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Engineering Short, Strong, Charge-Assisted Hydrogen Bonds in Benzoic Acid Dimers through Co-Crystallisation with Proton Sponge

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Abstract

A series of molecular complexes of the proton sponge 1,8-bis(dimethylamino)naphthalene (DMAN) with mono-substituted halobenzoic acids are reported, illustrating the designed exploitation of the characteristics of the proton sponge to induce short, charge-assisted hydrogen bonds in a predictable and reproducible manner. In every case, a DMAN molecule extracts a proton from the carboxylic acid group of the benzoic acid, as a result of which a recurrent supramolecular unit between a neutral and a

deprotonated benzoic acid molecule is formed featuring an extremely short, strong O-H \cdots O hydrogen bond, within a predominant crystallisation ratio of 1:2 (DMAN:benzoic acid).

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Introduction

Hydrogen bonding is one of the most utilised intermolecular interactions in crystal engineering as their directional nature lends itself to being used to control and direct the assembly process. Multi-component molecular complexes are known to alter significantly the physical properties when compared to the single components, with applications in varied areas including pharmaceutical¹ and optical materials.² Two general classes of material are possible, co-crystals where all components in the complex remain neutral, and salts where the molecules take ionic forms, offering the potential for the potential of charge-assisted hydrogen bonds; this is often the result of proton transfer and ΔpK_a values have widely been applied to predict which of these two classes is likely to form.³

Charge-assisted hydrogen bonds in general tend to be stronger than pure hydrogen bonds due to the additional electrostatic interactions involved, a consequence of one or more of the components carrying a charge. However, these have been far less studied as a design element in the assembly of multi-component molecular complexes.⁴ There is still much scope for developing understanding and implementation of such hydrogen bonds in terms of utilising them in the crystal engineering context.

DMAN (1,8-bis(dimethylamino)naphthalene) is known as the proton sponge due to its extremely high proton affinity. When crystallised in the presence of an acid co-former, it has a strong tendency to abstract a hydrogen atom from the acid and to incorporate it within an intramolecular N-H \cdots N hydrogen bond, forming the DMANH⁺ ion. The behaviour of the hydrogen atom within an N-H \cdots N hydrogen bond in such DMAN complexes has been studied previously using charge density^{5,6,7} including investigating the effects of weak hydrogen bonds on the location of the hydrogen atom with DMANH⁺ ions,⁷ and variable temperature X-ray diffraction.⁸ DMAN has previously been crystallised with a number of carboxylic

acids. These include benzene-1,2,4,5-tetracarboxylic acid,⁵ 4,5-dichlorophthalic acid,⁸ naphthalene-1,4,5,8-tetracarboxylic acid,⁹ benzene-1,2,3,4,5,6-hexacarboxylic acid,¹⁰ 1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidinecarboxylic acid,¹¹ 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid,¹² benzene-1,2,3-tricarboxylic acid,¹³ tartaric acid,¹⁴ maleic acid,¹⁵ 1,2-dichloromaleic acid,^{6,16} trifluoroacetate,¹⁷ 3,4-furandicarboxylic acid,^{8,18} and glutaric, suberic and dodecanedioic acids.¹⁹ In each case a protonated DMAN molecule is formed. The deprotonated acid molecule forms intramolecular O-H \cdots O hydrogen bonds^{5,6,8,15,16,18} or intermolecular charge-assisted O-H \cdots O hydrogen bonds.^{9,13,14} Only one of the latter, the complex with tartaric acid, is classified as a short, strong charge-assisted hydrogen bond with an O \cdots O distance of less than 2.5 Å.¹⁴ The role of weaker interactions such as $\pi\cdots\pi$ and C-H \cdots O weak hydrogen bonds in the three-dimensional self-assembly of a series of DMAN complexes with $Z' > 1$ were highlighted in a study of four organic salts.¹¹

There are a number of other examples where short, strong, charge assisted O-H \cdots O hydrogen bonds have been induced between carboxylic acid and carboxylate groups using other co-formers. These tend to be focused on creating extended architectures.^{20,21,22,23} A study of the Cambridge Structural Database based on the hydrogen phthalate ion, one of the common molecular ions utilised in this context, showed that *intramolecular* charge-assisted O-H \cdots O hydrogen bonds tended to be the shortest; in contrast, for this type of molecule, all but two of the *intermolecular* O-H \cdots O hydrogen bonds were longer than 2.5 Å, one of the exceptions being a sodium salt and the other a complex with diethylamine.²⁴

We have previously investigated the formation of charge-assisted hydrogen bonds by using strong acids.²⁵ Here we utilize instead a strong base, the proton sponge, and thus introduce a weaker acid as co-former. Our focus here is on investigating systematically the reliability of the formation of strongly hydrogen bonded acid:acid units, while also investigating the weaker interactions between these to explore the prevalence and structure-directing patterns of weaker interactions in the wider self-assembly process. Halobenzoic acids were used as the acid molecule in this study of DMAN-acid complexes to allow a systematic study of similar materials to be carried out with co-formers that would not be expected to provide competition for the stronger hydrogen bonding interactions, but also to investigate the balance

between halogen interactions and weaker hydrogen bonds in the wider self-assembly of the molecular complexes.

Experimental

X-ray diffraction data were collected at multiple temperatures using a Bruker Nonius Kappa CCD diffractometer, Bruker Apex II diffractometer or a Rigaku R-axis diffractometer, all equipped with an Oxford Cryosystems low temperature Cryostream device. The structures were solved by direct methods using SHELXS²⁶ and refined using SHELXL²⁷ within the WinGX program suite.²⁸

Neutron data were collected on the molecular complex of 2-iodobenzoic acid with DMAN on the Very Intense Vertical Axis Laue Diffractometer (VIVALDI)²⁹ at the ILL, Grenoble, France. No absorption corrections were deemed necessary due to the small size of the crystals. Orientation matrices were determined using the program LAUEGEN³⁰. Unit cell parameters were assumed to be the same as those determined from X-ray diffraction data as the Laue method at a continuous neutron source only allows for relative linear cell dimensions to be determined precisely. Reflections were integrated using ARGONNE_BOXES³¹ and normalized to a common wavelength, scaled and merged using LAUE4.³² The final refinements were performed using SHELXL²⁷ within the WinGX²⁸ program suite taking initial atomic coordinates from the X-ray structures. All hydrogen positional and anisotropic thermal parameters have been fully refined.

Different crystallisation temperatures and solvents were trialled for the preparation of all molecular complexes but only the solid forms reported below were obtained. The crystallisation conditions given gave rise to the best quality crystals for structural analysis. No anhydrous form of 4-fluorobenzoic acid with DMAN could be obtained and no hydrated forms other than those reported were obtained from any of the other tested conditions.

1:2 DMAN – benzoic acid (BA) molecular complex (1): a 2:1 molar ratio of BA and DMAN were dissolved in methanol and crystals were grown by slow evaporation of the solvent at a constant

temperature of 35 °C. The crystals formed were colourless prisms. Data were collected at 110, 200, and 300 K.

1:2 DMAN – 2-fluorobenzoic acid (2FBA) molecular complex (2): a 2:1 molar ratio of **2FBA** and **DMAN** were dissolved in dichloromethane and crystals were grown by slow evaporation of the solvent at room temperature. The crystals formed were colourless blocks. Data were collected at 100, 200, and 290 K.

1:2 DMAN – 2-chlorobenzoic acid (2CBA) molecular complex (3): a 2:1 molar ratio of **2CBA** and **DMAN** were dissolved in isopropanol and crystals were grown by slow evaporation of the solvent at room temperature. The crystals formed were colourless blocks. Data were collected at 100, 200, and 300 K.

1:2 DMAN – 2-bromobenzoic acid (2BBA) molecular complex (4): a 2:1 molar ratio of **2BBA** and **DMAN** were dissolved in diethylether and crystals were grown by slow evaporation of the solvent at room temperature. The crystals formed were colourless blocks. Data were collected at 110, 200, and 300 K.

1:2 DMAN – 2-iodobenzoic acid (2IBA) molecular complex (5): a 2:1 molar ratio of **2IBA** and **DMAN** were dissolved in acetone and crystals were grown by slow evaporation of the solvent at room temperature for crystals suitable for X-ray diffraction and 4 °C for crystals suitable for neutron diffraction. The crystals formed were colourless blocks. X-ray data were collected at 100, 200, and 300 K. Neutron data were collected at 30, 100, 200, and 300 K.

1:2 DMAN – 3-fluorobenzoic acid (3FBA) molecular complex (6): a 1:1 molar ratio of **3FBA** and **DMAN** were dissolved in diethyl ether and then crystals were grown by slow evaporation of the solvent at room temperature. The crystals formed were colourless blocks. Data were collected at 100 K.

