclinic space group  $P2_1/n$  where a half of both molecules are found in the asymmetric unit (Table 1). Again, inversion symmetry generates the remainder of each molecule. Unlike before, molecules of 4,4-BP are found to be disordered over two positions where after a free variable refinement returned a final value of .51/.49 for the major/minor components. In addition, the iodine and *para*-chlorine atoms, with respect to the iodine, are equally disordered over two positions and were modeled with a .50/.50 occupancy for each atom.

The ability of C<sub>6</sub>ICl<sub>5</sub> to form both I···N [I···N 2.956(7) Å; C–I···N 162.6(3)°] and Cl···N halogen bonds [Cl···N 3.205(20) Å; C–Cl···N 158.1(9)°] to the major site for 4,4-BP results in a one-dimensional chain (Figure 4). In drastic contrast to (C<sub>6</sub>I<sub>2</sub>Cl<sub>4</sub>)·(4,4-BP), the aromatic rings, namely the halogen-bond donor and acceptor, within (C<sub>6</sub>ICl<sub>5</sub>)·(4,4-BP) are nearly co-planar with an angle of 7.24° with regard to the major orientation (Figure 5). Again, molecules of C<sub>6</sub>ICl<sub>5</sub> engage in a face-to-face  $\pi$ - $\pi$  stacking arrangement that results in an infinite column of the donor that runs along the crystallographic *b* axis (Figures 5 and 6). These donors stack in a parallel and slightly offset pattern with a centroid-to-centroid distance of 3.8878(1) Å which is equal to that axis (Table 1).

Unlike (C<sub>6</sub>I<sub>2</sub>Cl<sub>4</sub>)·(4,4-BP), the secondary interaction between neighboring C<sub>6</sub>ICl<sub>5</sub> stacks within (C<sub>6</sub>ICl<sub>5</sub>)·(4,4-BP) is an infinite chain of Cl···Cl contacts. These are similar to the trifurcated X<sub>3</sub> synthon recognized in the structures of perhalobenzenes and trihalome-sitylenes [21,30]. In this structure, however, the infinite array of these non-covalent contacts [Cl···Cl 3.528(3) Å; C–Cl···Cl 148.1(3)° and 121.8(3)°;  $|\theta_1 - \theta_2| = 26.3(3)°$ ] appears between adjacent stacks of the donor along the crystallographic *b* axis (Figure 6). This closest chlorine–chlorine distance cannot be classified as either Type I or Type II due to the observed C–Cl···Cl bond angles [29]. In particular, Type I interactions should have a difference in bond angles equal to 0° while for Type II, the pair of angles should be close to 180° and 90°. Only half of the chlorine atoms on C<sub>6</sub>ICl<sub>5</sub> are found to interact in this type of Cl···Cl interaction.



**Figure 3.** X-ray structure of  $(C_6I_2Cl_4) \cdot (4,4-BP)$  illustrating the Type I Cl…Cl and Cl… $\pi$  interactions between nearest neighboring chains.



**Figure 4.** X-ray structure of ( $C_6ICl_5$ )·(4,4-BP) illustrating the I···N and Cl···N halogen bonds which generate the one-dimensional chain-like structure. The crystallographic disorder observed in both  $C_6ICl_5$  and 4,4-BP are shown. In particular, the observed disorder in  $C_6ICl_5$  is illustrated with the two colors (purple and green) on the same molecule.



**Figure 5.** X-ray structure of ( $C_6ICl_5$ )·(4,4-BP) illustrating the infinite homogeneous face-to-face  $\pi$ - $\pi$  stacking arrangement of the aromatic rings. The observed disorder in  $C_6ICl_5$  is illustrated with the two colors (purple and green) on the same atom. The disorder in 4,4-BP was removed for clarity.



**Figure 6.** X-ray structure of  $(C_6ICl_5) \cdot (4,4-BP)$  illustrating the infinite homogeneous face-to-face  $\pi - \pi$  stacking arrangement along with the infinite chain of Cl···Cl contacts. The observed disorder in  $C_6ICl_5$  is illustrated with the two colors (purple and green) on the same atom.

#### 3.3. Halogen Bond Energies Using Density Functional Theory Calculations

To enumerate the strength of both I···N and Cl···N halogen bonds within each cocrystal, a series of theoretical investigations using Density Functional Theory (DFT) calculations were performed. In particular, the M062X density functional was employed along with an aug-cc-pVTZ basis set. These halogen-bond strengths were calculated by using atomic positions determined from single-crystal X-ray diffraction data. The I···N halogen-bonding energy within (C<sub>6</sub>I<sub>2</sub>Cl<sub>4</sub>)·(4,4-BP) was determined to be -22.0 kJ/mol. In contrast, the I···N halogen bonding value for (C<sub>6</sub>ICl<sub>5</sub>)·(4,4-BP) yielded a lower value of -17.9 kJ/mol. In a similar approach, the strength of the Cl···N halogen bond within (C<sub>6</sub>ICl<sub>5</sub>)·(4,4-BP) was determined to be -7.4 kJ/mol. Interestingly, both of these energies are slightly lower than the published values for the co-crystal containing C<sub>6</sub>ICl<sub>5</sub> and *trans*-1,2-bi(4-pyridyl)ethylene which had values of -19.0 and -8.5 kJ/mol for the I···N and Cl···N halogen bonds, respectively [20]. These calculated binding energies support the presence of halogen bonds within these co-crystals.

#### 4. Conclusions

In this contribution, we report the structural diversity between a pair of co-crystals that differ only by the isosteric halogen-bond donor. This diversity is achieved by the type of secondary non-covalent interactions formed by the chlorine atoms on the given donor. In particular, these one-dimensional halogen-bonded chains either interact with neighbors via Type I Cl…Cl interaction or an infinite Cl…Cl contact that gives rise to the particular crystal packing. Currently, we are investigating the structures of related co-crystals with these donors and other symmetric bipyridine acceptors.

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