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## Two-point halogen bonding between 3,6-dihalopyromellitic diimides

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### MAIN TEXT

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## Abstract

The syntheses of 3,6-dichloro-, -dibromo-, and -diiodopyromellitic diimides—**ACI**, **ABr**, and **AI**, respectively—have been achieved. X-Ray crystallography of single crystals of **ACI** and **ABr** unveils the formation of extensive halogen-bonding networks in the solid-state as a consequence of interactions between the lone pairs on the carbonyl oxygen atoms with the  $\sigma$ -holes of the halogen atoms. Further, the solid-state superstructure of diiodopyromellitic diimide is characterised by the formation of associated halogen- $\pi$  dimers. The co-crystallisation of **ACI** or **ABr** with a 1,5-diaminonaphthalene derivative **DN** yields co-crystals of a mixed-stack charge-transfer (CT) complex which are supported by an expansive hydrogen-bonded network in addition to halogen-bonded belts that bring adjacent mixed-stacks into association with each other. 2,6-Dimethoxynaphthalene (**DO**) proved to be an effective CT complement to **AI**, yielding solvent-free co-crystals with superstructures which are comprised of a 1:2 ratio of **AI** to **DO**. This dimeric halogen-bonding motif is reminiscent of the formation of hydrogen-bonded dimers between carboxylic acids.

## Introduction

The development of noncovalent bonding interaction motifs is of crucial importance<sup>1</sup> to crystal engineers and chemists alike. As a consequence, an extensive range of hydrogen bonding<sup>2</sup> and aromatic CT<sup>2e,3</sup> motifs have been identified in both the solid state and solution phase. These and other noncovalent bonding interactions have been further exploited in supramolecular self-assembly processes,<sup>4</sup> as well as in diverse applications including molecular sensing<sup>5</sup> and organic electronics.<sup>3e,6</sup> The interaction known as halogen bonding<sup>7</sup>—namely, the noncovalent bonding interaction between a Lewis basic atom and a Lewis acidic halogen atom—has become

increasingly attractive because of its utility as a further source of influence which often acts<sup>7g</sup> orthogonally to other recognition motifs in supramolecular systems.

We became interested in exploring derivatives of the electron acceptor pyromellitic diimide (PMDI) in the context of our research<sup>6d</sup> into organic CT ferroelectric co-crystals. We hypothesised that, by replacing the two hydrogen atoms on the PMDI benzenoid core with halogens, the resulting halogenated PMDI would also become engaged in halogen-bonding interactions, especially since the electron deficient nature of PMDI would accentuate the Lewis acidity of the  $\sigma$ -holes<sup>7e</sup> in the aryl halides. Herein, we report (i) the syntheses of three 3,6-dihalopyromellitic diimides **AX** (**X** = **Cl**, **Br**, or **I**), (ii) the formation of dimeric two-point halogen-bonded networks in the solid-state superstructures of these three compounds, (iii) the formation of CT co-crystals of **ACl** or **ABr** with the electron-rich naphthalene derivative **DN**, and (iv) a 1:2 complex formed between **AI** and 2,6-dimethoxynaphthalene (**DO**).

## Experimental Section

### General Methods

Unless otherwise stated, compounds and solvents were purchased from commercial vendors (**4Cl** and **4Br** were obtained from Sigma Aldrich and TCI Chemicals, respectively) and were used as supplied without further purification. Compounds **DN**,<sup>8</sup> and **4I**,<sup>9</sup> were prepared following literature methods. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K on a Bruker Avance III 500 spectrometer, with a working frequency of 500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C. Chemical shifts are listed in ppm on the  $\delta$  scale and coupling constants are recorded in Hertz (Hz). Deuterated solvents for NMR spectroscopic analyses were used as received. Chemical shifts are reported in  $\delta$  values relative to the signals corresponding to the residual non-