2:1:1 DMAN - 3FBA hydrate molecular complex (7): a 1:1 molar ratio of **3FBA** and **DMAN** were dissolved in ethanol and then crystals were grown by slow evaporation of the solvent at room temperature. The crystals formed were colourless prisms. Data were collected at 110 K.

1:1 DMAN – 3-chlorobenzoic acid (3CBA) molecular complex (8): a 2:1 molar ratio of **3CBA** and **DMAN** were dissolved in diethylether and then crystals were grown by slow evaporation of the solvent at room temperature. The crystals formed were colourless blocks. Data were collected at 100 K.

1:1 DMAN - 3-bromobenzoic acid (3BBA) molecular complex (9): a 1:1 molar ratio of **3BBA** and **DMAN** were dissolved in a 10:1 v/v methanol water mix and then crystals were grown by slow evaporation of the solvent at room temperature. The crystals formed were colourless prisms. Data were collected at 100 K.

1:2 DMAN – 3-iodobenzoic acid (3IBA) molecular complex (10): a 2:1 molar ratio of **3IBA** and **DMAN** were dissolved in dichloromethane and crystals were grown by slow evaporation of the solvent at room temperature. The crystals formed were colourless prisms. Data were collected at 110, 200, and 300 K.

1:2:1: DMAN - 4-fluorobenzoic acid hydrate molecular complex (11): a 2:1 molar ratio of **4FBA** and **DMAN** were dissolved in acetonitrile and crystals were grown by slow evaporation of the solvent at room temperature. The crystals formed were colourless blocks. Data were collected at 100 K.

1:1 DMAN – 4-chlorobenzoic acid (4CBA) molecular complex (12): a 1:1 molar ratio of **4CBA** and **DMAN** were dissolved in methanol and crystals were grown by slow evaporation of the solvent at room temperature. The crystals formed were colourless blocks. Data were collected at 100 K.

1:2 DMAN – 4-bromobenzoic acid (4BBA) molecular complex (13): a 2:1 molar ratio of **4BBA** and **DMAN** were dissolved in a 1:1 v/v methanol acetone mix and crystals were grown by slow evaporation of the solvent at 4 °C. The crystals formed were pale brown blocks. Data were collected at 100, 200, and 300 K.

1:2 DMAN – 4-iodobenzoic acid (4IBA) molecular complex (14): a 2:1 molar ratio of **4IBA** and **DMAN** were dissolved in acetone and crystals were grown by slow evaporation of the solvent at room temperature. The crystals formed were pale purple blocks. Data were collected at 110, 200, and 300 K.

Results and Discussion

DMAN is a proton sponge, readily accepting a hydrogen atom between the two N atoms and thus it often forms molecular complexes where the co-components can act as hydrogen donors i.e. with molecular acids. The solid-state crystal structures of 14 molecular complexes of DMAN with benzoic acid and a series of monosubstituted halobenzoic acids (fluoro-, chloro-, bromo- and iodo- substituted) have been determined in this work. The predominant crystallisation ratio in these complexes is 1:2 (DMAN:acid) regardless of the molar ratio adopted at the start of the co-crystallisation. The only exceptions are the molecular complexes with 3-fluorobenzoic acid hydrate (**7**), 3-chlorobenzoic acid (**8**), 3-bromobenzoic acid (**9**) and 4-chlorobenzoic acid (**12**) which form 2:1:1, 1:1, 1:1 and 1:1 molecular complexes, respectively. In every case apart from complex (**7**), a short, strong, charge-assisted O-H \cdots O hydrogen bond is formed between two benzoic acid molecules, as a result of the transfer of a hydrogen from one of the benzoic acid molecules to the DMAN proton sponge molecule creating the expected protonated DMANH⁺ molecular ion. The strongly hydrogen bonded units are self-contained forming two molecular building blocks, a benzoic acid dimer and a protonated DMANH⁺ molecule; there is no extended hydrogen bonded network formed. The hydrogen bond data are summarised in Table 1; the hydrogen bonds in the carboxylic acid-carboxylate dimers formed are all seen to be short and strong, with intermolecular O-H \cdots O hydrogen bond distances below 2.5 Å (no such dimer is formed in complex **7**), and include the remarkably short O-H \cdots O hydrogen bond distance of 2.409(2) Å in complex **11**, among the shortest known. These units are predictable and recurrent. Despite the fact that these two molecular units are only connected by weak interactions such as C-H \cdots π and C-H \cdots O weak hydrogen bonds, there is a remarkable similarity in the role of these weaker interactions in directing the wider structural architecture.

DMAN Molecules

The DMAN molecule acts as a proton extractor, taking a hydrogen atom from an acid molecule into an N-H \cdots N intramolecular hydrogen bond. The geometries of the methyl groups of the DMAN molecules are distinctly different between the protonated and neutral DMAN cases (Figure 1). This makes it possible

to identify unambiguously the protonation state of the DMAN molecule even in cases where the data are of insufficient quality to determine reliably the hydrogen atom positions and in particular, where X-ray diffraction rather than neutron diffraction is used. The protonated DMANH⁺ molecule is present in all the molecular complexes reported. Where the DMANH⁺ molecule is formed, the primary hydrogen bonding interaction is an intramolecular N-H \cdots N hydrogen bond (Table 1); this unit is self-contained and only weak intermolecular hydrogen bonds can be formed to this hydrogen atom or to the remainder of the molecule. The N \cdots N distance is also shortened to reflect the presence of the charge-assisted hydrogen bond. In the absence of crystal packing effects, the hydrogen atom would be located centrally within this hydrogen bond, equally shared between the two N atoms, or disordered between the two N atoms. As a consequence of this protonation, the C-N distances (to the naphthalene core) in the DMAN molecule are lengthened from ~ 1.40 Å in neutral DMAN molecules to 1.43-1.49 Å in the DMANH⁺ molecules. The DMANH⁺ molecules tend to show an asymmetry of the C-N distances, with the longer distance of the two showing the greatest interaction with the hydrogen atom within the hydrogen bond indicated by the refined position of the hydrogen atom from Fourier difference methods and also through direct imaging of the electron density through Fourier difference maps. Direct imaging of the Fourier difference maps shows some ambiguity in the hydrogen atom position within the hydrogen bond, particularly in the presence of the heavier halogen atoms (see ESI); the refined hydrogen atom positions are therefore not necessarily reliable and conclusions about the precise positions of these atoms cannot be drawn from X-ray diffraction data. There is no evidence for temperature dependant behaviour such as proton migration. The precise behaviour of the hydrogen atoms is the subject of related work utilising neutron diffraction data, reported in an accompanying publication.³²

Where the crystallisation ratio is different from 2:1 benzoic acid:DMAN, neutral DMAN molecules are also present within the molecular complexes; these are the first such mixed protonation state DMAN complexes to be reported. The formation of molecular complexes in a different crystallisation ratio with different protonation states for the DMAN cannot be related to the pK_a values of the co-molecules (and

hence the ΔpK_a values) as the pK_a values for 3-bromobenzoic acid (3.81) and 4-chlorobenzoic acid (4.00), the two systems which show a 1:1 DMAN:benzoic acid ratio (**9** and **12**), lie in the mid-range of all of the co-molecules used (2.85-4.204).

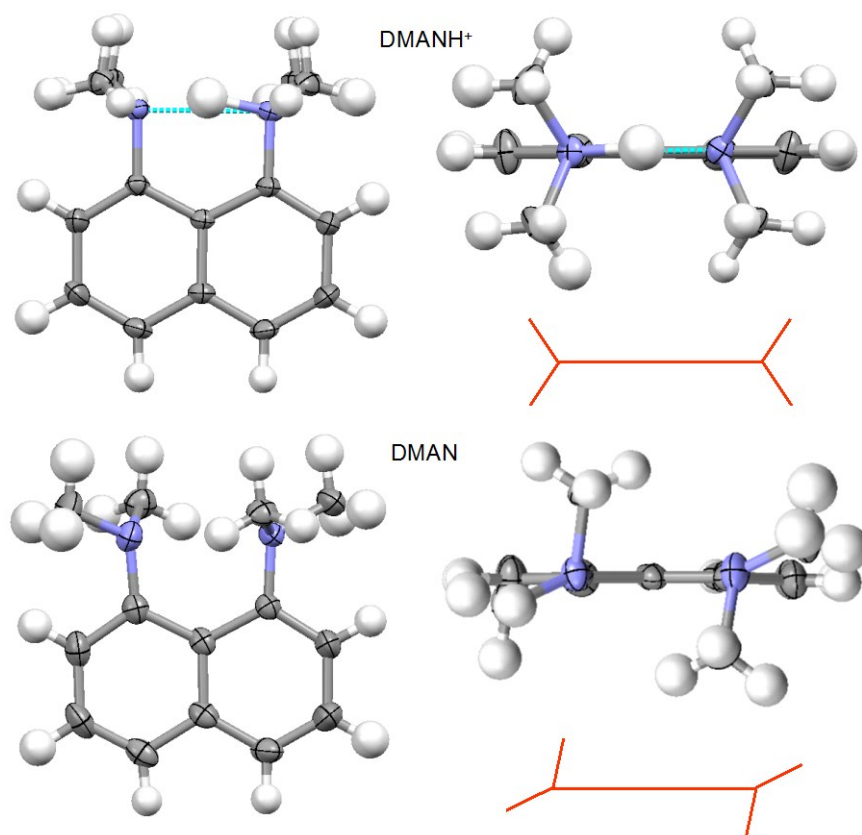


Figure 1. The difference in orientation of the methyl groups of DMAN between the protonated DMANH⁺ molecule (top) and neutral DMAN molecule (bottom). This offers an unambiguous indicator of the protonation state of the molecule.

Table 1. The hydrogen bond lengths for the two hydrogen bonds in each of the complexes.

Complex	T/K	N...N distance (Å)	N-H distance (Å)	H...N distance (Å)	O...O distance (Å)	O-H distance (Å)	H...O distance (Å)	Class
1	110	2.574(1)	1.25(2)	1.38(2)	2.477(1)	1.13(2)	1.35(3)	1
2	100	2.578(2)	1.30(3)	1.32(3)	2.447(2)	1.18(3)	1.28(3)	1
3	100	2.573(1)	1.08(2)	1.54(3)	2.444(2)	1.21(3)	1.24(3)	2
4	110	2.584(2)	1.22(3)	1.41(3)	2.455(2)	1.12(4)	1.35(4)	2
5 (X-ray)	100	2.566(3)	1.10(4)	1.50(4)	2.467(2)	1.07(4) [#]	1.40(4) [#]	4
5 (neutron)	100	2.567(2)	1.198(5)	1.414(5)	2.455(2)	1.207(4) [#]	1.249(4) [#]	4
6	110	2.604(2)	0.99(3)	1.66(3)	2.445(2)	1.13(4)	1.32(4)	1
7	100	2.588(1)	1.08(2)	1.56(2)	2.746(2) [*] 2.835(2) [*]	0.93(2) [*] 0.84(2) [*]	1.85(2) [*] 2.00(2) [*]	1
8	100	2.583(2) 2.789(5)	1.09(2) -	1.54(2) -	2.472(1)	1.05(2)	1.43(2)	1
9	100	2.604(7) 2.590(7) 2.791(7) 2.777(7)	1.13(5) 0.87(6) - -	1.52(5) 1.74(7) - -	2.455(6) 2.437(6)	1.2(1) 1.1(1)	1.3(1) 1.4(1)	2
10	110	2.580(3)	1.05(4)	1.57(4)	2.472(2)	1.15(4)	1.33(4)	2
11	100	2.564(3)	1.09(2)	1.51(2)	2.409(2)	1.16(3)	1.25(3)	-
12	100	2.602(1) 2.764(2)	1.00(2) -	1.65(1) -	2.478(2)	1.13(3)	1.35(3)	1
13	100	2.601(3)	0.95(3)	1.68(3)	2.477(3)	1.12(5)	1.37(5)	3
14	110	2.600(3)	1.07(3)	1.58(3)	2.474(3)	0.92(5) [§]	1.56(5) [§]	3

[#] Note that the hydrogen atom is most closely associated with the second benzoic acid molecule and therefore differs to that of all the other structures.

^{*} No link between benzoic acid dimers is formed. Here the second O is that of a water molecule and the hydrogen atom is attached firmly to the water.

[§] The H atom in this O-H...O hydrogen bond is placed in a distance constrained position and not freely refined – the thermal parameter is allowed to refine freely.

Benzoic Acid dimers linked by a single, short strong charge-assisted hydrogen bond

In all cases (except for the 1:2:1 DMAN 3-fluorobenzoic acid monohydrate (7)), a benzoic acid dimer is formed through a single short, strong, charge-assisted hydrogen bond between a neutral benzoic acid molecule and a deprotonated benzoic acid molecule. In general, this hydrogen bond is linear with the hydrogen bond axis lying in the same plane as the carboxylate group (Figure 2, left). However, the 4BBA and 4IBA units in complexes **13** and **14**, respectively, have an almost perpendicular arrangement for the molecules (Figure 2, right) with the hydrogen bond axis approximately perpendicular to the plane of the carboxylate group. The two most common hydrogen bonded motifs known for neutral benzoic acid molecules are the single hydrogen bonded catemer and the $R^2_2(8)$ hydrogen bonded ring where the carboxylic acid groups tend to lie in approximately the same plane.³⁴ In the singly hydrogen bonded dimers observed here, the carboxylic acid and carboxylate groups do not lie in the same plane and are twisted to different extents, in general tending slightly towards the catemer conformation where the torsion angle between the two carboxylic acid groups is greater than 90° . However, both the 3- and 4-chlorobenzoic acid molecular complexes (**8** and **12**, respectively) show an arrangement more similar to that of a hydrogen bonded ring where this torsion is less than 90° , while the 3-iodobenzoic acid molecular complex (**10**) has the two carboxylic acid groups lying almost exactly perpendicular to one another at the tipping point between the two.

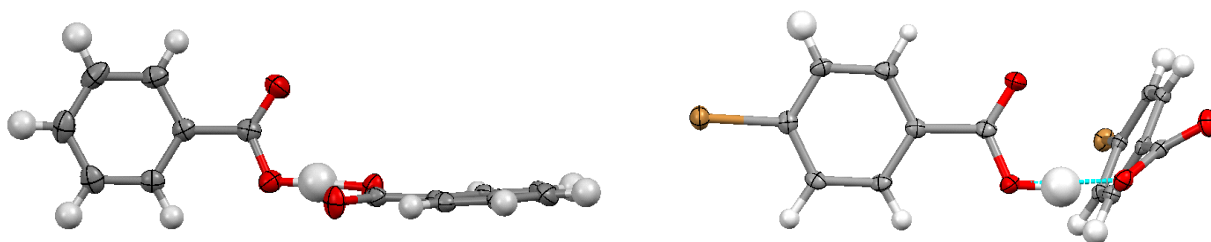


Figure 2. The two different configurations for the benzoic acid dimers. The most common linear configuration (left, BA; **1**) and the uncommon bent configuration (right, 4BBA; **13**).

The benzoic acid dimer is aligned such that one of the oxygen atoms not involved in the dimer hydrogen bond points towards the H atom in the N-H \cdots N intramolecular hydrogen bond of the DMANH⁺; this

orientation is supported by weak C-H \cdots O hydrogen bond interactions between the methyl groups of the DMANH⁺ and the O atom of the benzoic acid dimer. There are four broad classes which represent the orientation of the benzoic acid dimer relative to the DMANH⁺ molecule (Figure 3, Table 1). Classes 1 and 2 are similar and the most populated, where the dimer unit crosses the intramolecular hydrogen bond approximately perpendicular to the naphthalene ring. Classes 3 and 4 both have one of the benzoic acid molecules running approximately parallel to the intramolecular hydrogen bond; as a consequence of the increased steric bulk of the benzene ring of the adjacent benzoic acid molecule in close proximity to the methyl groups of the DMANH⁺ molecule, the N_{DMANH⁺} \cdots O_{BA} distances are longer reflecting the greater distance between the intramolecular hydrogen bond and the dimer. Class 3 contains only two structures, the 4BBA (**13**) and 4IBA (**14**) molecular complexes and this reflects the different geometry of the dimer unit. Class 4 is the anomalous molecular complex of DMAN with 2IBA (**5**).