deuterated solvents ( $\text{CD}_3\text{COCD}_3$ :  $\delta_{\text{H}}$  2.05 ppm,  $\delta_{\text{C}}$  29.84 ppm). X-Ray diffraction data were obtained on Bruker Platform and Kappa diffractometers, equipped with a  $\text{MoK}_\alpha$  (**ABr**) or  $\text{CuK}_\alpha$  (all other crystals) sealed-tube source and an APEX II CCD detector. Intensity data were collected using  $\omega$  and  $\phi$  scans spanning at least a hemisphere of reciprocal space for all structures (data were integrated using SAINT). Absorption effects were corrected on the basis of multiple equivalent reflections (SADABS). Structures were solved by direct methods (SHELXS)<sup>10</sup> and refined by full-matrix least-squares against  $F^2$  (SHELXL).<sup>10</sup> The structures were solved and refined using Olex2. The majority of the hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealised geometries. Crystallographic images were produced using UCSF Chimera.<sup>11</sup> Atom-to-atom distances were measured employing Mercury.<sup>12</sup>

### Synthetic Procedures

While the syntheses of some *N*-substituted dihalopyromellitic diimide derivatives and their precursors have been reported previously,<sup>13</sup> all of the parent diimides **AX** are unknown to date. Compounds **AX** (**X** = **Cl**, **Br**, or **I**, Fig. 1) were synthesised (Scheme 1) following similar synthetic routes to those in the literature.<sup>13c,d</sup> Oxidation of the appropriate 3,6-dihalodurene **1X** to the tetracarboxylic acid **2X**, followed by dehydration, yielded the dianhydride **1X**. Reaction of the anhydrides with  $\text{NH}_4\text{OAc}$  led to formation of the desired dihalogenated PMDIs **AX**, which precipitate out of the reaction mixture as a consequence of their low solubilities in AcOH. During the course of the synthetic optimisation, it was found, in agreement with the previous literature,<sup>13c,d</sup> that acetic acid was the ideal solvent because more polar solvents such as dimethylsulfoxide (DMSO) or even anhydrous dimethylformamide (DMF) could not be used as a reaction solvent at elevated temperatures. Highly coloured byproducts formed when reactions were conducted in these solvents, presumably as a consequence of the reactivity<sup>14,15</sup> of the aryl

halide. While *N*-methyl-2-pyrrolidone (NMP) could be used as a crystallisation solvent, highly coloured byproducts were still formed if NMP was used as a solvent for condensations between **AX** and primary amines.

### Typical procedure for the preparation of the **2X** compounds

**2Cl**: A mixture of **1Cl** (5.00 g, 24.6 mmol), KMnO<sub>4</sub> (20.0 g, 127 mmol), and *t*BuOH/H<sub>2</sub>O (1:1 v/v, 100 mL) was heated under reflux until the purple colour of the solution had disappeared, indicating complete consumption of KMnO<sub>4</sub>. The reaction mixture was then cooled to room temperature, and KMnO<sub>4</sub> (5.00 g, 31.6 mmol) was added carefully. The mixture was then heated under reflux for an additional 4 h, after which time EtOH (10 mL) was added to quench the remaining KMnO<sub>4</sub>. The brown solids were removed by hot filtration of the reaction mixture. After the filtrate had cooled to room temperature, it was acidified with 2 M HCl, and the solvent evaporated. The residue was dispersed in Me<sub>2</sub>CO and filtered to remove inorganic salts. The filtrate was collected and the solvent evaporated to yield **2Cl** as a white solid (5.57 g, 78.8%).  
<sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>, 125 MHz, 298 K): δ<sub>C</sub> (ppm) = 165.0, 136.3, 127.7.

**2Br**: In a similar manner to that described above for preparing **2Cl**, reaction of **1Br** (43.0 g, 147 mmol) and KMnO<sub>4</sub> (188 g, 1.19 mol total) in *t*BuOH/H<sub>2</sub>O (1:1 v/v, 500 mL) yielded **2Br** as a brown solid (50.4 g, 83.1%).  
<sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>, 125 MHz, 298 K): δ<sub>C</sub> (ppm) = 165.8, 138.4, 116.5.