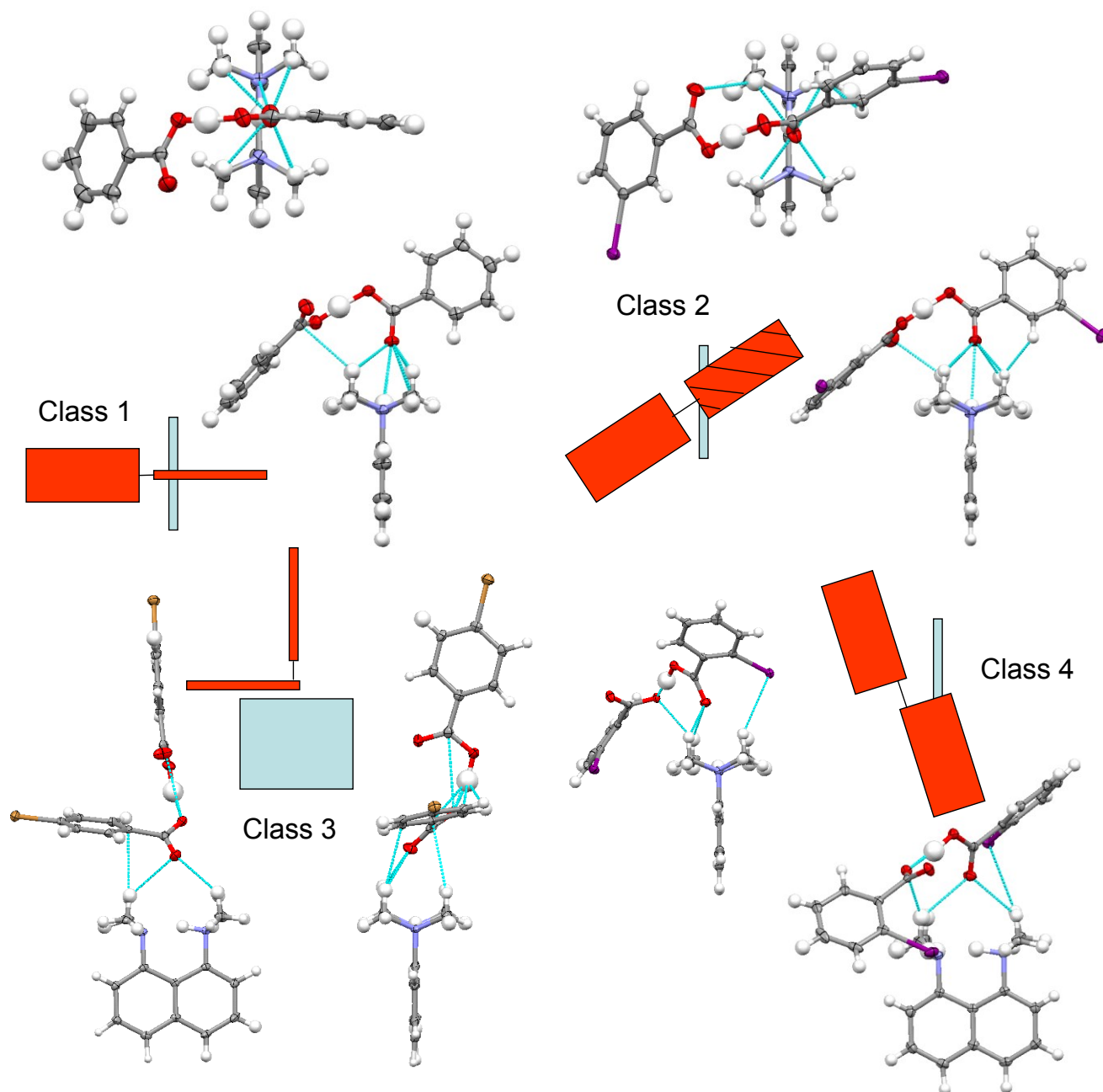
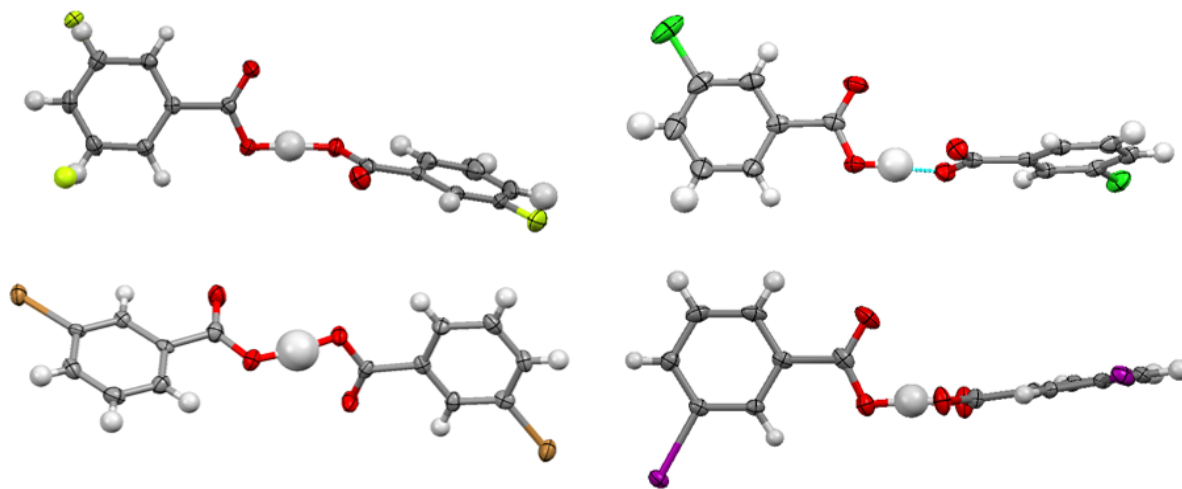


Figure 3. The four classes representing the arrangement of the benzoic acid dimers relative to the DMANH^+ molecule to which they are tethered.

The hydrogen atom of the acid dimer is almost always most closely associated with the benzoic acid molecule which is **not** interacting with the DMANH^+ molecule in the above way (i.e. the more deprotonated O atom is involved in the interaction with the DMANH^+ N-H \cdots N hydrogen bond), although the hydrogen atom is somewhat shared between the two molecules within the short, strong hydrogen bond (SSHB). Whilst the hydrogen atom positions from X-ray diffraction data cannot be relied upon, the location of the hydrogen atom can also be inferred from the C-O distances of the carboxyl and carboxylate groups. The 2IBA DMAN molecular complex (**5**) is an exception and here, the hydrogen atom sits closer to the 2IBA molecule which is tethered to the DMAN molecule via the above C-H \cdots O interaction. This could be inferred from the C-O bond lengths in the X-ray diffraction data, but has also been confirmed by neutron diffraction measurements. This may also explain or be a consequence of the unique orientation of the benzoic acid dimer above the DMANH^+ molecule. There is no evidence of temperature dependent behaviour of the hydrogen atom in any of these hydrogen bonds from the X-ray or neutron data.

Figure 4. The anomalous orientation of the 3IBA dimer (**10**; bottom right) with the I atom on the same



side as the H atom in the protonated COOH group and the 3CBA dimer (**8**; top right) where only one of the Cl atoms is on the same side as the hydrogen bond. For all other 2- and 3-substituted BAs, the halogen atom is always on the other side to the hydrogen bond ignoring disorder. Figure shows 3FBA (**6**) (top left), 3CBA (**8**) (top right), 3BBA (**9**) (bottom left) and 3IBA (**10**) (bottom right).

The two benzoic acid molecules within the dimers are independent in each of the complexes. There is a general correlation between the relative position of the halogen atom to that of the hydrogen atom in the hydrogen bond connecting the dimers in the asymmetrically substituted benzoic acids. In most cases, the halogen atom in the 2- and 3-substituted benzoic acids is orientated towards the side of the benzoic acid molecule with the non-protonated oxygen atom, neglecting any disorder (Figure 4). There are two exceptions to this; firstly, in the molecular complex of 3IBA with DMAN (**10**), the iodine atom on the benzoic acid molecule which is not tethered to the DMANH⁺ molecule lies on the same side of the benzoic acid molecule as the hydrogen bond (Figure 4). The second exception is in the 3CBA DMAN complex (**8**), where in this case, the halogen atom of the benzoic acid molecule which is tethered to the DMANH⁺ molecule lies on the same side of the molecule as the hydrogen bond.

Weak Hydrogen Bonds

There are a number of weaker interactions which are also prevalent in this series of complexes. Whilst the orientation of the benzoic acid molecule over the DMANH⁺ molecule shows some variation, one of the oxygen atoms of the dimer is always directed towards the N-H \cdots N hydrogen bond; this is surprisingly consistent given the nature of the intermolecular interactions which enforce this. The relevant O \cdots H distances are consistent with that of weak hydrogen bonds and may be assisted by the charged nature of each of the molecules. The refined hydrogen atom position within the N-H \cdots N hydrogen bond does vary from adopting a more central location to favouring one of the N atoms but Fourier difference maps show some ambiguity in the location of this atom (see ESI) and there is no discernable trend with the position of the benzoic acid dimer above this group. Neutron diffraction, where the hydrogen atom positions can be unambiguously identified and refined, is therefore necessary to investigate the nature of this weak interaction further and is the subject of a related paper.³³ As a consequence of the positioning of the benzoic acid dimer above the DMANH⁺ molecule, weak C-H \cdots O hydrogen bonds are formed from the four methyl groups of the DMANH⁺ molecules to the oxygen of the dimer (Figure 3). Slight variations in the position of the oxygen atom both in terms of the height above the DMANH⁺ molecule and small

translations relative to the centre of the N-H \cdots N hydrogen bond result in asymmetric hydrogen bonds to each of the four methyl groups, reflected by the C \cdots O distances. The asymmetry varies from complex to complex with no discernible trend identifiable.

A second type of C-H \cdots O hydrogen bond is always directed from one of the DMANH⁺ methyl groups towards one of the oxygen atoms of the second benzoic acid molecule in the dimer. This is within the same DMANH⁺ : benzoic acid dimer pair in most cases (Figure 5, left). The exception is the 4BBA (**13**) and 4IBA (**14**) complexes where the second molecule is no longer bent over the DMANH⁺ molecule and is directed away from the DMANH⁺ unit to which it is bonded; in this case, the interaction to the carbonyl oxygen of the untethered BA molecule is from a neighbouring DMANH⁺ methyl group (Figure 5, right).

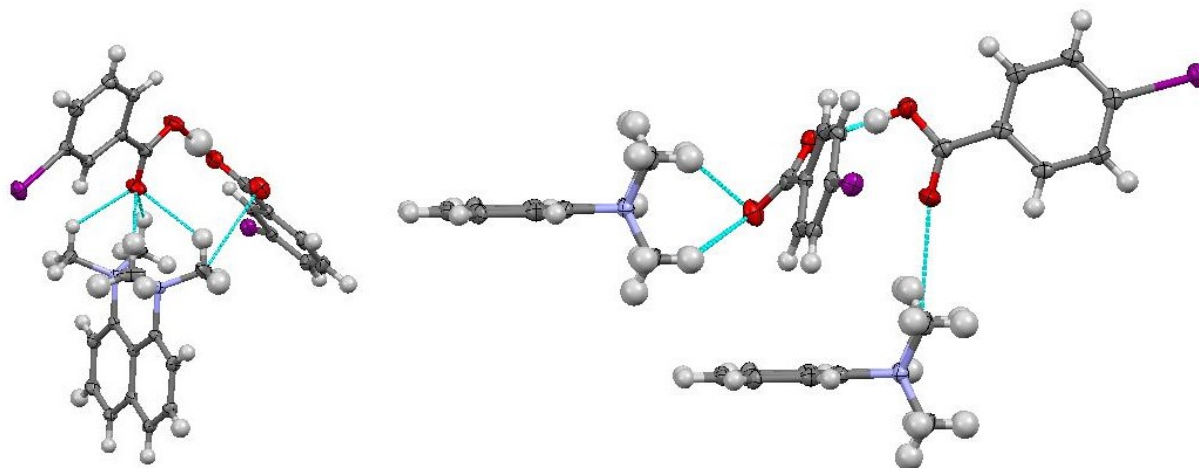


Figure 5. The weak hydrogen bonds between the methyl groups of the DMANH⁺ molecules and the untethered benzoic acid molecule. Left, DMAN 3IBA (**10**) where the weak hydrogen bond is within the same DMANH⁺ benzoic acid dimer pair; this forms in the majority of complexes. Right, DMAN 4IBA (**14**) where the orientation of the benzoic acid dimer prevents a weak hydrogen bond being formed within the DMANH⁺ benzoic acid dimer pair and therefore a weak hydrogen bond is formed to a neighbouring DMANH⁺ molecule; this is the same for the DMAN 4BBA complex (**13**).

Neutral DMAN co-existence

Four of the fourteen complexes crystallise in stoichiometries other than 1:2 (DMAN:acid) and have both neutral and charged DMAN molecules co-existing; these are the first reported examples of this co-existence and could not have been predicted by consideration of the ΔpK_a values; it is also notable that in no case is there “double deprotonation” of a benzoic acid dimer unit, emphasising the robustness of the motif and its key charge-assisted short hydrogen bond against the strong proton affinity of the additional, neutral, DMAN molecule present in these cases. There is no clear reason why these differing stoichiometries occur. Three complexes, the 4CBA (**12**), 3CBA (**8**) and 3BBA (**9**) complexes crystallise in 1:1 stoichiometries rather than 1:2. In all cases, the benzoic acid dimers still form, connected by a SSHB, and these are located above the DMANH^+ molecules with one of the O atoms directed towards the intramolecular $\text{N-H}\cdots\text{N}$ hydrogen bond. There are no significant interactions of the benzoic acid molecules or the DMANH^+ molecules with the neutral DMAN molecule. Due to the lack of interactions with this neutral DMAN molecule, there is 75:25 disorder of the methyl groups in the 4CBA complex (**12**) (Figure 6). There is no disorder in the 3BBA complex (**9**), although this has a particularly large asymmetric unit with four of each molecule type, comprising two neutral DMAN molecules, two DMANH^+ molecules and two hydrogen bonded 3BBA dimers.

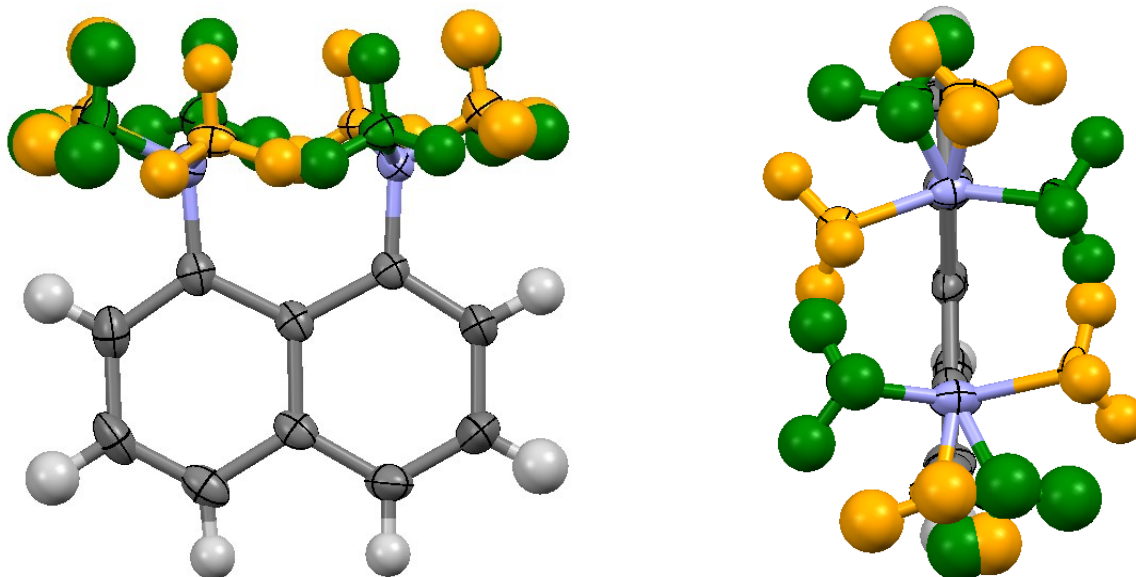
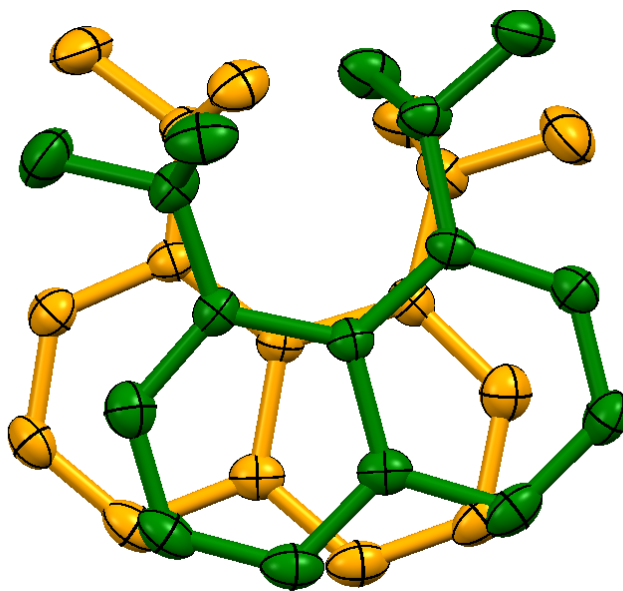


Figure 6. The disordered neutral DMAN molecule in the 4CBA complex (**12**). Green represents the major orientation (75%) and yellow, the minor component (25%).

Figure 7. The disordered neutral DMAN molecule in the 3CBA complex (**8**). The disorder is 50:50 about



a rotation axis the two colours show the two different positions that the DMAN molecule can adopt. Hydrogen atoms are omitted for clarity.