**2I**: In a similar manner to that described above for preparing **2Cl**, reaction of **1I**<sup>9</sup> (10.0 g, 25.9 mmol) and KMnO<sub>4</sub> (30.5 g, 193 mmol total) in *t*BuOH/H<sub>2</sub>O (1:1 v/v, 100 mL) yielded **2I** as a light-yellow solid (11.2 g, 85.4%).  
<sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>, 125 MHz, 298 K): δ<sub>C</sub> (ppm) = 167.4, 142.1, 91.2.

### Typical procedure for the preparation of compounds 3X

**3Cl**: A mixture of **2Cl** (4.00 g, 12.4 mmol) and Ac<sub>2</sub>O/AcOH (1:1 v/v, 20 mL) was heated under reflux for 8 h. The reaction mixture was then cooled to room temperature, and the precipitate isolated by filtration to yield **3Cl** as an off-white solid (1.22 g, 34.2%). <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>, 125 MHz, 298 K): δ<sub>C</sub> (ppm) = 158.6, 137.0, 129.5.

**3Br**: In a similar manner to that described above for preparing **3Cl**, reaction of **2Br** (50.0 g, 12.4 mmol) and Ac<sub>2</sub>O/AcOH (1:1 v/v, 400 mL) yielded **3Br** as a brown solid (24.7 g, 54%). <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>, 125 MHz, 298 K): δ<sub>C</sub> (ppm) = 159.1, 138.6, 117.3.

**3I**: In a similar manner to that described above for preparing **3Cl**, reaction of **2I** (10.0 g, 19.8 mmol) and Ac<sub>2</sub>O/AcOH (1:1 v/v, 80 mL) yielded **3I** as a yellow solid (5.91 g, 63.8%). <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>, 125 MHz, 298 K): δ<sub>C</sub> (ppm) = 159.8, 141.1, 89.0.

### Typical procedure for the preparation of compounds AX

**ACl**: NH<sub>4</sub>OAc (297 mg, 3.86 mmol) and **3Cl** (500 mg, 1.74 mmol) were added to AcOH (5 mL). The reaction mixture was left to stir at room temperature for 1 h, then heated under reflux for 8 h. The reaction mixture was then cooled to room temperature, and the precipitate isolated by filtration and washed with MeOH to yield **ACl** as an off-white solid (439 mg, 88.4%). An NMR spectrum could not be obtained on account of the poor solubility of the compound in standard deuterated solvents. The structure of the product was confirmed by X-ray crystallography of single crystals obtained by liquid-liquid diffusion of H<sub>2</sub>O into a saturated solution of **ACl** in NMP.

**ABr**: In a similar manner to that described above for preparing **ACl**, reaction of  $\text{NH}_4\text{OAc}$  (615 mg, 8.53 mmol) and **3Br** (1.00 g, 2.66 mmol) in AcOH (10 mL) yielded **ABr** as a white solid (680 mg, 68%).

**AI**: In a similar manner to that described above for preparing **ACl**, reaction of  $\text{NH}_4\text{OAc}$  (177 mg, 2.30 mmol) and **3I** (500 mg, 1.06 mmol) in AcOH (10 mL) yielded **AI** as a yellow solid (361 mg, 72.5%).

### Crystallisation Conditions

**General procedure.** Extended sonication and gentle heating were required in order to dissolve the majority of the **AX** compounds in *N*-methyl-2-pyrrolidone (NMP). Once the mixture was cooled to room temperature, the resulting solution was passed through a 0.45  $\mu\text{m}$  syringe filter into a 10-mL test tube. Fresh Milli-Q water (5 mL) was layered carefully on top of the NMP solution and the tubes were left in the dark.

**Crystals AX.** A mixture of pyromellitic diimide **AX** (X = Cl, Br, or I, 0.05 mmol) and NMP (5 mL) was crystallised following the general procedure. Crystals were observed to grow within 2 d.

**Co-Crystals ACl•DN and ABr•DN.** Mixtures of naphthalene donor<sup>8</sup> **DN** (0.09 mmol) and either pyromellitic diimide **ACl** or **ABr** (0.04 mmol) and NMP (5 mL) were crystallised following the general procedure. Dark needles were observed to grow within 7 d.