The 3CBA complex (**8**) also adopts the 1:1 DMAN:3CBA ratio but the disorder of the neutral DMAN molecule is quite different. The benzoic acid dimer motif persists in this structure and there is only one independent DMANH^+ molecule which is well defined. These are assembled in the same manner as the 1:2 complexes with the benzoic acid dimer above the $\text{N-H}\cdots\text{N}$ intramolecular hydrogen bond of the DMANH^+ molecule. The neutral DMAN molecule is 50:50 disordered about a two-fold rotation axis (Figure 7) and there is only half a molecule of this neutral species located in the asymmetric unit. The only interactions with the neutral DMAN molecule are weak $\text{C-H}\cdots\pi$ hydrogen bonds from methyl groups of the DMANH^+ molecule to the aromatic naphthalene ring on the neutral DMAN; the latter is sandwiched between two DMANH^+ molecules.

Hydrates

Two hydrate forms were also obtained with 3FBA (**7**) and 4FBA (**11**). Whilst an anhydrous form of 3FBA is also formed (**6**), the hydrate form of 4FBA was the only complex obtained with this co-former. The stoichiometry for the 4FBA complex (**11**) maintains the 1:2 DMAN:benzoic acid stoichiometry but with an additional water molecule included making a 1:2:1 DMAN:4FBA:H₂O complex. This stoichiometry was not maintained for the 3FBA hydrate (**7**).

Coexistence of neutral and charged DMAN molecules also occurs for the hydrated form of 3FBA with DMAN (**7**) and here the stoichiometry is 2:1:1 DMAN:3FBA:H₂O. This consequently results in the breaking of the benzoic acid homodimer motif with the second 3FBA molecule replaced by a water molecule; this hydrate form represents the only example amongst the complexes studied where this strong homodimer is not formed. A four molecule unit comprised of two 3FBA molecules (Figure 8) spaced by two water molecules is created; the charge on the carboxylate group is almost completely delocalized indicated by the equalization of the C-O distances, and one of the O atoms of the 3FBA molecule again sits above the DMANH⁺ molecule. Thus the four molecule 3FBA water unit connects two parallel DMANH⁺ molecules and the neutral DMAN molecule forms a C-H...F weak hydrogen bond from one of the methyl groups to a neighbouring 3FBA molecule and C-H... π interactions from aromatic H atoms to the aromatic ring of a second 3FBA molecule.

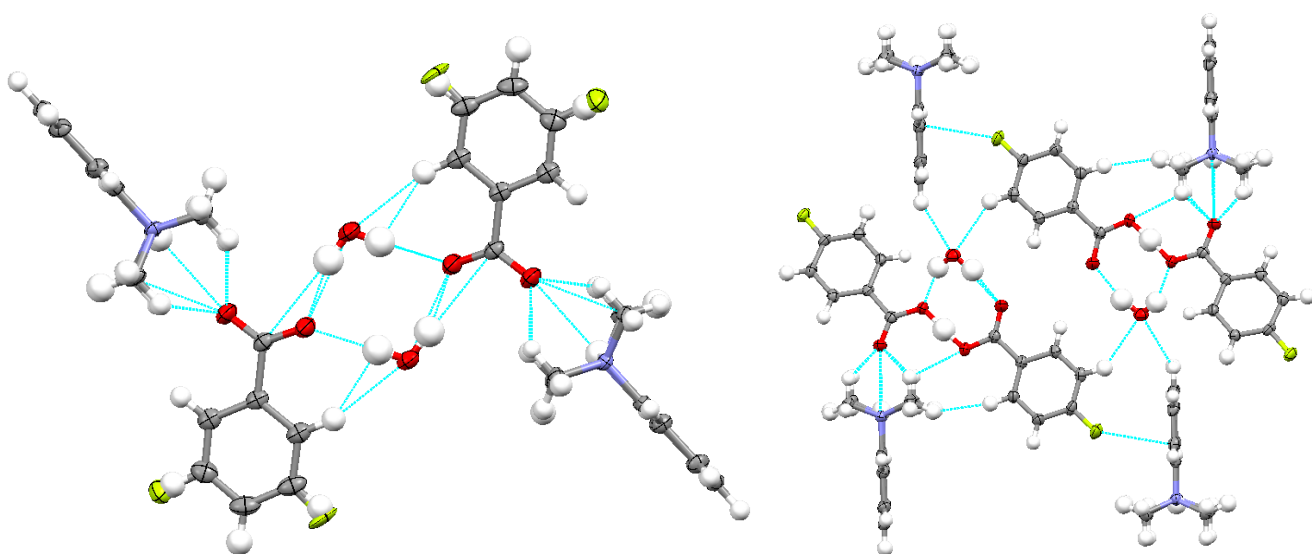


Figure 8. Left, the breaking of the benzoic acid dimer in the 3FBA hydrate complex (**7**). The stoichiometry is no longer 1:2 DMAN:3FBA and the water replaces one of the benzoic acid molecules. A four molecule hydrogen bonded unit is therefore formed which connects to two DMANH⁺ molecules. Note the fluorine atom of the 3FBA molecule is 75:25 disordered over two positions. Right, the role of the water molecule in the 4FBA hydrate complex. The benzoic acid dimer persists in this complex. The 4FBA hydrate complex (**11**) maintains the 2:1 4FBA to DMAN stoichiometry and thus the homodimer persists and only DMANH⁺ molecules are present. The role of the water molecule is thus different, forming two hydrogen bonds to a single 4FBA dimer, with one hydrogen bond to each molecule reinforcing the SSHB (Figure 8, right). The oxygen atom of the water molecule accepts two hydrogen bonds from an aromatic H atom on a neighbouring 4FBA molecule and a second from a DMAN molecule (Figure 8, right). Thus an extended stepped sheet structure is formed held together primarily by the weaker interactions with the DMANH⁺ rotated almost perpendicular to the 4FBA dimer units.

Halogen Interactions

Halogen interactions are found in this series of molecular complexes to different extents. They are, however, not a primary driving force in the molecular assembly. The fluorinated compounds show a tendency to form C-H \cdots F hydrogen bonds largely from DMANH⁺ methyl hydrogen atoms. These range in C \cdots F length from 3.027(3) Å (4FBA hydrate, **11**) to 3.526(2) Å (2FBA, **2**) and thus are significant interactions. One halogen bonded dimer is formed in the 3FBA complex (**6**) with two symmetry equivalent C-H \cdots F hydrogens forming the connecting links; the C \cdots F distance in this case is 3.242(2) Å.

The likelihood of halogen-halogen interactions forming increases as the substitution position is changed from *ortho* to *meta* to *para*. Halogen-halogen interactions are not prevalent for any of the 2-substituted benzoic acids, appearing only between the minor disordered component of 2BBA (**4**, distance 3.368(1) Å) and 2CBA (**3**, distance 3.381(1) Å, c.f. sum of van der Waals radii of 3.5 Å) with the ordered symmetry independent halobenzoic acid molecule in both cases. These cannot be considered driving forces behind the structure formation due to their small occupancies (15%). The heavier halogen atoms are also more

likely to form halogen-halogen interactions. In the 3BBA complex (**9**), a distorted type I Br \cdots Br interaction is found with a Br \cdots Br distance of 3.608(1) Å. The 4BBA (**13**), 3IBA (**10**), and 4IBA (**14**) complexes all show type II halogen-halogen interactions of Br \cdots Br or I \cdots I distances of 3.5887(4) Å, 3.7370(3) Å, and 3.8780(3) Å, respectively (c.f. sum of van der Waals radii for two Br atoms of 3.7 Å and two I atoms of 3.96 Å). Other prevalent interactions include C-H \cdots halogen, halogen \cdots π , and halogen \cdots O.

Perhaps surprisingly, the chlorine substituted complexes show a very small number of halogen interactions; the only complex in the three isomer series which shows halogen bonding is that of 4CIBA (**12**) where a type I Cl \cdots Cl interaction is formed. The Cl \cdots Cl distance in this case is 3.4822(7) Å which is only slightly less than the sum of the van der Waals radii for two chlorine atoms (3.5 Å). Neither the 2CBA (**3**) or 3CBA (**8**) complexes show any significant interactions involving the chlorine.

DMAN Stacking

Almost all of the molecular complexes show stacking of the DMANH⁺ molecules with the naphthalene rings tending to be parallel and overlapping with one another with the methylamino groups pointing in opposite directions (top-to-tail) and not directly overlaying with another DMANH⁺ molecule (Figure 9). The exceptions to this are the 3FBA complex (**6**) where the DMANH⁺ molecules are not parallel but are arranged in pairs and the 4BBA and 4IBA complexes (**13** and **14**) which do not show DMANH⁺ stacking in any form. The spacing of these units tends to increase when going from benzoic acid to 2-, 3- and 4-substituted benzoic acids. The stoichiometry of the complex significantly affects the range of these interactions. In the cases where the DMAN:benzoic acid stoichiometry is 1:2, isolated pairs of DMANH⁺ molecules are formed; in the case of BA (**1**) and 2IBA (**5**), these pairs are very staggered but in the remaining complexes there is significant overlap of the rings (Figure 9).