**Co-Crystal AI•(DO)<sub>2</sub>.** Pyromellitic diimide **AI** (10 mg, 0.02 mmol) was added to NMP (5 mL). Extended sonication and heating of the mixture was necessary in order to dissolve the majority of **AI**. Once the mixture was cooled to room temperature, naphthalene donor **DO** (4 mg, 0.02



mmol) was added to the solution, and immediately a coloured precipitate was formed. The supernatant was passed through a 0.45  $\mu\text{m}$  syringe filter into a 10-mL test tube. Fresh Milli-Q water (5 mL) was layered carefully on top of the NMP solution. Orange needles were observed to grow within 1 d.

## Results and Discussion

Single crystals of **ACl** and **ABr** suitable for X-ray diffraction were grown by liquid-liquid diffusion of  $\text{H}_2\text{O}$  into NMP solutions. X-Ray crystallography reveals (Table 1) that **ACl** and **ABr** crystallise isostructurally in the monoclinic  $P2_1/c$  space group (No. 14). The superstructures are solvent-free—the molecules are packed together tightly by a plethora of close contacts. The molecules are arranged (Fig. 2a and b) in a herringbone fashion in which the imide hydrogens engage in hydrogen-bonding interactions with nearby carbonyl oxygen atoms ( $[\text{O}\cdots\text{N}]$  distances: 2.88 and 2.89  $\text{\AA}$  for **ACl** and **ABr**, respectively). Belts of **ACl** and **ABr** molecules are formed as a consequence of significant two-point intermolecular halogen-oxygen-bonding interactions between adjacent molecules. These contacts are reminiscent of the hydrogen-bonded dimers formed<sup>2c</sup> between carboxylic acids. A search (See ESI) of the Cambridge Structural Database (CSD) with Conquest<sup>16</sup> reveals that this dimeric halogen-bonding motif is quite rare and has not been explored as a supramolecular motif. In both superstructures, the  $[\text{O}\cdots\text{X}]$  distances (Fig. 2c and d, red) are significantly less than the summation of the expected<sup>17</sup> van der Waals radii for  $[\text{O}\cdots\text{X}]$ , which are 3.25 and 3.35  $\text{\AA}$  for  $\text{X} = \text{Cl}$  and  $\text{Br}$ , respectively. Because of the rigid geometry of the molecules, the halogen atoms are in close proximity to both oxygen atoms of the *ortho* imide carbonyl groups. Even though the *intramolecular* halogen-to-oxygen distances are also less than the expected<sup>17</sup> van der Waals distances, halogen bonding between them is not expected<sup>18</sup> because the Lewis basic lone pairs on the oxygen atoms are not in the correct

geometry to interact with the halogen atom. The [Br $\cdots$ Br] distance (3.51 Å) in the solid-state superstructure of **ABr** is also shorter than the van der Waals distance (3.70 Å), and falls within the definition of a Type I<sup>7b</sup> halogen-halogen interaction—namely, the two [C–Br $\cdots$ Br] angles which define the interaction in question are the same (127°) as a result of the centre of inversion in the solid-state superstructure. In contrast, and presumably as a consequence of the **ACl** molecules favouring the more significant [O $\cdots$ Cl] interactions, the [Cl $\cdots$ Cl] distance (3.53 Å) is nearly equal to the expected van der Waals distance (3.50 Å). These Type I contacts arise typically from close-packing effects and are not considered<sup>71</sup> to be true halogen-bonding interactions, unlike the [O $\cdots$ X] interactions.<sup>19</sup> A side effect of the steric bulk of the halogen atoms is that the PMDI molecules do not lie completely flat in the solid-state superstructure—average torsional angles of 5.9 and 6.4° are present between the C=O and C–X bonds in **ACl** and **ABr**, respectively. Adjacent **ABr** and **ACl** molecules are essentially coplanar (Fig. 2e and f) with each other in a fashion that maximises directional halogen-bonding interactions. An intermolecular hydrogen-bonding interaction between imide groups is also evident in the crystal superstructures, with an [H–N $\cdots$ O] distance of 2.88 Å for both **ABr** and **ACl**. These interactions, which occur orthogonally to the halogen-bonding ones, also play a role in the herringbone assembly of the crystal structure.

Single crystals of **AI** suitable for X-ray diffraction were obtained by liquid-liquid diffusion between H<sub>2</sub>O and a solution of **AI** in NMP. The solid-state superstructure (Fig. 3) differs vastly from those of **ACl** and **ABr**. X-Ray crystallography reveals (Table 1) that **AI** crystallises in the triclinic  $P\bar{1}$  space group (No. 2) with an asymmetric unit containing one molecule each of H<sub>2</sub>O, NMP, and **AI**. The intermolecular [O $\cdots$ I] distance of 3.01 Å, which is 0.47 Å less than the expected<sup>17</sup> van der Waals distance, is even smaller than the [O $\cdots$ X] distances observed in the

solid-state superstructures of **ACl** and **ABr**. This observation agrees with the general halogen-bonding strength trend of  $I > Br > Cl$ . Additionally, there appear (Fig. 3c) to be  $[I \cdots \pi]$  interactions<sup>7i</sup> present in the superstructure. The distances between the planes defined by the central benzenoid rings alternate between 3.47 and 3.68 Å, providing evidence that pairs of **AI** molecules are Peierls distorted into dimers by these  $[I \cdots \pi]$  interactions. As a consequence of this distortion, the bend angle between the imide nitrogens and the centroid of the benzenoid ring in **AI** is about 174°. Each imide group in a molecule of **AI** engages in intermolecular hydrogen-bonding interactions with a molecule of NMP or H<sub>2</sub>O, with  $[H-N \cdots O]$  distances of 2.81 and 2.74 Å, respectively.

Subsequently, we attempted to co-crystallise compounds **AX** with electron-rich naphthalene **DN**<sup>8</sup> (Fig. 1). **DN** is characterised by diethylene glycol ‘arms’ which are capable of “locking” around suitable hydrogen-bonding sites in complementary molecules under the lock-arm supramolecular ordering<sup>6d</sup> (LASO) paradigm. It has been reported previously<sup>20</sup> that a compound similar to **DN**—with oxygen atoms in place of the NH functions on the naphthalene core—co-crystallises with PMDI to form a CT complex held together by a myriad of hydrogen-bonding interactions, similar to those found<sup>6d</sup> previously in LASO co-crystals. We discovered that liquid-liquid diffusion between H<sub>2</sub>O and solutions of **ACl** or **ABr** and **DN** in NMP produced large centimetre-long crystals of **ACl•DN** and **ABr•DN**, respectively, suitable for X-ray diffraction (Table 1). Complexes **ACl•DN** and **ABr•DN** were found to crystallise isostructurally (Fig. 4) in the monoclinic  $P2_1/c$  space group (No. 14). The superstructures are solvent-free and are characterised by an alternating mixed-stack between **ACl** or **ABr** and **DN** in which the diethylene glycol chains form interwoven hydrogen bonds with the imide hydrogens. The dimeric halogen-bonding motif observed in the solid-state superstructures of **ACl** and **ABr** were

found to hold together adjacent mixed-stacks in these co-crystals. The [O $\cdots$ Cl] distance (3.42 Å) in **ACI**•**DN** is, however, significantly larger than that (3.13 Å) in the solid-state superstructures of **ACI**, and also exceed the expected<sup>17</sup> van der Waals distance (3.25 Å). In **ABr**•**DN**, the [O $\cdots$ Br] distance (3.27 Å) compares more favourably to both the analogous interaction (3.13 Å) in **ABr** and the predicted<sup>17</sup> van der Waals distance (3.35 Å). These observations suggests that the CT from the electron-rich **DN** to the electron-poor **ACI** and **ABr** decreases the Lewis acidity of the halogen atoms significantly enough to weaken the halogen-bonding interactions. Indeed, the adjacent **ABr** and **ACI** molecules are no longer coplanar with each other in the co-crystals. In **ACI**•**DN**, the plane-to-plane distance between adjacent molecules of **ACI** is 1.58 Å, while in **ABr**•**DN**, only 1.30 Å separates the planes of the **ABr** molecules. The hydrogen-bonding tendencies of the imide groups in **ACI** and **ABr** are manifested by the presence of [H–N $\cdots$ O] interactions (2.82 and 2.81 Å, respectively) with the terminal oxygen atoms of the **DN** diethylene glycol chains.