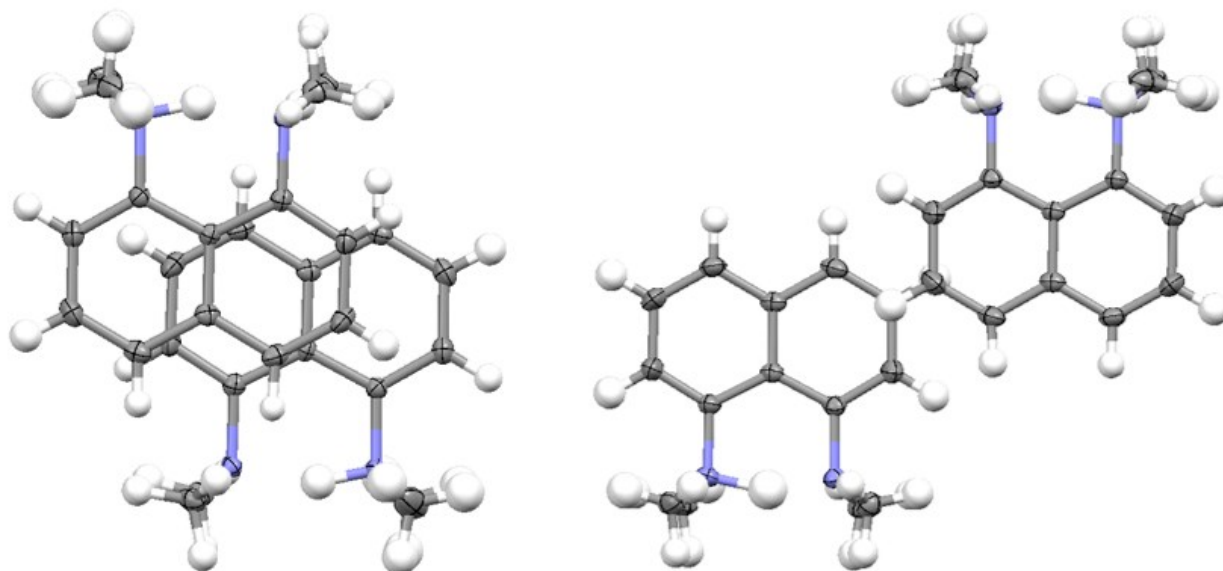
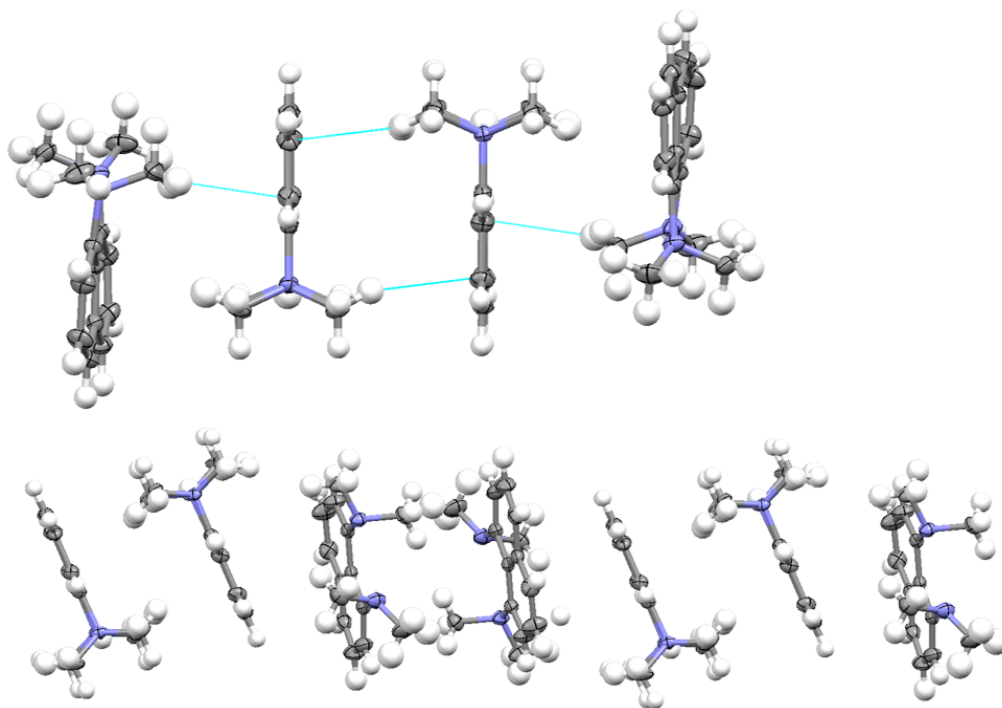


Figure 9. Pairs of parallel DMANH^+ molecules which are predominantly overlapped (left) but in the case of BA (**1**) and 2IBA (**5**) are significantly staggered (right).

Where the stoichiometry differs from 1:2, and where both neutral and protonated DMAN molecules co-exist, columns of DMANH^+ and neutral DMAN molecules tend to be formed. The exception to this is the 3FBA hydrate complex (**7**; in which there is no benzoic acid dimer formed) where discrete four molecule stacks are formed with a pair of parallel DMANH^+ molecules sandwiched by neutral DMAN molecules which are not parallel (Figure 10). There are two complexes with channel structures. The 3BBA (**9**) and 4CBA (**12**) complexes both have 1:1 stoichiometries and therefore have similar wave-like

channels of stacked pairs of alternating DMAN and DMANH⁺. The DMAN and DMANH⁺ pairs are rotated by approximately 90° relative to one another and are not parallel, inducing the wave.

Figure 10. Extended stacking of mixed DMANH⁺ and neutral DMAN. Top, the four molecule isolated units of the 3FBA hydrate complex (7) where a DMANH⁺ pair is sandwiched by two neutral DMAN



molecules. Bottom, wavy chains of alternating pairs of DMANH⁺ and DMAN formed in the 1:1 complexes of 3BBA (9) and 4CBA (12).

The only examples in which there is no pairing of DMANH⁺ or DMAN molecules are the 4BBA (13) and 4IBA (14) complexes. In these cases, only DMANH⁺ molecules are present, but the hydrogen bonded benzoic acid dimer is bent. It is likely that this unusual dimer geometry is the driving force behind the quite different packing (Figure 11).

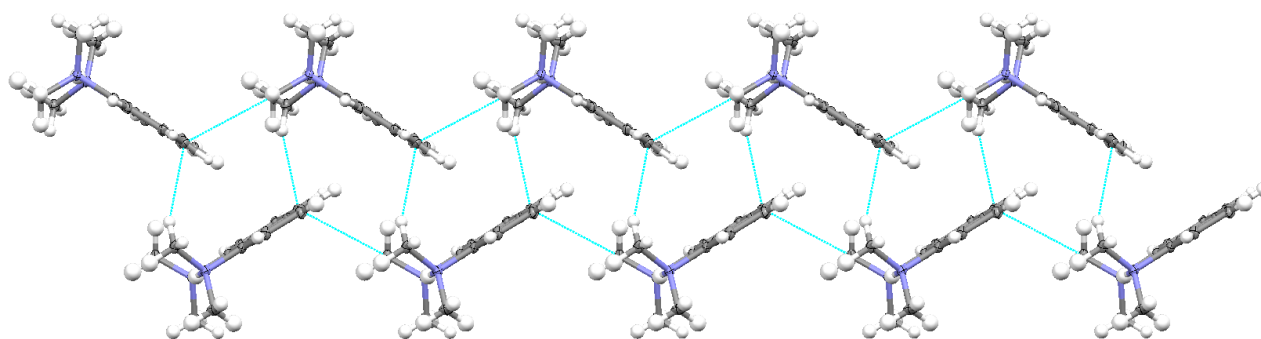


Figure 11. The differing chains of DMANH⁺ molecules in the 4BBA (**13**) and 4IBA (**14**) complexes.

Propensity for disorder

The relatively weak interactions, particularly involving the untethered benzoic acid molecule, results in a reasonably high propensity for disorder. The relatively small size of fluorine and the relatively weak intermolecular interactions it tends to form means that there is disorder of the F atom over two positions in both the 2FBA (**2**) (~95:5) and 3FBA (80:20 for the anhydrous, **6**, 75:25 for the hydrate, **7**) complexes (Figure 12). The symmetry of the molecule in 4FBA (**11**) precludes such disorder from happening in that case.