Despite repeated attempts, no co-crystals were formed between **AI** and **DN**. All of our attempts only yielded crystals of **AI**•(H<sub>2</sub>O)•(NMP). An explanation for this outcome may be found in the steric bulk of **AI** which prevents the formation of the CT complex. Looking down a mixed-stack in **ACI**•**DN** or **ABr**•**DN** reveals (Fig. 4c and d) that the halogen atoms are positioned closely on top of the  $\pi$  bonds in **DN**, a situation which may be difficult to replicate with the large electron clouds associated with iodine atoms. We posited that utilising<sup>19</sup> a differently substituted naphthalene would allow for an alternate stacking geometry. Indeed, simply mixing compounds **AI** and 2,6-dimethoxynaphthalene (**DO**) in NMP resulted in the immediate formation of a pink/orange precipitate. Careful co-crystallisation of **AI** with **DO** (Fig. 1) yielded orange needles suitable for X-ray diffraction (Table 1), an observation which confirms that the altered

substitution pattern of the naphthalene favours the formation of a CT complex. The superstructure (Fig. 5) of the co-crystal—which is in the triclinic  $P\bar{1}$  (No. 2) space group—consists of mixed-stacks of **AI** and **DO**, and additional molecules of **DO** oriented in a herringbone fashion between the mixed-stacks, resulting in an overall 1:2 ratio of donors to acceptors in the crystal. A side view of the mixed-stacks reveals (Fig. 5) that the face-to-edge molecules of **DO** are packed around the iodine atoms, suggesting that this unexpected packing motif most likely arises as a consequence of the bulk of the iodine atoms. The **AI** imide groups engage in the formation of weak hydrogen-bonded dimers, with [H–N···O] distances of 3.16 Å. To our surprise, there are no apparent halogen-bonding interactions in this assembly despite their prominence in the solid-state superstructure of **AI**, no doubt a consequence of the crystal packing forces that direct the formation of the 1:2 complex observed in the superstructure of the co-crystal.

## Conclusions

In summary, we have synthesised dichloro-, dibromo-, and diiodopyromellitic diimide. The solid-state superstructures of these compounds reveal that the halogen atoms engage in dimeric two-point intermolecular halogen-bonding interactions with adjacent oxygen atoms. Isostructural and solvent-free co-crystals obtained between dichloro- or dibromopyromellitic diimide and a 1,5-diaminonaphthalene derivative exhibit weakened halogen-bonding interactions between the charge-transfer mixed-stacks. Diiodopyromellitic diimide co-crystallised with 2,6-dimethoxynaphthalene in the form of a 1:2 complex. Presently, we are evaluating the materials properties of these co-crystals, while also exploring the utility of this dimeric halogen-bonding motif in solution.<sup>7h,21</sup>

## Acknowledgements

We thank Dr. Amy A. Sarjeant, Charlotte L. Stern, and the personnel in the Integrated Molecular Structure Education and Research Center (IMSERC) at Northwestern University for their assistance in the collection of some raw X-ray crystallographic data. This research is part (Project 34-949) of the Joint Center of Excellence in Integrated Nano-Systems (JCIN) at King Abdul-Aziz City for Science and Technology (KACST) and Northwestern University (NU). The authors would like to thank both KACST and NU for their continued support of this research. D.C. was supported by a NSF Graduate Research Fellowship; he also gratefully acknowledges support from a Ryan Fellowship awarded by the NU International Institute for Nanotechnology (IIN). A.K.B. acknowledges Fulbright New Zealand for a Fulbright Graduate Award and the New Zealand Federation of Graduate Women for a Postgraduate Fellowship Award.

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