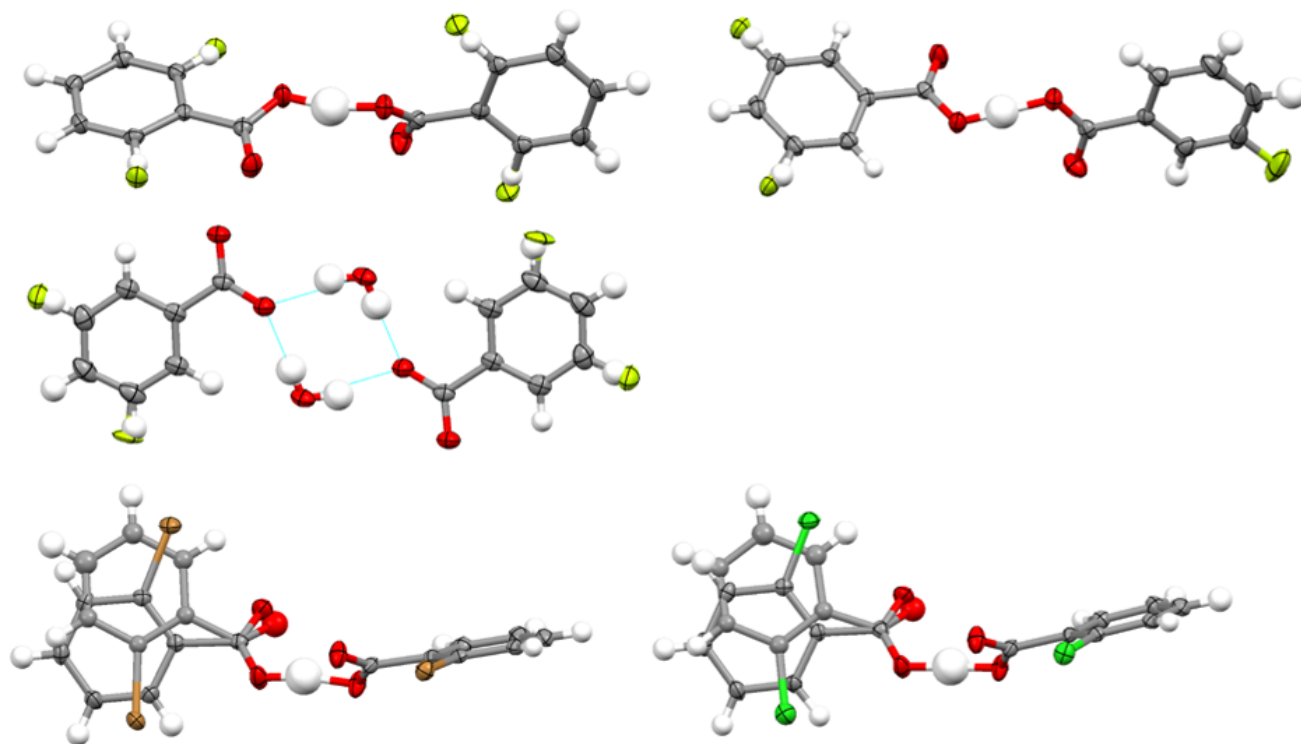


Figure 12. Disorder of the benzoic acid molecules. Top left, 2FBA (**2**); top right, 3FBA (**6**); middle, 3FBA hydrate (**7**); bottom left, 2BBA (**4**); bottom right, 2CBA (**3**).

Disorder of one of the benzoic acid molecules is also found for most of the 2-substituted benzoic acid molecules, with the exception of 2IBA (**5**). Both 2CBA (**3**) and 2BBA (**4**) show whole molecule disorder of the untethered benzoic acid molecule over two positions in an 85:15 ratio (Figure 12). The halogen atoms of the major component of both complexes are not involved in any significant interactions, perhaps explaining the presence of the disorder. In the 2IBA complex (**5**), the I atom is significantly larger in size and is involved in an $I \cdots \pi$ interaction with a neighbouring aromatic ring of a 2IBA molecule, locking the molecule into one position.

The DMANH^+ molecules are always ordered. However, there is disorder of differing types observed for some of the neutral DMAN molecules co-existing in the complexes. The neutral DMAN molecules in the 3BBA (**9**) and 3FBA hydrate (**7**) complexes are not disordered in any way. The DMAN in the 4CBA complex (**12**) only shows disorder of the methyl groups as there are two possible crystallographic

arrangements of the molecule in the same configuration (Figure 6). However, in the 3CBA complex (**8**), there is whole molecule disorder of the neutral DMAN molecules (Figure 7). There is no obvious reason why the disorder in the latter should be more complex.

Conclusions

Fourteen molecular complexes of DMAN with benzoic acid and mono halo substituted benzoic acids are reported. DMAN is a proton sponge, and in the majority of cases, extracts a hydrogen atom from the carboxylic acid of a benzoic acid molecule which hydrogen bonds with a second neutral benzoic acid molecule and the stoichiometry is 1:2 DMAN:benzoic acid. The hydrogen bond between the two benzoic acid molecules can be classified as a charge-assisted SSHB with O \cdots O distances less than 2.5 Å; this predictable motif has thus been engineered by use of the proton sponge to induce such hydrogen bonds. The induced short, strong charge assisted hydrogen bonds include, in complex **11**, the remarkably short O-H \cdots O distance of 2.409(4) Å, one of the shortest yet known for a benzoic acid type dimer. Use of the proton sponge, DMAN, is therefore a reliable route towards inducing such SSHBs and can be regarded as a reliable crystal engineering design strategy. The DMAN molecule in each case extracts the hydrogen atom into a charge-assisted intramolecular N-H \cdots N hydrogen bond. These two motifs, the benzoic acid dimer and the DMANH⁺ molecule, are isolated units with no other strong hydrogen bonding capability available. Despite this, the assembly of these units relative to one another is remarkably similar across the complexes studied, with an oxygen atom of one of the benzoic acid molecules pointing directly down at the N-H \cdots N hydrogen bond; the position of this O atom is, in general, asymmetric with respect to the two N atoms and might be expected to influence the position of the H atom within this intramolecular hydrogen bond. There are some exceptions to this 1:2 stoichiometry and it is not clear why these particular cases should occur. Despite the differing stoichiometry, the short, strong charge-assisted hydrogen bonded benzoic acid dimer is still formed in all cases except the hydrated complex **7**. Two hydrates were also formed, one with 3FBA (**7**) where an anhydrous form was also identified and a second with 4FBA (**11**) where no anhydrous form was obtained. The benzoic acid dimer is maintained in the 4FBA complex,

but a water molecule is inserted between benzoic acid molecules in the 3FBA hydrate, breaking the homodimer motif. Again there is no obvious reason why the role of the water molecule in the two should differ.

Halogen interactions are not prevalent in these complexes and cannot be considered a driving force behind the assembly of the extended structures. However, interactions involving the heavier I atoms are more common than those involving the lighter halogen atoms. Stacking of the DMAN molecules in a top-to-tail manner is prevalent and where the stoichiometry is 1:2, pairs of DMANH⁺ molecules are isolated from one another. In the cases where the stoichiometry is 1:1, channels of alternating pairs of neutral and charged DMAN molecules are formed.

These complexes provide an ideal set of systems in which the extent of weak hydrogen bonding and the distance limitations of such an interaction can be investigated. The ambiguity of hydrogen atom positions derived from X-ray diffraction prevents any conclusions on this to be drawn in this study. This is the subject of a related paper utilising neutron diffraction for its ability to resolve accurately hydrogen atom positions.³³

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Supporting Information Available. Tables of crystallographic data, Fourier difference maps of selected hydrogen bonds. Crystallographic data have been deposited with the Cambridge Structural Database CCDC nos: 1443267-1443300

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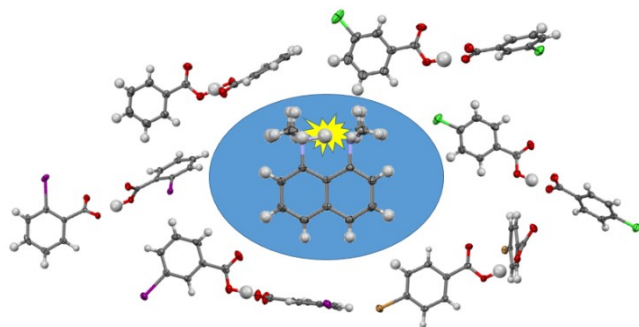
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Engineering Short, Strong, Charge-Assisted Hydrogen Bonds in Benzoic Acid Dimers through Co-Crystallisation with Proton Sponge

Lynne H. Thomas, Andrew O. F. Jones, Andras A. Kallay, Garry J. McIntyre, and Chick C. Wilson



Short, strong, charge-assisted hydrogen bonds have been engineering into 14 molecular complexes involving the proton sponge. The reliability of these interactions are demonstrated and this provides a route for accessing very short O-H \cdots O hydrogen bonds.